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FONKSİYONEL POLİAMİDLER

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FUNCTIONAL POLYAMIDES

Ph. D. THESIS

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PREFACE

I owe a dept of gratitute to my supervisor Prof.Dr.Yusuf YAĜCI, who has so materially contributed to my understanding of the subject.

I would like to express my deep appreciation to my colleagues, expecially Dr.A.ÖNEN, Doç.Dr.M.H.ACAR, Doc. Dr. G.HIZAL. My thanks is also due to Doç.Dr. N.BIÇAK for his constractive comments and criticisim which helped to improve my work.

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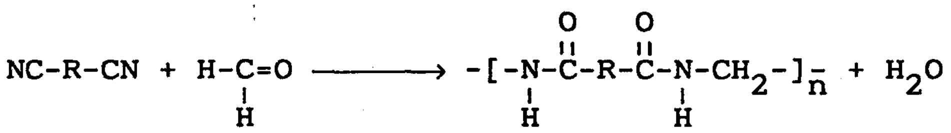
Finally, I sincerely thank to my parents for their patiance, understanding, and encouragement during all stages involved in the preparation of this thesis.

CONTENTS

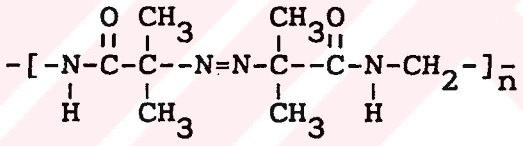
SUMMARY

The polyamides can be prepared by the low temperature solution method by condensing dinitriles with formaldehyde in the presence of strong acid such as sulfuric acid or formic acid according to the following reaction.



$$NC-R-CN + H-\underset{H}{C}=O \longrightarrow -[-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-CH_2-]_n- + H_2O$$

In this work, we synthesized polymeric azo initiator from formaldehyde and the well known azo initiator 2,2'-azobis(isobutyronitrile) (AIBN). The resulting polyamide has the following structure,



$$-[-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-N=N-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-CH_2-]_n-$$

This initiator was used to prepare block copolymers by sequential decomposition. Detailed studies on the synthesis and characterization were also carried out.

The synthesis of polyamides containing thioether groups achived by using dinitrile (containing thioether group) with formaldehyde under similar conditions.
The obtained polyamides were shown to coordinate mercury with a high degree of selectivity.

In addition, the oxidation of thioether group present in the dinitrile compound made it possible to synthesize corresponding polysulfones.

ÖZET

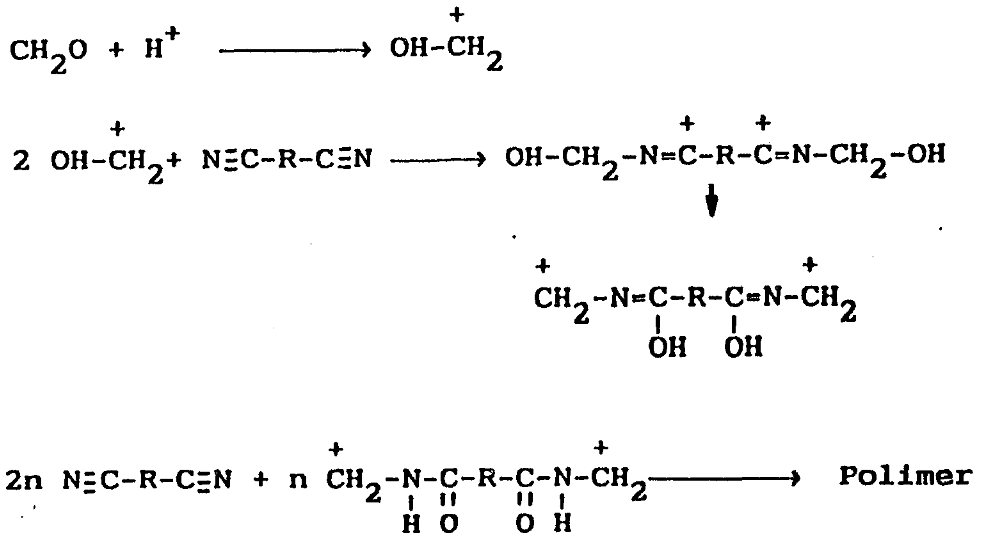
FONKSİYONEL POLİAMİDLER

Polimer bilimi oldukça yeni bir dal olmasına rağmen son otuz yılda çok hızlı bir şekilde gelişmiştir. Sentetik polimerler olarak bilinen lifler, plastikler, sentetik kauçuklar, endüstride çok çeşitli ve geniş uygulama alanı bulmuştur. Bu tür maddeler doğal kauçuk, odun, metaller gibi giderek azalan doğal kaynaklar yüzünden alternatif malzemelerdir.

Günümüzde yeni polimerik malzemelerin üretimi yerine varolan polimerlerin modifikasyonu bilimde ve endüstride önem kazanmıştır. Blok kopolimer sentezleri bu bakımdan yeni polimerik malzemelerin bilinen ticari polimerlerden üretilmelerine olanak sağlamaktadır.

Katyonik, anyonik, veya kondenzasyon polimerizasyonuyla elde edilen polimerik azo başlatıcılar, radikal mekanizma üzerinden graft ve blok kopolimer sentezinde kullanılmaktadır.

Bu çalışma, dinitril fonksiyonu içeren monomerler ile trioxan arasındaki reaksiyondan yararlanılarak çeşitli poliamidlerin sentezini ve bunların bazı özelliklerinin incelenmesini içermektedir. Bu tür reaksiyonun genel mekanizması aşağıdaki gibidir.



$$CH_2O + H^+ \longrightarrow OH-\overset{+}{CH_2}$$

$$2\ OH-\overset{+}{CH_2} + N{\equiv}C-R-C{\equiv}N \longrightarrow OH-CH_2-N{=}\overset{+}{C}-R-\overset{+}{C}{=}N-CH_2-OH$$

$$\downarrow$$

$$\overset{+}{CH_2}-N{=}\underset{OH}{\underset{|}{C}}-R-\underset{OH}{\underset{|}{C}}{=}N-\overset{+}{CH_2}$$

$$2n\ N{\equiv}C-R-C{\equiv}N + n\ \overset{+}{CH_2}-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-R-\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{N}}-\overset{+}{CH_2} \longrightarrow \text{Polimer}$$

Isı etkisi ile bozunabilen azo grubu içeren poliamid sentezi, 2,2′-azobis(isobutilonitrile) (AIBN) veya 2,2′-azobis (cyclo- heksanonitrile) (V-40) ile trioksanın sülfirik asit içindeki reaksiyonundan elde edilir. Reaksiyon 0 ^{o}C de gerçekleştirilerek azo grubunun reaksiyon sırasında ısısal olarak bozunmaması sağlanmıştır. Sülfirik asit ve AIBN in çeşitli mol oranlarında karıştırılması ile elde edilen polimerlere ait deneysel bulgular Tablo 1 verilmiştir.

Tablo 1 Trioksanın sülfirik asit içinde AIBN ile polimerleşmesi^{a}.

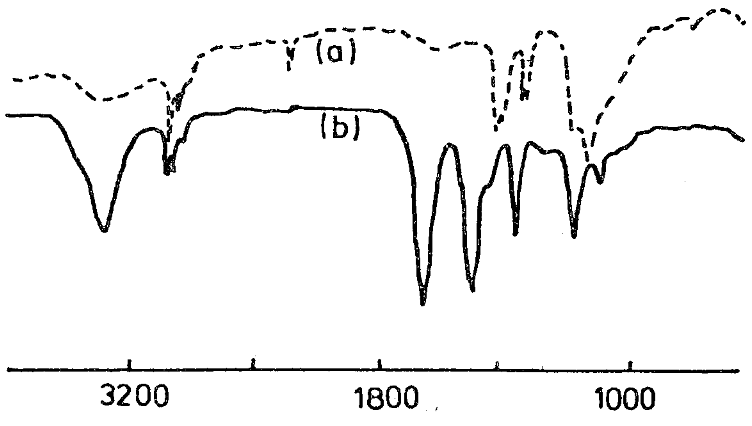
Kod	H_2SO_4/AIBN (mol/mol)	Trioksan (mol)	Verim (%)	$\eta_{sp/c}$^{b} (dl/g)
PA-1	5	0.0017	51.01	-
PA-2	10	0.0017	48.02	2.3
PA-3	15	0.0017	32.36	1.5
PA-4	20	0.0017	40.81	0.7
PA-5	25	0.0017	32.58	0.09

a : Sıcaklık: 0 ^{o}C, reaksiyon süresi: 60 dak.

b : DMSO/CH_2Cl_2 (1/1, v/v) karışımında 25^{o}C de ölçüldü.

Tablodan görüldüğü gibi polimer verimi ve molekül ağırlığı sülfirik asit içinde AIBN konsantrasyonu arttıkça artmaktadır.

AIBN ve poliazoamid'in IR spekturumu aşağıdaki gibidir.



Sekil a: AIBN'nin, b: Azo içeren poliamidin IR spektrumu

Elde edilen bu poliazoamidler, stirenin radikal polimerleşmesinde başlatıcı olarak kullanılmıştır. Azo grubunun kısmi parçalanması ile elde edilen polistiren zincirindeki azo grubu sayısı direkt olarak polimerizasyon süresi ile ilgili olduğu ısısal bozunma deneylerinden bulunmuştur. Deney sonuçları aşağıdaki Tablo2 de gösterilmiştir.

Tablo 2 Azo grubu içeren polistirenin 70^oC de benzende bozunması .

Kod	$\bar{M}_{no} \cdot 10^{-3}$	$\bar{M}_{ni} \cdot 10^{-3}$	N_s
4	43.9	20.05	1.2
5	70.9	35.4	0.84
6	54.1	49.4	0.04

Metilmetakrilat'da aynı şekilde poliazoamid başlatıçısı ile polimerleştirilmiştir.

Elde edilen polimerler ikinci monomer varlığında polimerleştirilerek blok kopolimerler sentezlenmiştir.

Blok kopolimerleşme deneyinde başlatıcı olarak azo grubu içeren polistiren kullanıldığında, çok miktarda homopolimer oluştuğu gözlenmektedir. Ancak blok kopolimer içinde ikinci monomerin yüzdesi polimerleşme süresi arttıkça artmaktadır. Bunun sebebi oluşan birincil radikallerin birleşmesi veya prepolistirendeki azo grubunun parçalanmaması olarak açıklanabilir. Benzer sonuçlar başlatıcı olarak azo grubu içeren polimetilmetakrilat kullanıldığında da elde edilmiştir. Deney sonuçları Tablo 3 gösterilmiştir.

Son yıllarda polimer alanındaki yapılan çalışmalarda polimer-metal komplekslerine önem verilmiştir. Şelat oluşumu metal iyonlarının çözeltiden ekstrakte edilmesinde çok kullanılmaktadır. Yapısında tioeter grubu bulunduran polimerlerin seçimli olarak civa bağladığı bulunmuştur. Bu amaçla β,β'(etilenditiyol)dipropionitril, formaldehitle sülfirik asit içinde 0^oC polimerleştirilmiştir. Deneysel bulgular Tablo 4 verilmiştir.

Tablo 3 Azo Grubu İçeren Prepolimerlerden blok kopolimer sentezi.

Kod	Prepolimer (g/l)	Monomer	Zaman (dak)	Dönüşüm (%)	Elde edilen ürunlerin yüzdesi			Block kopolimer bileşimi
					PSt (%)	PMMA (%)	PSt-b-PMMA (%)	PMMA (%)
7	PSt	MMA	60	3.6	45.1	36.4	18.5	77.6
8	PSt	MMA	120	7.4	50.1	45.1	4.8	83.3
9	PMMA	PSt	60	1.9	23.0	70.5	6.5	32.3
10	PMMA	PSt	120	2.3	30.1	60.1	9.7	26.7

Tablo 4 EDP ile trioksanın sülfirik asit içindeki polimerleşmesi.[a]

Kod	H_2SO_4/EDP (mol/mol)	Trioksan (mol.10^{-4})	Dönüşüm (%)	$\eta_{sp/c}$[b] (g/dl)
PATE-1	10	3.3	69.56	0.32
PATE-2	15	3.3	80.04	0.33
PATE-3	20	3.3	45.96	0.30
PATE-4	30	3.3	74.6	0.03

a: Reaksiyon sıcaklığı: 0°C, süresi: 90 dak.

b: N-metilpirrolidon içinde 30°C da ölçüldü.

Polimerlerin ve metal iyonlarının N-metilpirolidon içindeki çözeltisi karıştırıldığında, civa iyonunun varlığında kompleksleşme sonucu sarı renkli bir çökelti oluşurken, diğer iyonların varlığında ise sadece bulanma gözlenmiştir. Bu sonuçlar bize polimerin seçimli olarak civa iyonunu tuttuğunu gösteriyor. İyon tutma deneylerinin sonuçları Tablo 5 de gösterilmektedir.

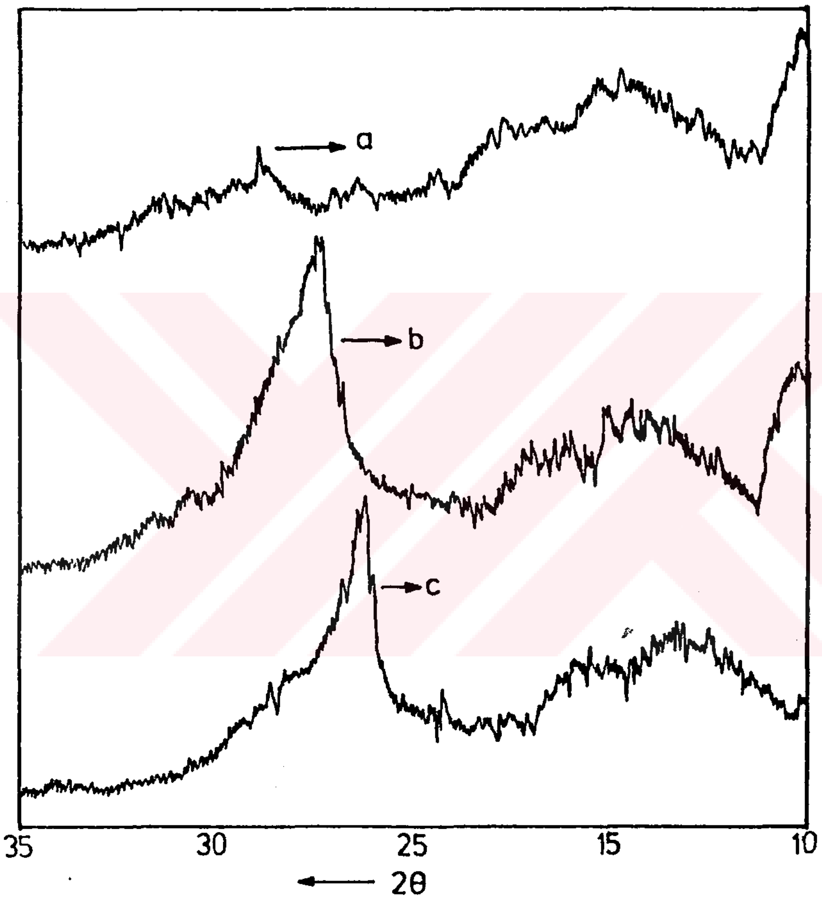
Tablo 5 PATE'nin şelat yapabilme özellikleri.

	$Zn(Ac)_2$[a]	%[b]	$Cd(Ac)_2$[a]	%[b]	$Hg(Ac)_2$[a]	%[b]
Standart	0.5	-	0.5	-	0.08	-
PATE 1	0.465	7	0.417	3.8	0.06	25
PATE 2	0.462	7.6	0.481	3.8	0.048	40
PATE 3	0.465	7	0.477	4.6	0.069	42
PATE 4	0.469	7.6	0.481	3.8	0.048	40

a : Çözeltideki serbest iyon derişimi.

b : PATE ekstraksyonu sonunda çözeltide kalan serbest iyon derişimi.

β,β'(etilenditiol)dipropionitril dioksanda çözündükten sonra hidrojen peroksitle sülfona yükseltgenmiştir. Sülfon dinitril daha önce uygulanan yöntemle sülfürik asit içinde trioksan ile polimerlestirilmiştir. Elde edilen polisülfon organik çözücülerde çözünmemektedir. Bu sebeple polimerlerin çözünürlüğünü arttırmak için adipoil segmenti polimere ilave edilmiştir. Kopolimerlerin kristal yapısı x ışınları kırınımı yöntemiyle incelenmiştir.



Şekil Poliamidlerin x ışını kırınım ölçümleri, (a) Poliamid sülfon (b) Poliadipoilsülfon (% 80 sülfon % 20 adipoil) (c) Poliadipoilsülfonamid (% 80 adipoil % 20 sülfon).

CHAPTER 1. OBJECTIVES OF THE WORK

The object of the work described in this thesis was to prepare functional polyamides for various purposes.

Recently there has been a significant growth of interest in the preparation of block copolymers with novel physical and chemical properties. Various methods to synthesize these polymers have been known for a long time. Radical polymerization processes with multifunctional initiators which have either several O-O or N=N groups in a molecule is one approach to obtain block copolymers and are studied in detail.

It is also well known that dinitriles readily react with formaldehyde under mild conditions in the presence of strong acid to yield polyamides. Therefore it seemed quite appropriate to prepare multifunctional azo initiator by a similar polyamidation reaction and selecting suitable dinitrile compound possessing azo group in the structure.

Compared with other methods of block copolymerization the use of multifunctional azo initiators have the advantage of being applicable to wide variety of monomers polymerizable with free radical mechanism. Moreover, because of the presence of many thermo-labile azo groups, it is possible to adjust the molecular design of the polymer which effects the final properties of the resultant block copolymers.

Cation binding of polymeric products is frequently required in order to broaden the applicability of polymers. Quite often, cation binding property serves the purpose of extraction, purification and separation of metal ions which can be achieved by the attachement of suitable groups into polymers.

Polyamidation methods may be employed to impart these groups by using dinitrile compounds with thioether groups. Obviously, oxidation of these groups to sulfones prior to polyamidation would cause some property changes. Thus, polyamidesulfones may be attained via condensation of sulfone dinitriles with formaldehyde which may find application in the development of high-tech devices.

CHAPTER II. INTRODUCTION

II.1. Definition of Polymers

Polymer is a large molecule constructed from many smaller repeating units which are called monomers. Monomers are covalently bonded together in any conceivable pattern. The properties of polymers are directly related with the type of monomer.

When only one species of monomer is used to build up a macromolecule, the product is called as a homopolymer. If the chains are composed of two types of monomer unit, polymer is called copolymer. When three or more different monomers are incorporated in one chain, a terpolymer results.

II.2. Polymerization Reactions

II.2.1. Classification of Polymerization Reactions

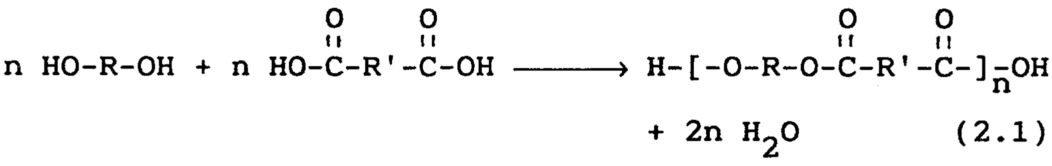
Various methods are used to classify polymerization reactions in encyclopedia and text books. For example classification based on stochiometry, polymerization mechanism, the nature of propagating species, product structure, the nature of monomers [1-3]. The classical subdivision of polymers into two main group was made around 1929 by Carothers as addition and condensation types and the processes as addition polymerization and condensation polymerization [4].

Although detailed information on the free radical and condensation polymerization exists in the most of the polymer text books, we would like to give introductory knowledge on these processes since they are related to the scope of this work.

II.2.2. Condensation Polymerization

Condensation reaction produces a polymer or a small molecule. Products depend on the functionality of reactants. Functionality is the average number of reacting groups per reacting molecule. Functional groups can be -OH, -COOH, -COCl etc.. If the functionality is less than two it produces low molecular weight condensation product.

The typical examples being the condensation of an acid with an alcohol to yield low molecular weight ester. However, two or more functional groups containing acid and alcohol gives polyester (2.1)



$$n\ HO{-}R{-}OH + n\ HO{-}\overset{O}{\overset{\parallel}{C}}{-}R'{-}\overset{O}{\overset{\parallel}{C}}{-}OH \longrightarrow H{-}[{-}O{-}R{-}O{-}\overset{O}{\overset{\parallel}{C}}{-}R'{-}\overset{O}{\overset{\parallel}{C}}{-}]_n{-}OH + 2n\ H_2O \qquad (2.1)$$

A condensation polymerization begins with producing dimer when the concentration of dimers increase, trimers, tetramers and oligomers combine each other and form high molecular weight product. Last step rather slower than the others because the concentration of reactive groups decreases as the length of chain increases. For this reason long reaction times are required to achieve high conversion.

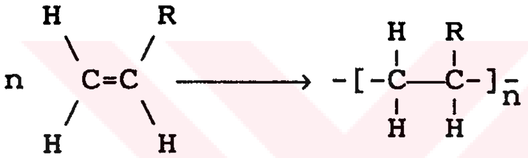
In the condensation reactions at least two functionality is needed but this is not the case when addition reactions are employed. Long chains are readily obtained from opening multiple bonds or strained rings. Such reactions invariably proceed by a chain reaction mechanism and resulting polymers have a repeating unit which is identical in composition to the monomer and are formed without loss of any portion of the monomer molecules. Polymerization begins with the addition of an initiator which reacts with the monomers to produce active center. Active center reacts with another monomer to produce active molecule these steps are called initiation step.

Polymerization then proceeds by successive addition of more monomer molecules to the active end of growing chain. This steps are called propagation steps. The addition of monomer to active center will proceed until the reactive center destroyed by chemical reaction or until the supply of monomer is finished.

For the ring-opening process, ring strain has a very important role [5]. Ring strain is a thermodynamic property that is caused either angular deformation or steric interaction of substituents on the ring atoms.

Addition polymerization is classified into two main groups, free radical and ionic polymerization according to structure of growing site which is created by free radical or ionic initiators.

The monomers involved in free radical polymerization generally contain a vinyl (carbon-carbon double bond) linkage. The polymerization process involves opening up the double bond. The net reaction can be envisaged :



$$n\,\mathrm{CH_2{=}CHR} \longrightarrow -[-\mathrm{CH_2}-\mathrm{CHR}-]_n- \qquad (2.2)$$

The complete polymerization proceeds in three main stages : Initiation, propagation, termination.

Initiation : The process may be initiated by several ways; spontaneous or induced decomposition of an initiator, photo induced reaction of vinyl monomer, reaction of initiator with monomer, thermally induced reaction between two monomers.

Decomposition of initiator : $I \xrightarrow{k_d} 2\,R\cdot$ (2.3)

Photoinduced monomer reaction : $M + h\upsilon \longrightarrow M\cdot$ (2.4)

Reaction of initiator with monomer :

$$I + M \xrightarrow{k_d} R\,M\cdot \;+\; \text{residue} \qquad (2.5)$$

Thermally induced monomer reaction : $2\,M \longrightarrow \cdot M\text{-}M\cdot$ (2.6)

Where (I) represents initiator molecule, (M) represents monomer and (R·) represents the free radical.

This primary radical reacts with an other monomer to form a new radical.

$$R\cdot + M \xrightarrow{k_i} M_1\cdot \qquad (2.7)$$

k_d and k_i are the rate constants of decomposition and initiation steps.

Propagation contains the growth of M_1 by adding to another monomer, this step repeats incereasing the chain by one monomer unit at a time.

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \qquad (2.8)$$

Where kp is the rate constant of propagation.

Theoretically, the chain can continue to propagate until all monomer in the system has been consumed. In fact, free radicals are particularly reactive. They can easily react and become inactive covalently bonded molecule. This step is called termination.

Termination of chains can take place several ways. The most important termination reaction is the interaction of two active chain ends.

First one is the combination of two radicals :

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tc}} M_n - M_m \qquad (2.9)$$

Second one is dispropotionation with hydrogen abstraction from one end to give two dead polymer chains, one is being an unsaturated and the other is saturated.

$$M_n\cdot + M_m\cdot \xrightarrow{k_{td}} M_n + M_m \qquad (2.10)$$

k_{tc} and k_{td} are the rate constants oftermination by coupling and disproportionation, respectively.

II.3. Polyamidation Reactions

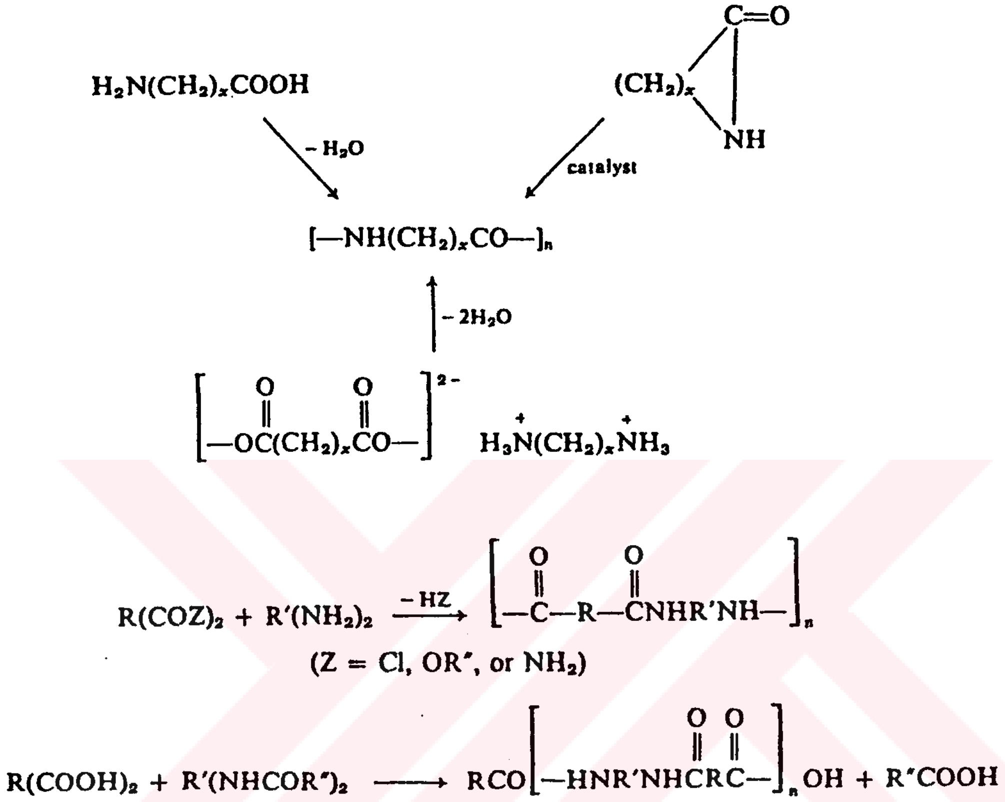
Polymeric amides are found in the nature in the many polypeptides which continue a variety of amide organisms and the composition of silk and wool.

The reaction of dibasic acids with diamines was reported in the early literature to give low molecular weight cyclic amides as infusible and insoluble products [6]. It was Carothers who first recognized that polymeric amides were formed by the reaction of diamines with dibasic acids [7].

The major methods of preparing polyamides summarized in scheme 1 and 2 .

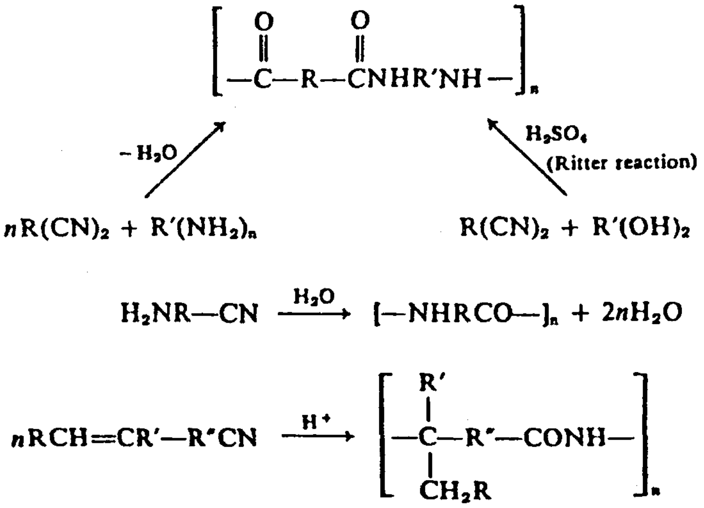
SCHEME 1

The General Preparative Methods for the Synthesis of Polyamides.



SCHEME 2

Miscellaneous Methods for the Synthesis of Polyamides from Nitriles



Polyamides with molecular weights above 7000 are useful because they possess properties which allow them to be spun into fibers [8,9].

Cross-linked polyamides may be prepared from polyfunctional amino acids, triamines, or tri carboxylic acids, etc.

Some of the main uses of polyamides or naylons are for synthetic fibers for tyre, carpet, stocking and upholstery industries. Use of polyamides as molding and extrusion resin for plastics industry is also of increasing importance.

II.3.1. Amidation of Dibasic Acid with Diamines.

In order to achieve a good reactant balance, the diammonium salt is first prepared by the reaction of diamine with dibasic acid as shown in equation 3.1.

$$\begin{array}{r} n\ H_2N\text{-}R\text{-}NH_2 + n\ HOOC\text{-}R'\text{-}COOH \longrightarrow n\ [R'(COO)_2)^+(R(NH_3)^-] \\ \Big\downarrow \begin{array}{l} \text{Heat} \\ -\ 2n\ \ H_2O \end{array} \\ \text{-[-CO-R'-CO-NH-R-NH-]}_n\text{-} \end{array} \tag{2.11}$$

The salt is conveniently formed by bringing together alcoholic solutions of equivalent amounts of reactants and following the reactions electromatically. The salts can be converted to polyamides either by fusing them under reduced pressure or by heating them in an inert solvent such as cresol or xylenol.

II.3.2. Amidation of Dicarboxylic Acid Esters with Diamines

The preparation of polyamide by aminolysis of reactive esters proceeds under mild conditions and without racemization [10]. For example, phenyl esters of some substituted malonic acid derivatives condese with aliphatic diamines to produce heat-stable high molecular weight polyamides at about 200-210 °C under reduced pressure. However, heating the free malonic acid with the same diamines caused only decarboxylation at 115-185 °C.

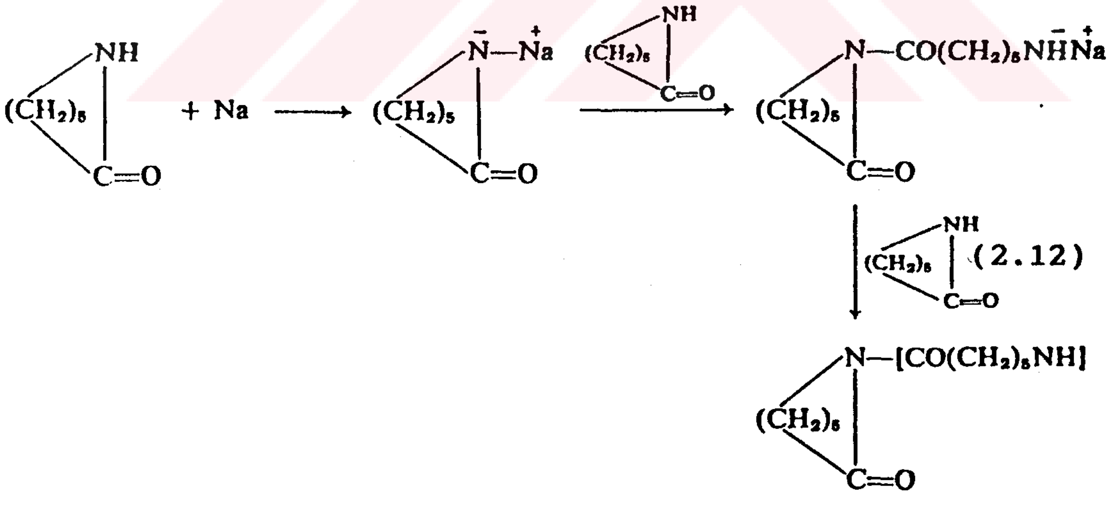
II.3.3. Condensation of Amino Carboxylic Acids and Their Derivatives

Amino carboxylic acids condense in the absence of catalyst at approximatelly 260 °C to librate water. The reaction may be accelareted by the use of reduced pressure. In the case of nylon 7 and 11 the probability of occurance of intramolecular dehydration to form 8 or 12 membered ring lactams is very remote, but nevertheless approximately 0.5 %do from in both cases.

It is noticeable that polyamides which contain even-number of polymethylene groups, melt higher than the odd-numbered ones [11].

II.3.4. Condensation of Lactams

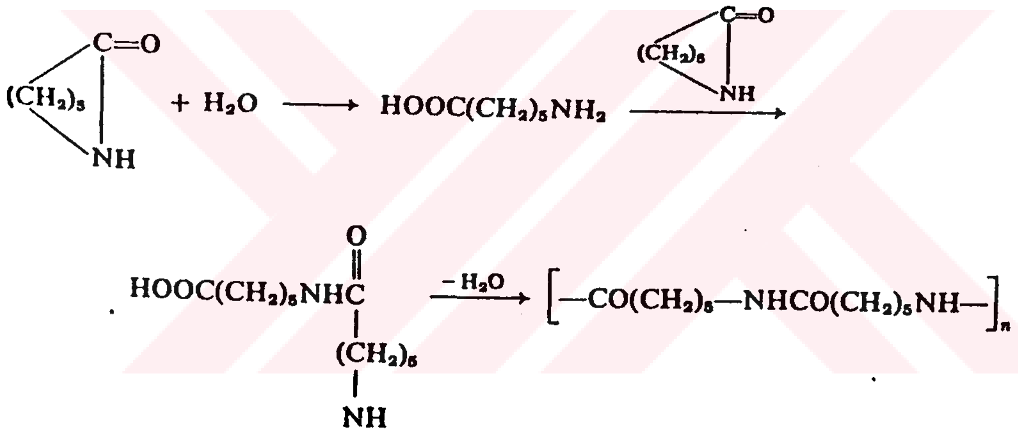
Lactams may be polymerized under acidic or basic conditions to give polyamide by an addition type reaction [12]. The polymerization of caprolactam can be given as an example for both cases. Caprolactam can be polymerized smoothly and rapidly by heating at 200-280 °C in a closed vessel with inert atmosphere in the presence of alkali or alkaline earth metals. The alkaline metals such as sodium or lithium are more effective than calcium and magnesium [13].


(2.12)

Lactams can also be polymerized to nylon 6 in the presence of catalytic amounts of hydrogen chloride

[14,15]. Lactams polymerize at a rate corresponding to the following order of lactam ring size : 8 > 7 > 5 and 6. These results are related to the relative basicities of the ring lactams towards hydrogen chloride.

Water can also initiate the polymerization of lactams at elevated temperature. Water reacts with lactam to give amino acid which then initiate polymerization by proton transfer from the carboxylic acids.



(2.13)

II.3.5. Low Temperature Polycondensation of Diacid Chlorides with Diamines

The Schotten-Baumann reaction can be applied to the preparation of polyamides using bifunctional reagents. Since the reaction is very rapid at room temperature, it can be carried out at low temperature in solution or by an interfacial polycondensation technique [16,17].

In the solution polycondensation method the reaction is carried out in a single inert liquid in the presence of an acid acceptor. The polymer may precipitate out of the solution or it may be soluble.

In the interfacial polycondesation method the reaction is carried out at the interface of two immiscible solvents. The amine is dissolved in water and acid chloride is dissolved in the hydrocarbon layer [18]. The organic solvent is the most important variable since it controls partition and diffusion of the reactants between the two immiscible phases, the reaction rate, solubility and swelling of permeability of the growing polymer.

The advantage of the interfacial polymerization process is that it is a low-temperature process requiring ordinary equipment. It also allows one to prepare those polyamides that are unstable in the melt polymerization process. Random or block copolymers can easily be prepared depending on the reactivity of the reactants and their mixture.

The reaction between 4,4'-Diaminodibenzo-18-crown-6 and 4,4'-Azo-bis(4-cyanopentanoyl chloride) can be given as an example of interfacial polycondensation reaction [19]. This reaction leads to the formation of polyamide possesing crown ether units in the main chain.

II.3.6. Condensation of Dinitriles and Formaldehydes

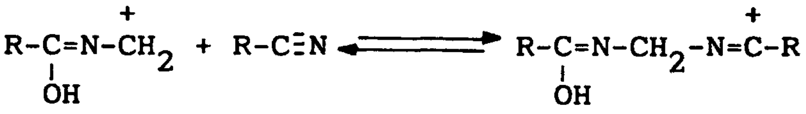
The reaction between nitriles and aldehydes which have been studied occasionally, after discovery of a novel method for preparation of polyamides in acid solution at room temperature [20,21,22].

The reaction between nitriles and formaldehyde is exothermic and occurs at room temperature with remarkable ease to give high yields of methylene-bis-amides (often over 90 %). The reaction is effected by adding a mixture of nitrile and formaldehyde (preferably as trioxane which is soluble in most liquid nitriles) to an excess of 85 % sulfuric acid solution, keeping the temperature at 30 °C by cooling. At the end of the reaction, mixture is poured into an excess of ice and water. Water insoluble solids are usually precipitated. The reaction of nitriles with formaldehyde appears to proceed by a carbonium ion mechanism and may be presented by the series of equations.

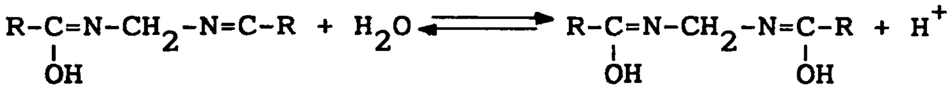
$$CH_2O + H^+ \longrightarrow HO\text{-}CH_2^+ \qquad (2.14)$$

$$HO\text{-}CH_2^+ + R\text{-}C\equiv N \rightleftharpoons R\text{-}\overset{+}{C}{=}N\text{-}CH_2\text{-}OH \qquad (2.15)$$

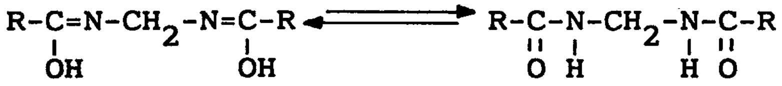
$$R\text{-}\overset{+}{C}\equiv N\text{-}CH_2\text{-}OH \rightleftharpoons R\text{-}\underset{OH}{C}{=}N\text{-}\overset{+}{C}H_2 \qquad (2.16)$$



$$R\text{-}\underset{OH}{C}{=}N\text{-}\overset{+}{C}H_2 + R\text{-}C\equiv N \rightleftharpoons R\text{-}\underset{OH}{C}{=}N\text{-}CH_2\text{-}N{=}\overset{+}{C}\text{-}R \qquad (2.17)$$



$$R-\underset{\substack{| \\ OH}}{C}=N-CH_2-N=C-R + H_2O \rightleftharpoons R-\underset{\substack{| \\ OH}}{C}=N-CH_2-N=\underset{\substack{| \\ OH}}{C}-R + H^+ \quad (2.18)$$

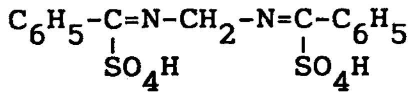


$$R-\underset{\substack{| \\ OH}}{C}=N-CH_2-N=\underset{\substack{| \\ OH}}{C}-R \rightleftharpoons R-\underset{\substack{\| \\ O}}{C}-\underset{\substack{| \\ H}}{N}-CH_2-\underset{\substack{| \\ H}}{N}-\underset{\substack{\| \\ O}}{C}-R \quad (2.19)$$

The amidation reaction provides highest yields with formaldehyde but other aldehydes such as acetaldehyde, butrylaldehyde and chloral can be used to give compounds of the type R-CO-NH-C(R')H-NH-CO-R where R' is $-CH_3$, $-C_3H_7$, $-CCl_3$. Aldehydes which contain hydrogen atoms on the atom adjacent to the carbonyl group undergo a number of self-condensation reactions under the influence of sulfuric acid, and therefore give remarkedly lower yields in the reaction with nitriles.

The reaction is general with nitriles and gives derivatives which are normally high melting solids. Of special interest is the reaction of formaldehyde and acrylonitrile which yields methylene-bis-acrylamide, a useful monomer for vinyl polymerization. For this reaction 95 % sulfuric acid was used as a solvent and a catalyst.

Eventhough the reaction is presented by a carbonium ion mechanism it is possible that sulfates are formed as intermediate products. Evidence for the formation of sulfur- containing compounds has been obtained by effecting the benzo nitrile-formaldehyde reaction in an acetic-sulfuric acid mixture and pouring the resulting solution into excess of acetic acid. Crude intermediate can be presented as below.



$$C_6H_5-\underset{SO_4H}{\underset{|}{C}}=N-CH_2-N=\underset{SO_4H}{\underset{|}{C}}-C_6H_5 \qquad (2.20)$$

Owing to its ionic character, the reaction of nitriles with formaldehyde is influenced greatly by acid strength of reaction system. Phosphoric acid, methane sulfonic acid and formic acid or mixture of these acids with sulfuric acid can be used to induce the reaction between nitriles and formaldehyde at room temperature. When only formic acid is used, higher temperatures are required to bring about the reaction.

In general, yields and reaction rates vary widely with the nature of the aldehyde, nitrile and acid strengh used for the reaction.

This new method of obtaining polymers permits the preparation of a type of polyamide which can not be obtained by conventional method of heating a diamine with a dibasic acid since monomethylenediamine is unstable in the free state [23]. Besides from yielding a new polyamide structure, this method differs from the usual procedure for polyamide preparations (heating at 200-300 °C) in that it is exotermic and proceeds rapidly at room temperature.

II.4. Block Copolymers

Block copolymers are defined as having a linear arragement of blocks of varying monomer composition [24]. That is, a block copolymer is a combination of two or more polymers joined end to end.

The increasing importance and interest in block copolymers arises mainly from their unique properties in solution and in the solid state which are a consequence of their molecular structure. In particular, sequences of different chemical composition are usually incompatible and therefore have a tendency to segregate in space.

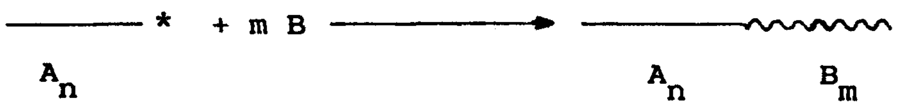
Their sequential arrangement can vary from A-B structures containing two segments only, to A-B-A block copolymers with three segments to multiblock -(-A-B-)-system possessing many segments as shown below schematically.

A-B block copolymer ;  (2.21)

A-B-A block copolymer ;  (2.22)

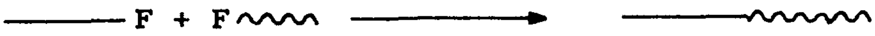
-(-A-B-)- block copolymer ;  (2.23)

There are two general methods for synthesis of block copolymers. In the first, active site on a macromolecular chain are created which then initiate the polymerization of a monomer. The polymerization may be radical, anionic, or cationic, and for one active site, can be presented as below.



(2.24)

The second method, is the reaction between chemical functional groups which presented at the ends of different polymers. This type is a kind of condensation reaction. With difunctional species, the reactions lead to multi block copolymers, also called segmented copolymers. It can be shown as below.



(2.25)

II.4.1. Anionic Block Copolymerization

Copolymerization which proceed through anionic active center show some very interesting features. In the first place the proportions of two monomers in an anionically prepared copolymer are usually quite different from those found when the copolymerization initiated by free radicals. A particularly good example is the monomer pair, styrene and methylmetacrylate. Using equimolar feed in normal temperature the free radical initiated copolymer contains 50 % of both. On the other hand, a copolymer obtained under similar conditions using one group addition anionic initiator contains very little styrene indeed. So great is the change in composition with initiator type.

In the anionic system, termination or transfer reactions can not take place. This special advantages lead to observe very narrow molecular weight for production of "talior-made" block copolymer.

This method leads to development of new class of materials which are called thermoplastic elastomers.

II.4.2. Cationic Block Copolymerization

Block and graft copolymerization by cationic polymerization is complicated by transfer, leading to contamination of the product by homopolymer. However, successful sequential block copolymerization of styrene and substituted aziridines were possible when the aziridines were initiated by living polystyrene at lower temperature [25].

The work of Kennedy on the block and graft polymerization utilizing alkyl aluminium halide initiators is particularly impressive because these initiators migrate transfer and several of products look attractive from a commercial point of view. Kennedy examined the idea of reactive end groups or pendant groups on a polymeric back-bone as co-initiator with the alkyl aluminium halide to polymerize a second monomer [26]. This system can be represented as shown below.

$$\text{Polymer-Cl} + \text{Et}_2\text{AlCl} \longrightarrow \text{Polymer}^{+} + \text{Et}_2\text{AlCl}_2^{-} \qquad (2.26)$$

$$\text{Polymer}^{+} + \text{M} \longrightarrow \text{Polymer-M}^{+} + \text{n M} \longrightarrow \text{Copolymer} \qquad (2.27)$$

II.4.3. Preparation of Block Copolymers by Radical Polymerization

Radical copolymerization have been practisized for many years and polymers so made, industrially outweigh those made by any other method.

During the simultaneous polymerization of two monomers A and B, characterized by their reactivity ratios r_A and r_B the probability of forming large sequences of A and B is very small. Accordingly, the radical polymerization of a mixture of monomers usually does not lead to block copolymer. However creation of free radical sites or generating species such as azo or peroxide on a given polymer can then initiate polymerization of a second polymer.

Radical block copolymerization leads inevitably to more or less homopolymer so that the products require careful separation before the block copolymer characterized.

The synthesis of block copolymer via radical mechanism has several advantages: One of these, all monomer containing at least one double bond can be polymerized radically therefore a wide choice of monomer combinations are avaible. Another one is that, radical polymerizations are considerably less sensitive to impurities than ionic techniques.

II.4.3.1. Azo Polymers

Azo-containing polymers can be formally classified according to a variety of criteria. The thermal stability of the -N=N- group is the principal criterion. A further subdivision can be made according to the position of the -N=N-group. Main-chain azo groups, and side chain azo groups.

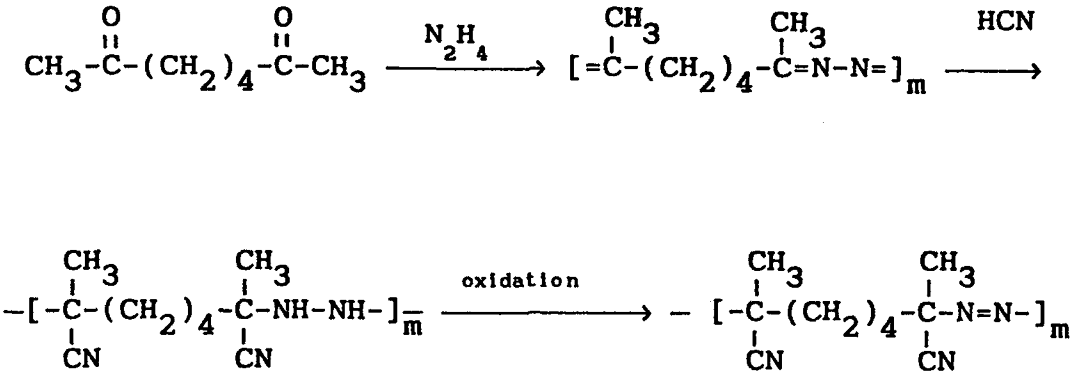
For main-chain azo group, each monomer unit contains a stable or unstable azo function which can be shown below.

$$-(-R-N=N-R-)_n- \quad ; \quad -(-R-N=N-R-)_n-(R-)_m- \qquad (2.28)$$

Side-chain azo groups in which the branches form the main chain. In the copolymer, at least one component contains an azo function as shown below.

$$-(-R-)_n- \quad ; \quad -(-R-)_n-(-R'-)_m- \qquad (2.29)$$

For the synthesis of the labile main-chain azo groups involved the conversion of aliphatic diketones having at least four carbon atoms between the carbonyl functions to polyazines, which are converted to polyhydrazonitriles by addition of HCN, the latter are transformed into polymeric azo compounds by oxidation [27].



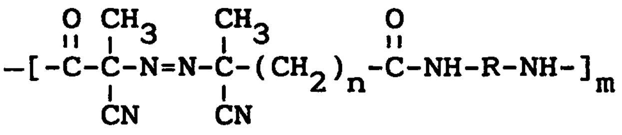
$$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{N_2H_4} [=\overset{\overset{CH_3}{|}}{C}-(CH_2)_4-\overset{\overset{CH_3}{|}}{C}=N-N=]_m \xrightarrow{HCN}$$

$$-[-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-(CH_2)_4-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH-NH-]_m \xrightarrow{\text{oxidation}} -[-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-(CH_2)_4-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-]_m$$

(2.30)

An alternative synthesis is to polymerize reactive AIBN analogues with suitable comonomers or bisphenol A which is shown below [28].

Acide chloride + Diamine ⟶



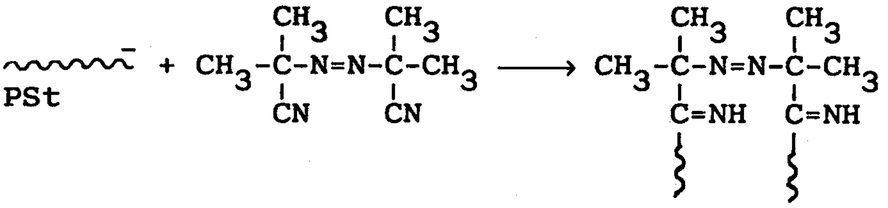
$$-[-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}-NH-R-NH-]_m$$

(2.31)

Polymers containing more than one azo group per chain can also be formed during the foregoing reaction by radical combination.

$$\sim\sim N{=}N\sim\sim\cdot + \cdot\sim\sim N{=}N\sim\sim \longrightarrow \sim\sim N{=}N\sim\sim N{=}N\sim\sim \quad (2.32)$$

Another method of producing polymers containing one or more labile azo group is termination of anionicaly polymerized polystyrene by addition of AIBN [29].



$$\underset{PSt}{\sim\sim\sim^{-}} + CH_3-\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{\underset{\wr}{C=NH}}{C}}-N=N-\overset{CH_3}{\underset{\underset{\wr}{C=NH}}{C}}-CH_3$$

(2.33)

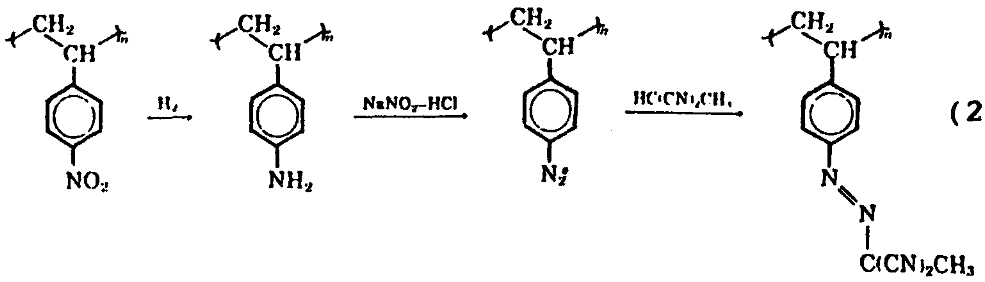
One of recent studies on preparing macroazonitriles containing crown ether moieties and various amounts of -N=N- units in the main-chain is based on solution condensation between cis-diaminodibenzo-18-crown-6 and adipoylchloride or terphtaloyl chloride with addition of ACPC [30].

Almost all polymers containing labile azo groups can be utilized for the synthesis of block copolymers. For example, polyazo esters were heated in the presence of a monomer M_1. The resulting azo-containing block copolymer could be used for the subsequent polymerization of another monomer M_2 to form an ABC-type block copolymer [31,32].

$$\text{Polyazoester} \xrightarrow[\text{heat}]{M_1} \sim\sim N{=}N \sim\sim (M_1)_n \xrightarrow[\text{heat}]{M_2} M_1 \sim\sim M_2 \quad (2.34)$$

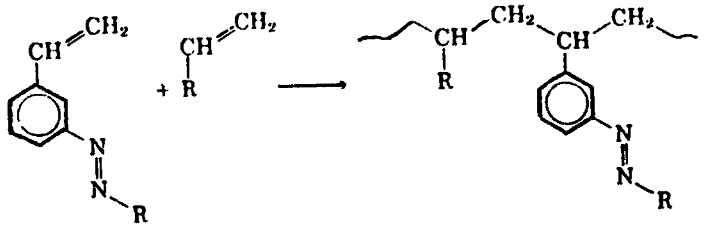
Many different synthetic routes are available for the production of polymers which contains stable azo functions in the backbone chain. Some of aromatic polyamides and esters can be given as examples of this class.

Two main synthetic routes are available for the synthesis of branched azo group containing polymers. In the first, the azo groups are introduced into a prepolymer which is indicated below.



(2.35)

In the second route, monomers containing an azo group, in addition to a polymerizable functioality, are copolymerized with other monomers [33].



(2.36)

This kind of prepolymers can be used as initiators for the production of graft copolymers.

II.5. Polysulfides

During the last several decades the synthesis of polymers with high sulfur content was investigated with the aim of improving chemical stability and viscoelastic properties over those of polymeric sulfur. Polysulfide can be shown with formula $-(-R-S_x-)-$ (R most often alkylene, oxaalkylene or arylene groups) .

The first example of a polysulfide synthesis was the polycondensation of 1-2 dichloroethylene with sodium tetrasulfide, followed by polysulfides based on bis(2-chloroethyl) ether and bis(2-chloroethyl)formal [34]:

$$n\ [Cl\ CH_2\text{-}O\text{-}CH_2)_2O + n\ NaS_x \longrightarrow$$

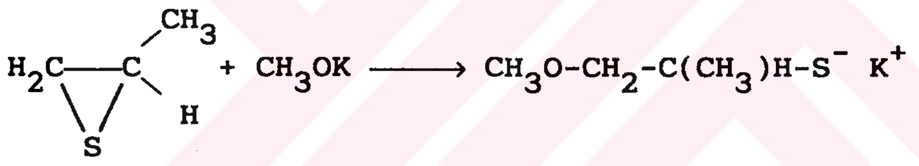
$$-[-CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}S_x\text{-}]_{\bar{n}} \quad (2.37)$$

The resulting polysulfides have high molecular weight, and are inert to organic solvents with good weatherability and aging properties. The reduction of high molecular weight polymer in reactive liquid results oligomers which is terminated with sulfuryl groups [35].

Remarkable progress has been made recently on the synthesis of polysulfide polymers by other routes, such as ring-opening polymerization of cyclic polysulfide as well as addition and condensation copolymerization of elemental sulfur.

For ring-opening polymerization , only three and four membered monomers, thrianes, and thietanes, respectively, are able to polymerize. Polymerization proceeds via both ionic and cationic mechanism and is particularly irreversible [36,37]. Only tetrafluorothiirane polymerizes radically [38].

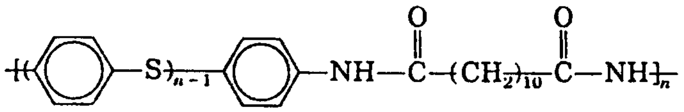
Anionic polymerization can initiate with alkali metals or their complexes with alcohol, thiol or amide.



$$+ \ CH_3OK \longrightarrow CH_3O\text{-}CH_2\text{-}C(CH_3)H\text{-}S^- \ K^+ \qquad (2.38)$$

The living site can be terminated with appropriate compound.

The most widely used synthetic route for the preparation of polysulfide polymers is based on the reaction between dihalide and sodiumpolysufide as an example of polycondensation reaction [39,40]. Polyamides can be similarly obtained by condensation of (4-aminophenyl-w-aminopoly(thio-1,4- phenylene) with 1,12-dodecanedionic acid catalyzed by $P(OC_6H_5)_3$ in N-methylpyyrolidone-quinoline [41].



(2.39)

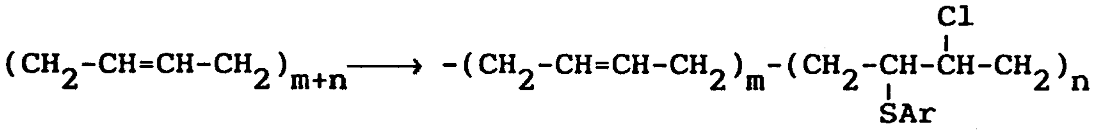
Glass-transition temperatures of polymer increase with increasing poly(phenylenesulfide) content [42].

Only methods such as oxidative coupling of thiols are used only rarely [43,44]. But reductive coupling of acryldisulfonyl halide and acids results in poly(arylenedisulfide)s in good yield.

$$X\text{-}R\text{-}Y \longrightarrow -(R\text{-}S\text{-}S)_n- \qquad (2.40)$$

$X{=}{-}SO_2Cl \quad Y{=}{-}SO_2F \quad R{=}1,4\text{-phenylene}$

The introduction of sulfide groups into polymers usually improves some physical and chemical properties such as thermostability and solubility. In order to enhance the solvent resistance of rubbers, cis-1,4-polybutadiene has been modified with p-toluenebenzenesulfenyl chlorides [45,46].

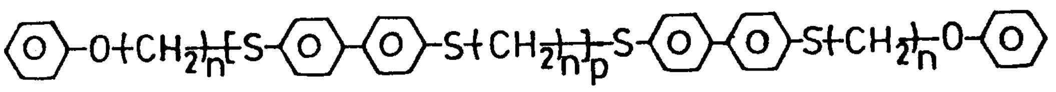


$$(CH_2\text{-}CH{=}CH\text{-}CH_2)_{m+n} \longrightarrow -(CH_2\text{-}CH{=}CH\text{-}CH_2)_m\text{-}(CH_2\text{-}\underset{\displaystyle SAr}{CH}\text{-}\overset{\displaystyle Cl}{CH}\text{-}CH_2)_n$$

$Ar = p\text{-}CH_3C_6H_4,\ C_6H_5$ (2.41)

The overlap of d-orbitals of the sulfur atoms in the modified polymer unit with π-orbitals of the neighbouring unreacted double bond activates the later and may thus be responsible for the block structure of the polymer [46].

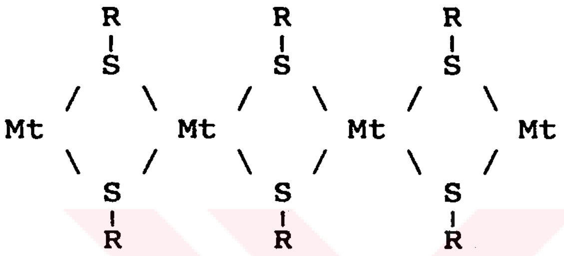
Some of the aliphatic aromatic mixed polysulfides exhibit liquid crystaline properties. Shaffer and his co-workers were prepared a polymer from bisbenzenthiol and polymethylene dihalide. This polymer has lower transition temperatures and broader mesophase thermal stability than other polyesters [47].


(2.42)

II.5.1 Organometallic Polymers Containing Sulfur

Various metals belonging to the 1B, 11B, 1VA, V111A groups of the periodic table form covalent or coordination bonds with divalent sufur. This ability is used in the separation of metal ions by maens of their fixation on a sulfur containing polymer. Both mono and bidantate ligands bearing sulfur atoms give polymer metallic salts or complexes. The presence of readily polarizable sulfur atoms confers electro-conductivity. Other polymers belonging to this class exhibit catalytic activity due to their polynuclear structure and can be used as models of metalloenzymes. Insolubility in common inorganic and organic solvents is a common property of polymers containing sulfur-metal linkages in the main chain and precludes their precise characterization (micro structure molecular weights, etc.).

Reactions of both mono and polythiols or their derivatives with transition metal salts or complexes is a versatile method of preparation of coordination polymers. Thus it was proposed as early as 1935 that palladium mercaptides have linear polymeric structure [48]. The square planar structure as proposed for diamagnetic insoluble Ni(11) thiolates [49].

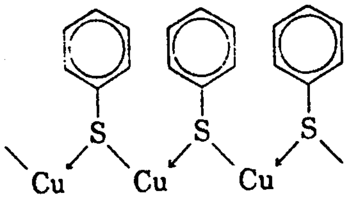


Mt = Pd, Ni

R = C_2H_5, C_6H_5

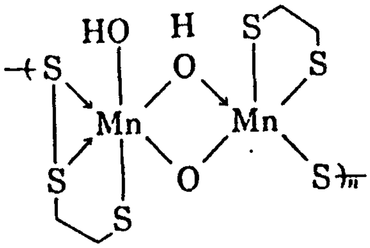
(2.43)

More recently a number of sulfur bridged polymers have been prepared by reactions of metallic derivatives (eg. cupric or cuprous chloride, mercuric chloride, silver acetate, lead acetate or niceltetracarbonyl) with 1,4- benzenedithiol at elevated temperature [50].



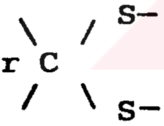
(2.44)

Manganese-dithiolate coordination polymers has catalytic activity to this polynuclear complex which was obtained by the reaction of potassium permanganete with chelating thiols (eg. 1,2-ethanedithiol, 3,4-toluenedithiol) in aqueous ethanol [51].

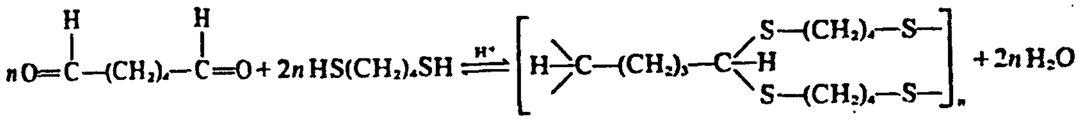


(2.45)

Sulfur containing polymers which can selectively bind mercury would furnish real advantages. The widespread occurrence of mercury as a pollutant in industrial wastes and the difficulties encountered in removing it with conventional ion exchange resins is one of these. Another application is found in the therapeutic use in mercury poisoning where such a resin could bind the mercury which precipitates in the enterohepatic circulation and remove it via fecel excreation [52]. Several types of chelating polymers have been described which are, in fact, effective in the toxic effects of mercury.

All of them contain sulfur, either as -SH groups or  groups [53].

This type of polymer can be prepared by the basic condensation reaction between dialdehyde and dithiol in the presence of HCl as catalyst. This reaction type previously used to prepare low molecular weight chelating agents with a high selectivity for mercury(II).



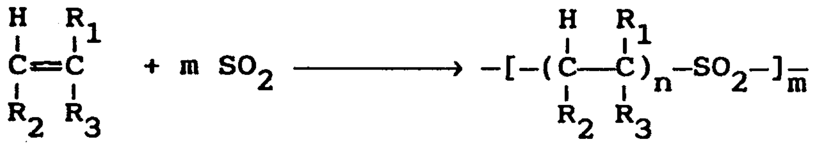
(2.46)

This polymer, under similar conditions can bind only small amount of Cu(11), Pb(11), Ni(11) or Co(11) ions. The selectivity to Hg(11) can be explained by soft acid, base interaction which was first explained by Pedersen [54].

II.5.2. Polysulfones

Both alifatic and aromatic polysulfones have important applications. Poly(arylene sulfone)s belong to the class of high performance engineering thermoplastics that retain useful mechanical properties up to about 473 K. Their thermal and oxidative stability is due to the presence of the sulfonyl group. Polymers with analogous structure, but containing other groups and bringing aromatic moieties, have inferior high temperature characteristics.

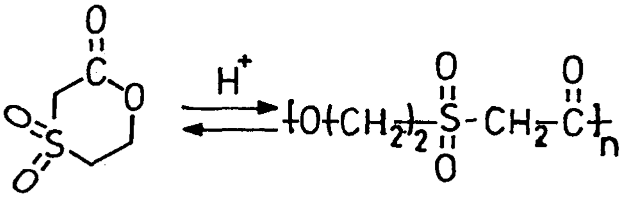
Olefin-sulfurdioxide copolymers (poly(olefin-sulfone)s, poly(alkylenesulfone)) are obtained by free radical reaction of olefins with sulfurdioxide. In principal class, the hydrocarbon and sulfonyl residues alternate, as shown below [55].



$$\underset{R_2\ \ R_3}{\overset{H\ \ R_1}{C{=}C}} + m\ SO_2 \longrightarrow -[-(\underset{R_2\ \ R_3}{\overset{H\ \ R_1}{C{-}C}})_n-SO_2-]_{\overline{m}} \qquad (2.47)$$

Second method of preparation is oxidation of polysulfide. Atactic poly(olefin sulfone) has been prepared from atactic polyepisulfide and polysulfone with one, two or more than two main chain carbon atoms per alkyl residue are obtained [56].

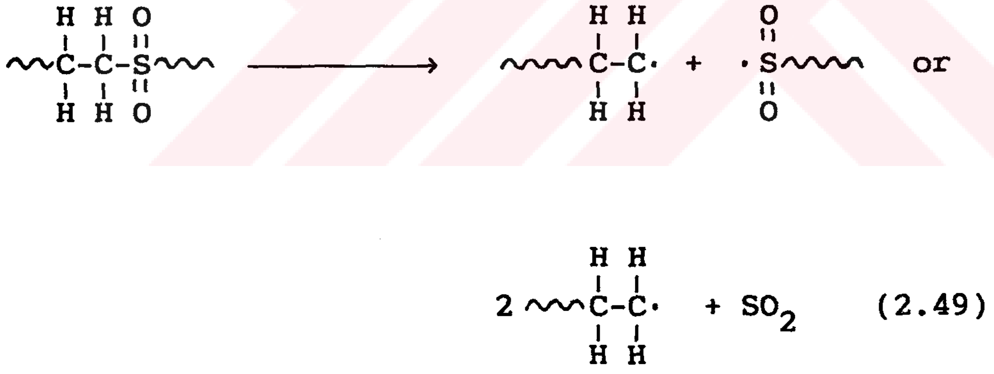
A poly(alkylsulfonylester) is formed by opening the cyclic monomer with an acidic catalyst [57].



(2.48)

The polysulfones of ethylene, propylene, butadiene, and other dienes as well as poly(methylene sulfone)s dissolve in strong acids. Poly(1,4-decaline sulfone) and poly(methylene sulfone)s are resist to alkalis, but poly(olefin sulfone)s have the characteristic susceptibility to alkalis, of β-disulfones [58]. Liquid ammonia, aqueous sodium hydroxide, and amines degrade poly(olefin sulfone)s to cyclic disulfones. The thermal stability of poly(butadiene sulfone) increased by hydrogenetion of the double bonds and that of poly(1,3- cyclohexadiene sulfone) is increased by aromatization [59].

The radiation chemistry of poly(olefine sulfones) has attracted the interest of researchers during the past decade, because this class of polymers was found to exhibit rather high radiation sensitivity in terms of main-chain rupture [60]. Radiation chemical yields for main-chain scission of the order of G(S)=10 scission per 100 eV where determained for poly(olefin sulfones) such as poly(butene-1-sulfone) and poly(hexene-1-sulfone). These results, together with the fact that radiation induced main-chain rupture initiates depolymerization in many cases even at room temperature, were the basis for intense studies aimed at employing poly(olefin sulfones) as highly sensitive resist materials in electron beam and X-ray lithography [61,62]. Upon free radical polymerization , many olefines, such as butane-1 or hexene-1, form alternating 1:1 copolymers with sulfur dioxide having the base unit $-CH_2-CHR-SO_2-$. From the results of the studies mentioned above it was inferred that, under the influence of high energy radiation, C-S bonds are split preferentially to C-C bonds as shown below [63,64].



$$\sim\!\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\underset{O}{S}}\sim\!\sim \longrightarrow \sim\!\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\cdot + \cdot\overset{O}{\underset{O}{S}}\sim\!\sim \quad \text{or} \quad 2\sim\!\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}\cdot + SO_2 \qquad (2.49)$$

Olefine sulfone copolymers and methylmethacrylate and β-substituted acrylate copolymers have been investigated as e-beam positive resist [65]. Compared with olefine sulfone copolymers, acrylate- and methylacrylate-based polymers have excellent film-forming properties but lower sensitivities.

CHAPTER III. EXPERIMENTAL

III .1. Materials

III.1.1. Purification of Materials

III.1.1.1. Trioxane (Aldrich)

It is crystalized from sodium-dried diethylether and dried in air. Drying in an oven or vacuum was delibaretly avoided since it sublimizes easily.

III.1.1.2. 2,2'azobis(isobutyronitrile) (AIBN) (Aldrich)

It was recrystalized from methanol. Dried under vacuum and stored in a refrigerator.

III.1.1.3. Styrene (Petkim)

Washed with 5% NaOH to remove inhibitors, then with water, dried with $CaCl_2$ several hours and distilled under reduced pressure ($50^oC/25mmHg$). Middle fraction was collected and freshly used.

III.1.1.4. Methylmethacrylate (AkrilKimya)

Washed with 5% NaOH to remove inhibitors, then with water, dried with $CaCl_2$ and distilled under reduced pressure (46°C/100mmHg) middle fraction was collected, freshly used.

III.1.1.5.Tetrahydrofuran(Merck)

Refluxed over KOH to remove peroxides and then distilled over sodium wire (66.5 ℃/760 mmHg).

III.1.1.6. Dichloromethane (Merck)

Shaken with portions of conc. H_2SO_4 until acid phase became colorless, then washed successively with water, aq. 10% Na_2CO_3 and water. Dried with $CaCl_2$ and distilled over $CaCl_2$ (40 $^{\circ}$C) and stored over 4 A molecular sieve.

III.1.1.7. Dimethyl Sulfoxide(Merck)

Dried with CaH_2 and peroxides were removed and then distilled over wire (76.5-75.8 $^{\circ}$C/mmHg), and stored over 4 A molecular sieve.

III.1.1.8. Dioxane

It was shaken with KOH solution, until inorganic phase is no more black. Organic phase distilled over sodium. Middle fraction was collected and stored over 4 A molecular sieve.

III.1.1.9. Benzene (Merck)

Purified by shaking with conc. H_2SO_4, then washed with dilute NaOH solution and water, dried with $CaCl_2$ and then distilled over sodium wire (80.1°C/760mmHg).

III.2.Preparation of Materials.

III.2.1. Preparation of β',β(ethylenedithiol)diproionitrile (EDP)

In a 250 ml. two-necked flask fitted with a reflux condenser and a $CaCl_2$ drying tube, freshly prepared 200mgNaOEt, 9.4 g. (0.1 mol) ethanedithiol in 50 ml. dioxane were placed and kept in an ice-water bath. From a dropping funnel 11.2 g. (0.21 mol.) acrylonitrile was added dropwise in 30 min.. The temperature of the mixture increased during this addition. The mixture was then precipitated in water. Recrystallization from benzene gave white crystals (yield 18.9 g. 91 %) mp. 92 °C. IR spectrum of this compound is shown in Fig.3.1

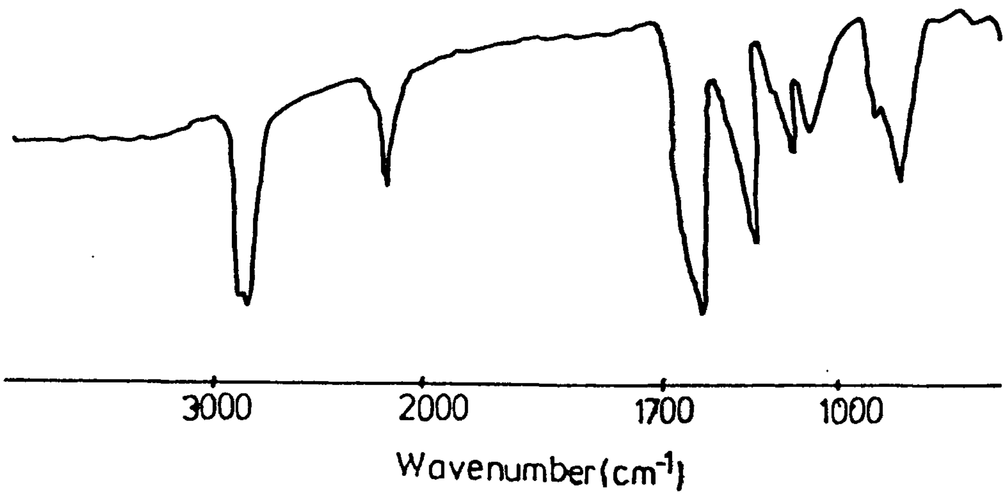


Fig. 3.1 IR Spectrum of EDP.

III.2.2. Preparation of β,β′ (ethylendisulfone) dipropionitrile (EDSP).

0.5 g. β,β′(ethylenedithio)dipropionitrile was dissolved in 10 ml. dioxane and 2 ml. 30 % H_2O_2 was added dropwise. The mixture stirred overnight while the product precipitates. Solubility of the product decreases by cooling. Therefore solution was first cooled then filtered off, washed with cold dioxane and ether then dried under vacuum. Yield is 46% , mp.127 ^oC.

III.3. Techniques

III.3.1. Polyamidation

Polymerization of 2,2'azo bis(isobutyronitrile) with formaldehyde was carried out as follows. Trioxane (0.15 g ,0.0017 mol.) was dissolved in a given amount of 95% sulfuric and AIBN (0.88 g., 0.005 mol.) were added with vigorously stirring over a period of 10 min. at 0 ^oC. Rapid polymerization occursimmadiatelly after the addition of AIBN and the viscosity of the solution increased gradually during the polymerization process. After 90 min the solution was poured into ten-fold excess water or acetone. The resulting polymer was filtered and dried under vacuum at room temperature.

Polyamidation of 2,2'azobis(cyclohexanonitrile), β,β′(ethylenedithio)dipropionitrile, β,β′ (ethylene-disulfone)dipropionitrile with trioxane was carried out in a similar ways.

III.3.2. Free Radical Polymerization

Polymerization of styrene and methylmethacrylate using polyamide, which was obtained from AIBN and trioxane as macro azo-initiator was studied.

Polymerization was carried out in a tube, which has appropriate volume for solvent and monomer, with standart socket joint for connection to the high vacuum line. Given amount of azo-containing polyamide was dissolved in dimethyl sulfoxide-dichloromethane mixture which is 1:1 by volume and required volume of freshly distilled styrene or methylmethacrylate is added to the tubes. Then tubes were connected to the high vacuum system by means of manifold with standart sockets. It is shown in Figure 3.2.

Polymerization tubes are immersed in a Dewar flask, which contains liquid nitrogen, to froze content. After their contents are frozen, they are degassed about 5 min., then let it to melt. Freeze-thaw technique is repeated three times before sealing tubes. These samples are polymerized by placing them into a constant temperature bath at 60 ^{o}C. After the required time, the tubes are quickly immersed into the cold water bath and are opened by applying hot point. The content of samples are poured into the ten-fold excess amount of methanol to precipitate polymers. The resultant polymers are filtered off and dried in a vacuum and weighted.

The % conversion can be calculated from the equation which is indicated below.

$$\% \text{ Conversion} = \frac{\text{Weight of obtained polymer (g.)}}{\text{Weight of monomer (g.)}} * 100 \qquad (3.1)$$

III.3.3. Thermal Degradation of Azo-Containing Polystyrene

The thermal degradation experiments were also carried out in sealed tubes. 50 mg. azo containing polystyrene was dissolved in 5 ml. benzene, and then excess amount of N,N diphenylpicrylhydrazyl (DPPH) (2 mg.) added to the tubes as radical scavenger. Tubes were degassed with freeze-thaw technique , sealed and finally immersed into a constant temperature bath at 70 °C. A great care must be taken to prevent illumination of tubes from light. At the end of given time, tubes are opened and poured into excess amount of methanol to precipitate the polymer. The resultant polymers are filtered off and washed with methanol to get rid off excess DPPH and dried in a vacuum. Molecular weights of polymers were determined with gel permeation chromatography (GPC).

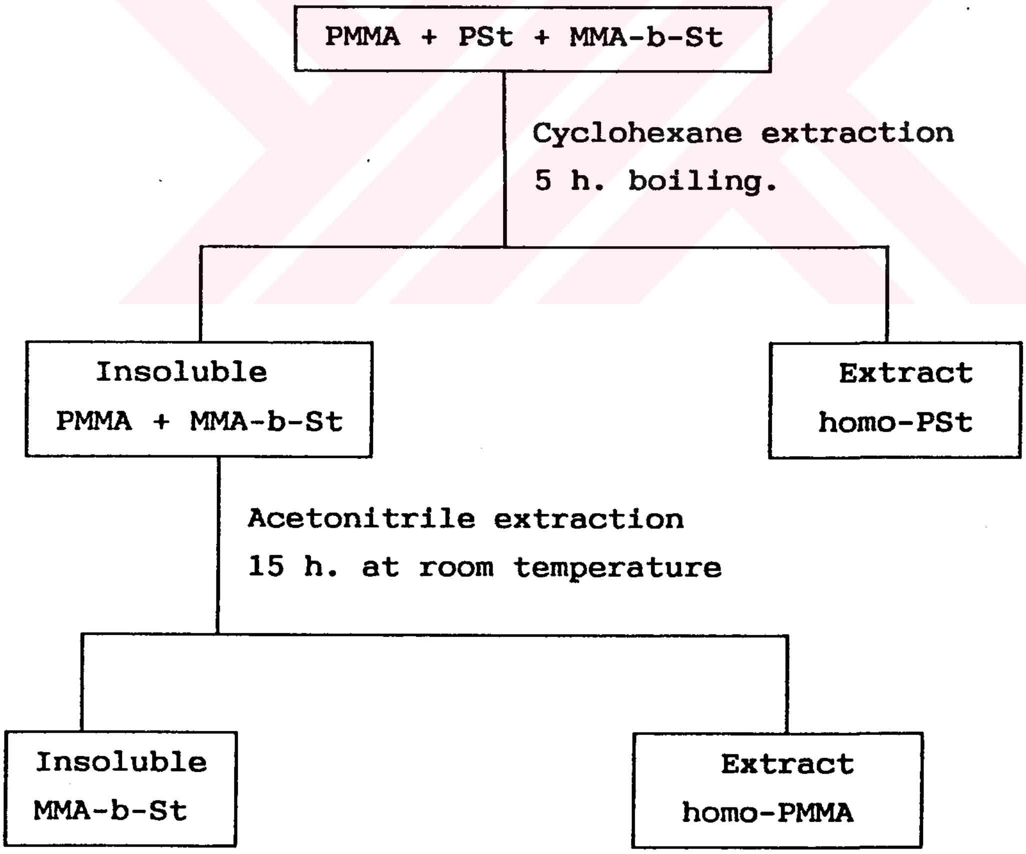
III.3.4. Free Radical Block Copolymerization

Appropriate solutions of obtained prepolymers (azo containing polystyrene or polymethylmethacrylate and monomers (methylmethacrylate or styrene) were placed in a polymerization tube, followed by degassing in the usual manner and then sealed. Tubes are immersed in constant temperature bath at 70 °C. At the end of given time, polymer solution was precipitated into methanol. The mixture of block copolymer and homopolymers were separated by successive extraction in boiling cyclohexane and acetonitrile according to the scheme 3.1.

Then the extracted homopolymers and block copolymer were precipitated in methanol dried under vacuum, and weighed, composition of polymers, molecular weights were determined by ^{1}H NMR and GPC, respectivelly.

Scheme 3.1

Purification of Copolymer



III.3.5. Interaction of Poly(amidethioether) with Metal Ions.

The solution of metal salts ($Zn(Ac)_2$, $Cd(Ac)_2$ and $Hg(Ac)_2$) was prepared in N-methylpyyrolydone so as the concentration of these metal salts 10^{-3} M. 2 ml. of these metal salt solutions were added to 2 ml. solution of poly(amidethioether) (5.10^{-4} g/l in N methylpyyrolidone) at room temperature. The temperature was then raised to 70 °C. In the case of mercury salt, yellow colored precipitate formed immediately. In the other cases, the solutions became only slightly cloudy. Subsequently, metal binded polymers were filtered off. The concentration of Hg(11), Zn(II), and Cd(11) ions in the remaining solution was determined by spectroscopic measurements.

UV measurements were used to determine the concentration of Hg(II) ions. For this purpose $0.65.10^{-3}$M dithione solution was prepared in NMP, red colored complex observed after addition of mercury ions containing poly(amidethioether) solution.

Atomic absorption method was used to determine the concentration of free zinc and cadmium ions in the solution. For this purpose, filtered solutions was diluted and directly injected to the atomic absorption instrument.

III.4. Apparatus

III.4.1. High Vacuum System

A pyrex high vacuum line contains, B-14 sockets, mercury diffusion pump, Edwards two stage rotary oil pump and two liquid nitrogen traps, one between diffusion pump and manifold, the other between diffusion and backing pumps. The vacuum obtained is usually about 10^{-4} torr. Schematic representation of high vacuum system is shown in Fig. 3.2.

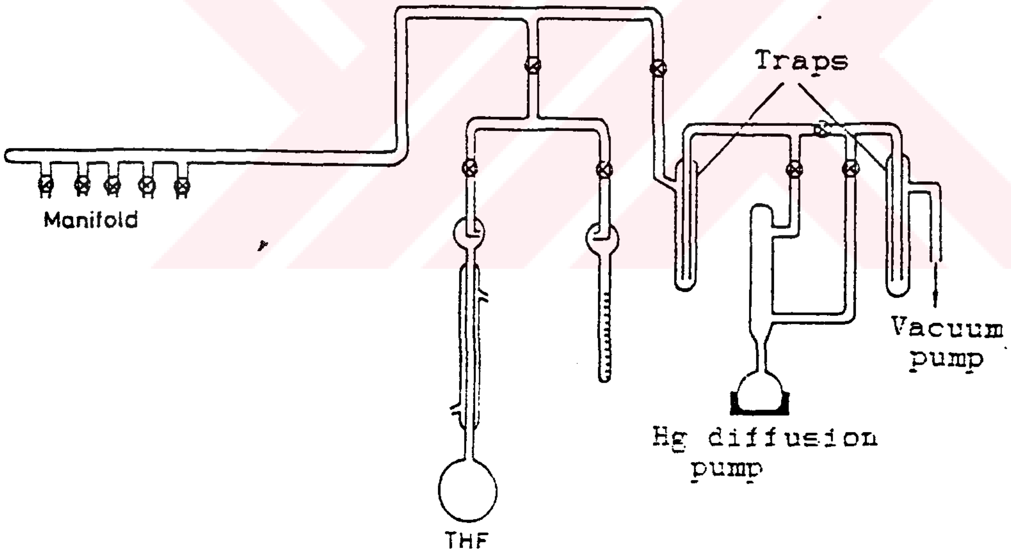


Figure 3.2. Schematic representation of high vacuum system.

III.4.2. ^{1}H-NMR Spectroscopy

^{1}H-NMR spectra were recorded on Varian EM 390 , Bruker SD 1823 in $CDCl_3$, CD_2Cl_2 or DMSO-d_6, using tetramethylsilane as internal standard.

III.4.3. IR Spectroscopy

IR spectra were recorded on Jasco FT-IR 5300 and Shimadzu IR-400 using KBr discs.

III.4.4. UV Spectroscopy

UV spectra were recorded by Shimadzu UV 160 A using N-methylpyyrolidone as a solvent.

III.4.5. Atomic Absorption

Atomic absorption measurements were made with Beckman Model 1272 flame atomic spectraphotometer.

III.4.6. Differential Scanning Calorimetry

Perkin-Elmer DSC-II type instrument was employed to determine melting and thermal decomposition of azo-containing polyamide and other related compounds. Approximately 1 mg. of sample was put directly to the standard aluminum pan. Nitrogen gas passed over the sample holders during the measurements with a rate of 20 ml/min and heating rate of 8 ^{o}C/min.

III.4.7 Viscosity Measurements

Canon-Fenske viscosimeter was used for this purpose. The concentration of the polymer solution was 1 g/dl in DMSO/CH_2Cl_2 mixture at 25 C.

Viscosity was calculated from the equation below [66,67].

$$\eta_{sp} = \frac{t-t_o}{t_o} - 1 \qquad (3.2)$$

t = flow rate of the polymer solution.
t_o = flow rate of the solvent.

III.4.8. Gel Permeation Chromatography

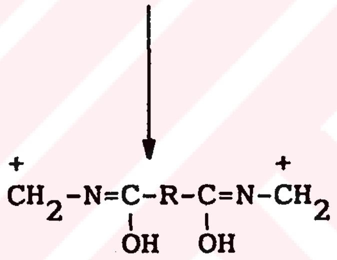
The $\bar{M}_n$ values of obtained polymers, which can dissolve in THF, were calculated from GPC according to polystyrene standard samples, using Knauer M-64 Instrument and THF as eluent at flow rate of 1ml/min. at 20 min.. One Shodex-GPC/A- 803 and two Ultrapac Coloumn 2139-560 columns were used for measurements.

CHAPTER IV. RESULTS AND DISCUSSION

New azo-containing polyamides were synthesized by the reactions of trioxane with 2,2'-azobis(isobutyronitrile) or 2,2'-azobis(cyclohexanonitrile). The reaction mechanism is shown below.

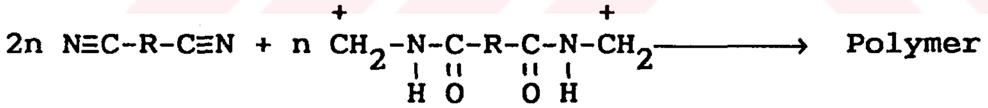
$$CH_2O + H^+ \longrightarrow OH-\overset{+}{C}H_2 \qquad (4.1)$$

$$2\ OH-\overset{+}{C}H_2 + N\equiv C-R-C\equiv N \longrightarrow OH-CH_2-N=\overset{+}{C}-R-\overset{+}{C}=N-CH_2-OH \qquad (4.2)$$



$$\overset{+}{C}H_2-N=\underset{OH}{C}-R-\underset{OH}{C}=N-\overset{+}{C}H_2$$

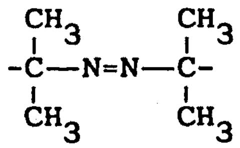
(4.3)



$$2n\ N\equiv C-R-C\equiv N + n\ \overset{+}{C}H_2-\underset{H}{N}-\underset{O}{\overset{}{C}}-R-\underset{O}{C}-\underset{H}{N}-\overset{+}{C}H_2 \longrightarrow \text{Polymer}$$

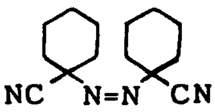
(4.4)

R: In the case of AIBN



$$-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-$$

In the case of V-40



Results of polymerization in various molar ratios of sulfuric acid and AIBN are summarized in Table 4.1.

Table 4.1. Polymerization of AIBN with Trioxane in H_2SO_4[a]

CODE	H_2SO_4/AIBN (mol/mol)	Trioxane (mol)	Yield (%)	$\eta_{sp/c}$[b] (dl/g)
PA-1	5	0.0017	51.01	-
PA-2	10	0.0017	48.02	2.3
PA-3	15	0.0017	32.36	1.5
PA-4	20	0.0017	40.81	0.7
PA-5	25	0.0017	32.58	0.09

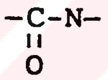
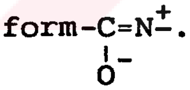
a : Temperature $^{o}0$ C, reaction time 60 min.
b : Measured at 25 ^{o}C in DMSO/CH_2Cl_2 (1/1, v/v).

As can be seen from the Table 4.1, the yield of polymerization and molecular weight of the polymers increased by increasing concentration of AIBN in sulfuric acid.

The resultant polyamides, which were prepared from AIBN and trioxane, were soluble in sulfuric acid, formic acid, m-cresol a mixture of DMSO/CH_2Cl_2 (1,1;v,v), and partially soluble in acetone.

All amides show a carbonyl absorption band known as the Amide I band. Its position depends upon the degree of hyrogen bonding, and thus on the physical state of the compound. The C=O absorption of amides occurs at longer wavelengths than "normal" carbonyl absorbtion due to the resonance effect. Secondary amides have strong Amide I band in the region 1650 cm^{-1} when examined in the solid state.

Primary amides show two N-H stretching bands resulting from symmetrical and asymmetrical N-H stretching. Secondary amides and lactams show only one N-H stretching band. As in the case of O-H stretching, the frequency of N-H stretching is reduced by hydrogen bonding, through to a lesser degree.Overlapping occurs in the observed position of N-H and O-H stretching frequencies so that an unequivocal differentiation in structure is sometimes impossible. For secondary amide N-H stretching band appears at about 3320 cm^{-1}.

Amides, pyrroles, and indoles absorb from $\delta \sim 8.5$,to $\delta \sim 5.0$; the effect on the absorbtion position of concentration, solvent, and temperature is generally smaller than amines. The nonequivalance of protons on the nitrogen atom of primary amide and the methyl groups of N,N-dimethylamides is caused by hindered rotation around the  $-\underset{\underset{O}{\|}}{C}-N-$ bond because of the contribution of the canonical form  $-\underset{\underset{O^{-}}{|}}{C}=N^{\pm}-$.

The infrared and ^{1}H-NMR spectra of polyazoamides were recorded by using KBr disc and by dissolving in $CD_2Cl_2/DMSO-d_6$ respectivelly. The related spectra are shown in Figures 4.1 and 4.2.

The polyamide structure was easily characterized by strong -NH streching band appearing at 3300 cm^{-1}, and C=O streching band at 1650 cm^{-1}, N=N streching band at 1500 cm^{-1}. The spectra of C≡N are characterized by weak to medium absorption in the triple bond stretching region at 2200cm^{-1}. The disappearance of nitrile absorption band shows us that all nitrile functions consumed in the reaction.

The NMR spectrum of polymer displays signals at 1.2 ppm(-CH3= c), 3.9 ppm (-CH2= a), 8.5 ppm (-NH= b).

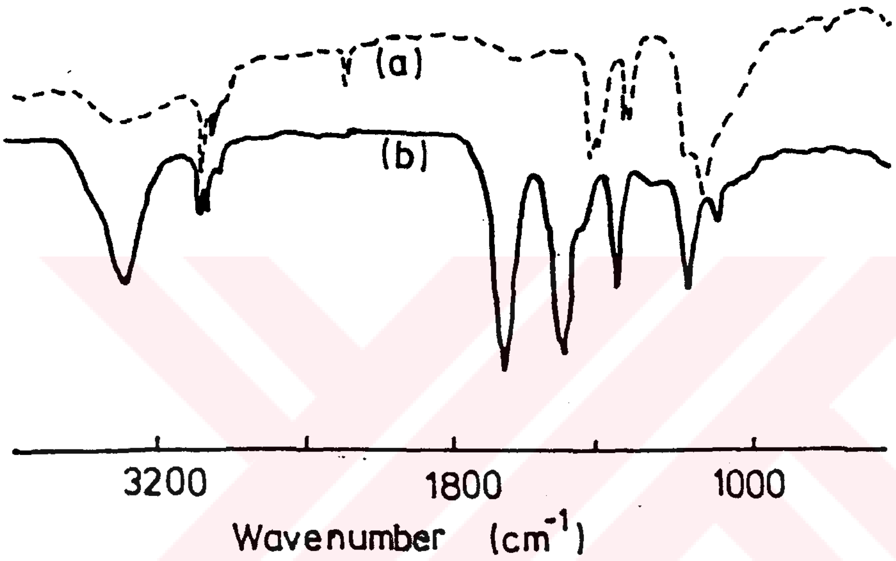


Figure 4.1 Infrared spectra of (a) AIBN (----) and (b) polyamid obtained from AIBN(——).

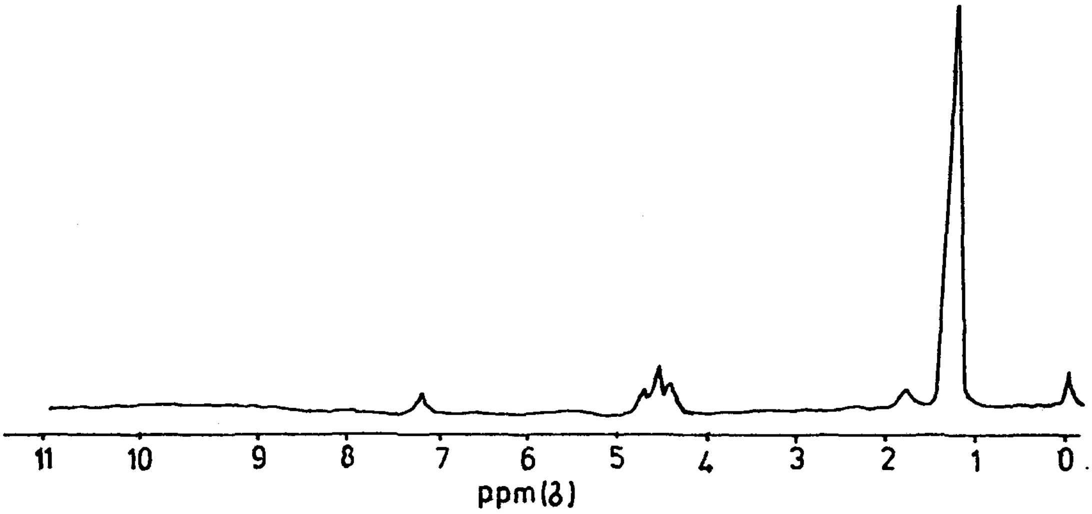


Figure 4.2 ^1H NMR spectrum of polyamide obtained from AIBN.

Decomposition of the azo-containing polyamides were studied by DCS. Fig.4.3 shows typical DSC trace for the decomposition. As can be seen from the figure, polyamide melts at 415 K (142 ^{o}C), decomposition rate constant for polyamide could not be clearly determined due to the interferance of secondary reactions observed in the studied temperature range.

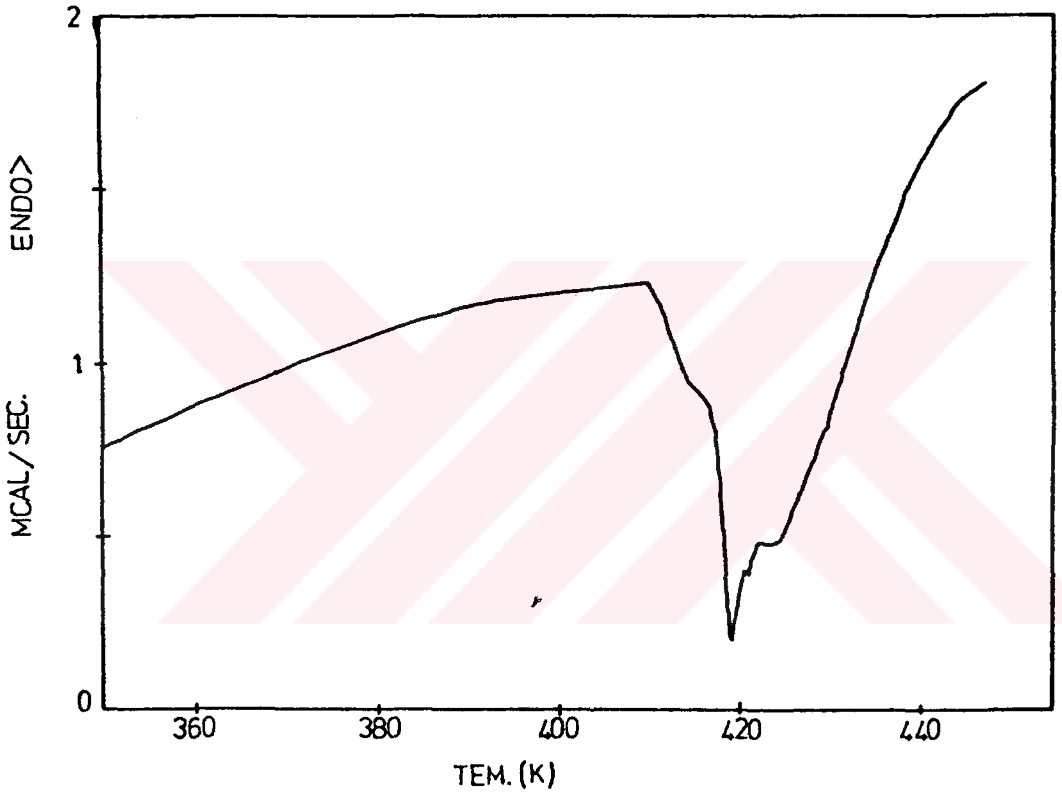


Figure 4.3 DSC trace for the decomposition of polyazoamide

The other polyamide, which was obtained from the reaction between trioxane and V-40, has similar spectral properties. IR and ^{1}H-NMR spectra are shown in Figure 4.4 and 4.5.

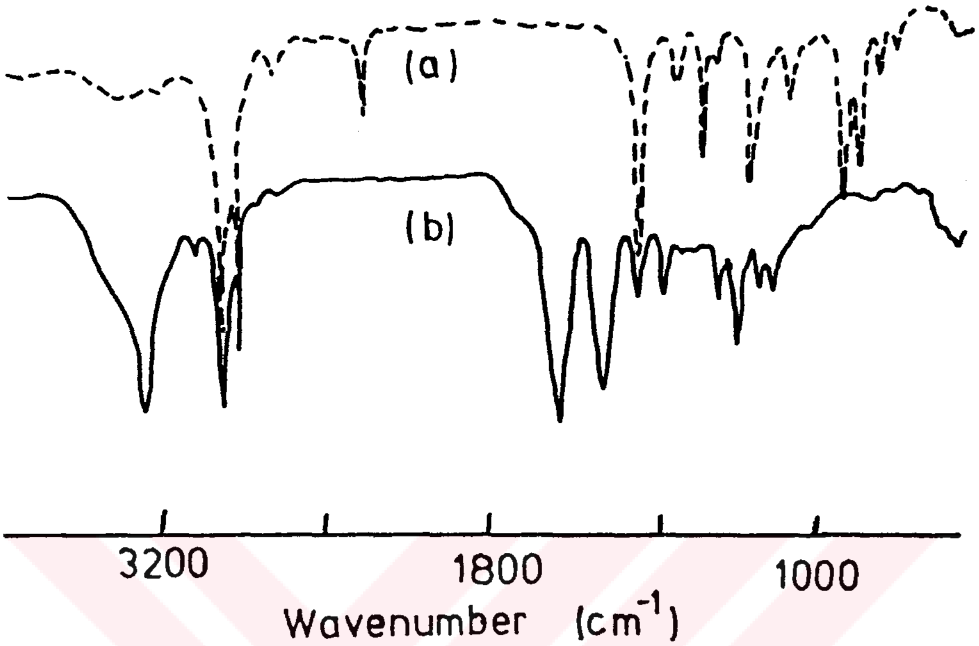


Figure 4.4 Infrared spectra of (a) V-40 (-----) and (b) polyamide obtained from V-40 (———).

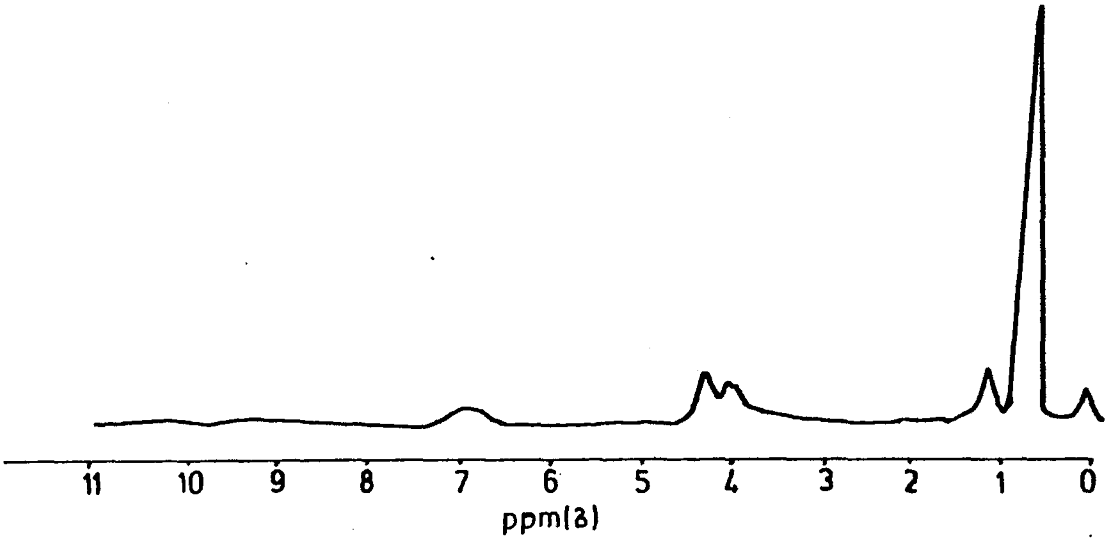


Figure 4.5 ^{1}H NMR spectrum of polyamide obtained from V-40.

IV.1. The Use of Polyazoamide for Free Radical Polymerization

Azo-containing polyamide was used to initiate the polymerization of styrene or methylmethacrylate. It is observed that PA-2 has higher viscosity than the other polyamides. For this reason PA-2 was used as polymeric azo initiator throughout the work so as to increase labile N=N groups.

Styrene and methylmethacrylate were used as representative monomers to test the efficiency of polyamide for initiating capability in free radical polymerization. Results are collected in the Table 4.2.

Table 4.2. Polymerization of St and MMA initiated by PA-2.

Monomer (mol/l)	[PA-2] (g/l)	Conversion (%)	$\eta_{sp/c}^{a}$ (dl/g)	$\bar{M}_n.10^{-5}$	$\bar{M}_w/\bar{M}_n$
St [4.5]	10	7.39	0.41	0.943	1.48
St [6.8]	10	4.34	0.53	1.131	1.59
St [6.8]	5	4.31	0.68	1.276	1.66
MMA [4.5]	10	37.07	0.53	2.017	1.72
MMA [6.7]	10	30.75	0.59	2.618	2.01
MMA [6.7]	5	27.47	0.74	4.987	1.34

a : Measured at 30 ^{o}C in toluene.

Molecular weight of polymers increases with decreasing initiator concentration, as expected in these process.

For the detailed investigations on the effect of the polymerization conditions and on the number of azo groups in the resultant polymers, several experiments were performed. The results are summarized in Table 4.3 and Fig.4.4.

Table 4.3 Polymerization[a] of Styrene with PA-2 at 60 ^{o}C.

Run	[M] (mol/l)	[PA/2] (g/l)	Time (min)	Conversion (%)	$\bar{M}_n.10^{-3}$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	8.48	10	30	3.16	43.9	2.66
2	8.48	10	60	7.53	70.9	2.01
3	8.48	10	90	16.93	54.1	2.17

a : in CH_2Cl_2/DMSO (1,1;v;v)

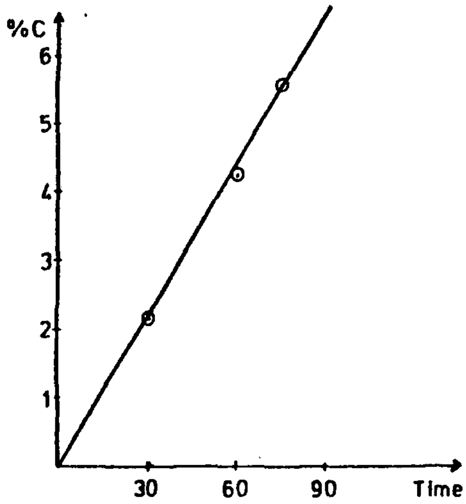
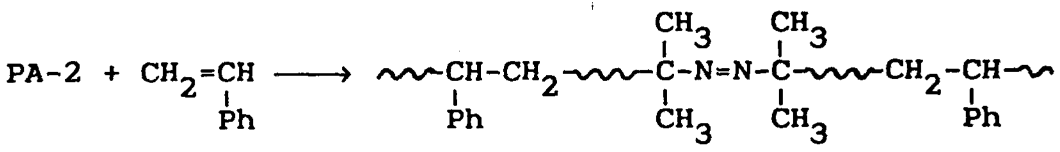


Figure 4.6 Time-conversion curves for the polymerization of styrene initiated by polyazoamide.

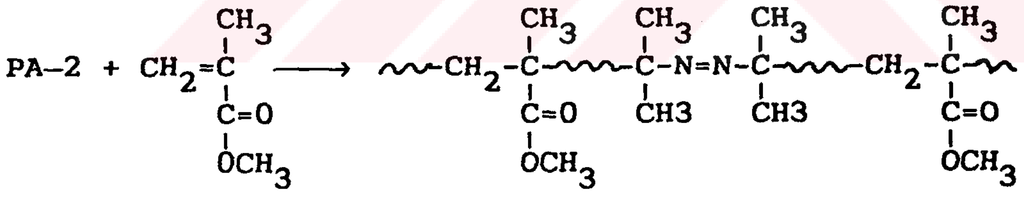
As can be seen from the Table 4.3 , the conversion of polymerization is directly propotional to the reaction time which is the typical aspect of radical polymerization.

The overall reactions of PA-2 with styrene and methylmetacrylate are shown separetly below.



$$\text{PA-2} + CH_2{=}\underset{Ph}{CH} \longrightarrow \sim\!\underset{Ph}{CH}-CH_2\sim\!\underset{CH_3}{\overset{CH_3}{C}}-N{=}N-\underset{CH_3}{\overset{CH_3}{C}}\!\sim CH_2-\underset{Ph}{CH}\!\sim$$

(4.5)



$$\text{PA-2} + CH_2{=}\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}} \longrightarrow \sim CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}\sim\!\underset{CH3}{\overset{CH_3}{C}}-N{=}N-\underset{CH3}{\overset{CH_3}{C}}\!\sim CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}\!\sim$$

(4.6)

Azo groups present in the main chain of the resultant polymers may decompose upon heating as will be shown below.

IV.2. Thermal Decomposition of Azo-containing Polystyrene

As it is known for a design of the block copolymer, it is essential to synthesize a prepolymer having desired number of remaining scissible azo groups in the main chain since azo concentration regulates the segment length of sequences.

Azo group content in the polymer is expected to decrease with increasing polymerization time of styrene or methylmethacrylate. This was evidenced by studies on the thermal degradation of the resultant polymers. The thermolysis of the azo groups was almost complete after 5 hour heating at 70 °C. Fig.3.7, Table 4.4 summarize the thermolysis data of three azo containing polystyrene obtained at different polymerization times.

Table 4.4 Thermolysis of Azo-containing Polystyrene at 70 °C in benzene.

Run	$\bar{M}_{no} \cdot 10^{-3}$	$\bar{M}_{ni} \cdot 10^{-3}$	N_s
4	43.9	20.05	1.2
5	70.9	35.4	0.84
6	54.1	49.4	0.04

The number of azo groups which cause chain scissions per macromolecule can be calculated from the equation below.

$$Ns = \frac{M_{no}}{M_{ni}} - 1 \qquad (4.7)$$

$\bar{M}_{no}$ and $\bar{M}_{ni}$ indicate the number average molecular weights before and after thermolysis respectively. Molecular weight changes during the thermolysis are calculated by GPC. The GPC chromatograms are shown in Figure 4.8.

Number of azo group per molecule decreases significantly as the polymerization time increases. It should also be noted that molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of the polymer increases after thermolysis, indicating irregular location of scissible azo groups.

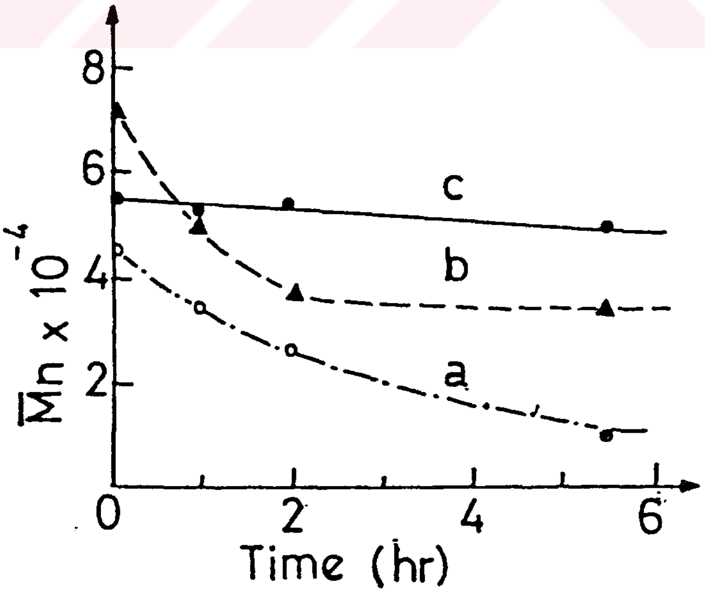


Figure 4.7 Thermolysis of Azo-containing Polystyrenes obtained from (a) Run 1, (b) Run 2, (c) Run 3.

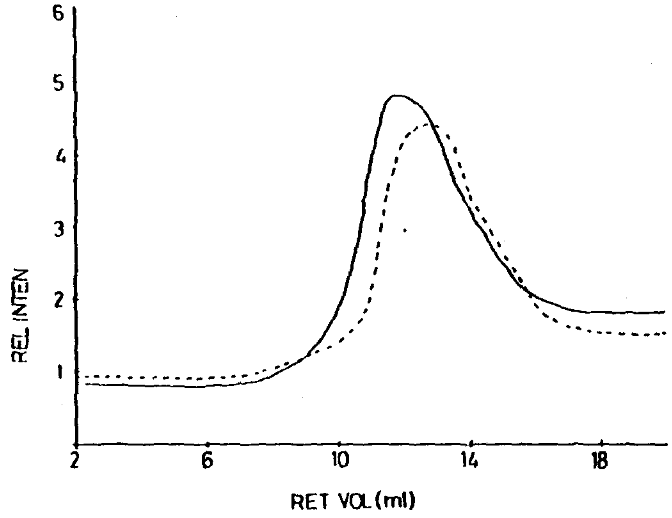
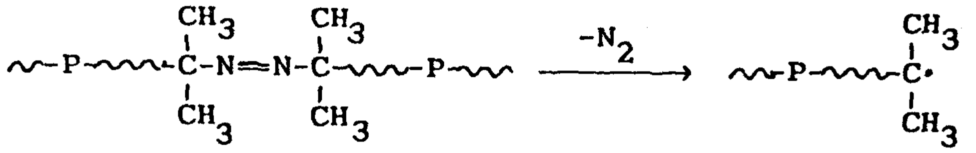


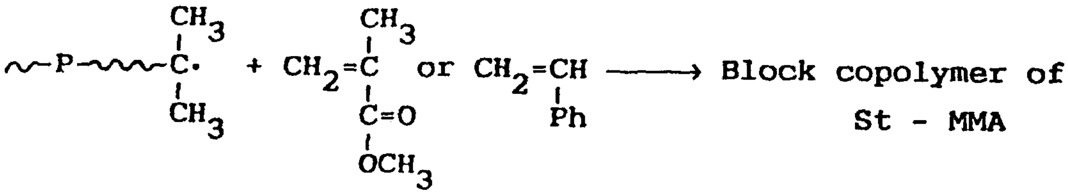
Figure 4.8 GPC Chromatograms of Polystyrene (a) Before thermolysis, (b) After thermolysis.

IV.3. Block Copolymerization by Using Polymeric Azo Initiator

The polymeric azo initiators were used in the synthesis of block copolymers. These second stage polymerizations were carried out in bulk. The main reactions involved in the block copolymer preparation with the azo containing polystyrene or methylmethacrylate are ;



$$\sim P \sim \underset{CH_3}{\overset{CH_3}{C}}-N{=}N-\underset{CH_3}{\overset{CH_3}{C}}\sim P \sim \xrightarrow{-N_2} \sim P \sim \underset{CH_3}{\overset{CH_3}{C}}\cdot \qquad (4.8)$$

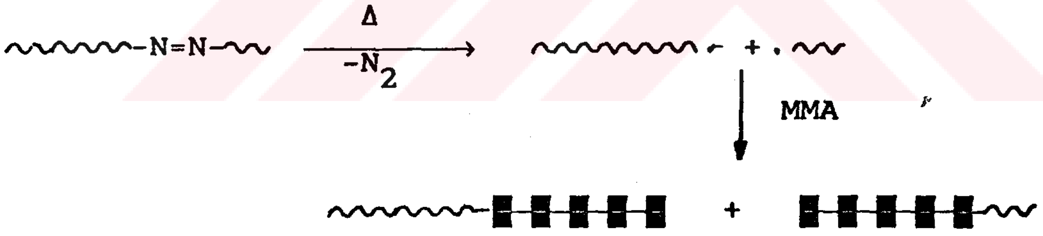


$$\sim P \sim \underset{CH_3}{\overset{CH_3}{C}}\cdot + CH_2{=}\underset{\underset{OCH_3}{C{=}O}}{\overset{CH_3}{C}} \text{ or } CH_2{=}\underset{Ph}{CH} \longrightarrow \text{Block copolymer of St - MMA}$$

P : Polystyrene or polymethylmethacrylate (4.9)

Typical results concerning block copolymerization of styrene and methylmetacrylate using azo containing polystyrene or polymethymethacrylate are presented in the Table 4.5.

Significant amount of homopolymers are formed. The formation of homopolymer increases with increasing polymerization time. Homopolystyrene formation may be due to the primary radical combination of polystyrene attached radicals in the block copolymerization step. Polystyrene molecules which for any reason fail to acquire labile azo groups during the synthetic procedure in the fist step also contribute to the presence of polystyrene. Rather low yield of block copolymer is probably resulted from the decomposition of randomly distributed azo group in the polystyrene chains. The overall reaction can be written as follows,



(4.10)

∿∿ : PSt segment ▮-▮-▮-▮- : PMMA segment

Block copolymers were freed from homopolymers by extraction method. Block copolymers which contain short polystyrene segments are expected to show solubility properties similar to homo polymethylmethacrylate. This was evidenced by spectral investigation of acetonitrile soluble portion of the

Table 4.5 Block copolymerization using azo-containing prepolymers of 70° in bulk.

Run	Prepolymer (g/l)	Monomer	Time (min)	Convertion (%)	Composition of the reaction mixture PSt (%)	PMMA (%)	PSt-b-PMMA (%)	Block copolymer composition PMMA (%)
7	PSt	MMA	60	3.6	45.1	36.4	18.5	77.6
8	PSt	MMA	120	7.4	50.1	45.1	4.8	83.3
9	PMMA	PSt	60	1.9	23.0	70.5	6.5	32.3
10	PMMA	PSt	120	2.3	30.1	60.1	9.7	26.7

reaction. GPC analysis clearly indicates this behaviour as well as the block copolymer formation. Fig.4.9 shows the GPC chromatograms recorded with the azo containing prepolystyrene and block copolymer extraction. The new peak at higher molecular weight is ascribed to the block copolymer. It is interesting to note the apperance of a new peak at lower molecular weight which may be attributed to the further decomposition product i.e. polystyrene with short chain. This peak shifted to higher molecular weight with longer reaction time indicating addition of methylmetacrylate units. These observations are entirely consistent with the assumption of random decomposition of the prepolystyrene.

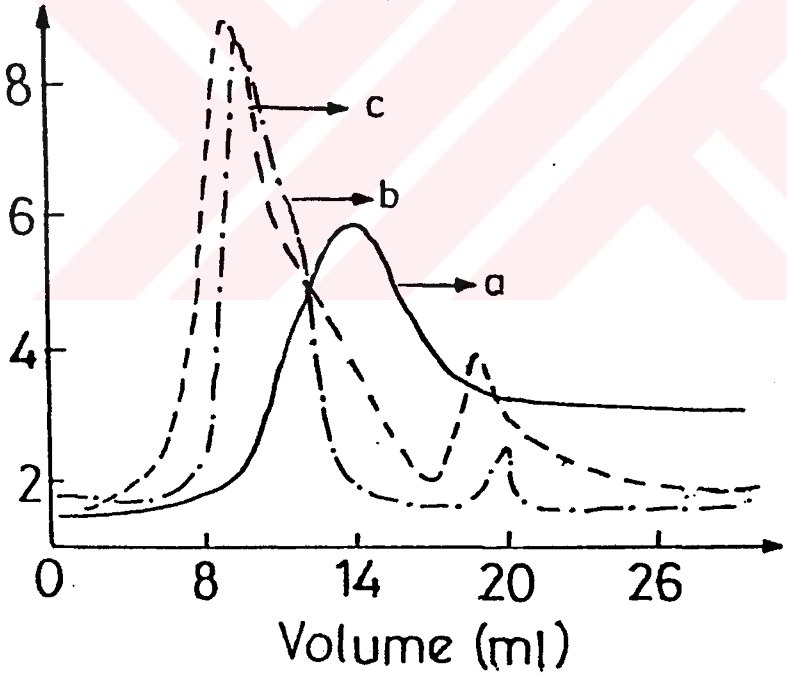


Figure 4.9 GPC Chromatogram recorded for the products formed on block copolymerization. (a) Azo-containing prepolystyrene (Run 2); (b) purified block copolymer (Run 7) (c) purified block copolymer (Run 8).

The Infrared spectrum of the purified block copolymer show characteristic bands of C=O from methylmetacrylate at 1720 cm^{-1} in addition to that of PSt at 690, 810, 2940 and 3040 cm^{-1}(aromatic and alifatic C-H bands). On the other hand, characteristic amide streching -NH band appears at 3300 cm^{-1}. This shows that the final block copolymer contains amide group which already exists in the prepolystyrene. It is shown in Figure 4.10.

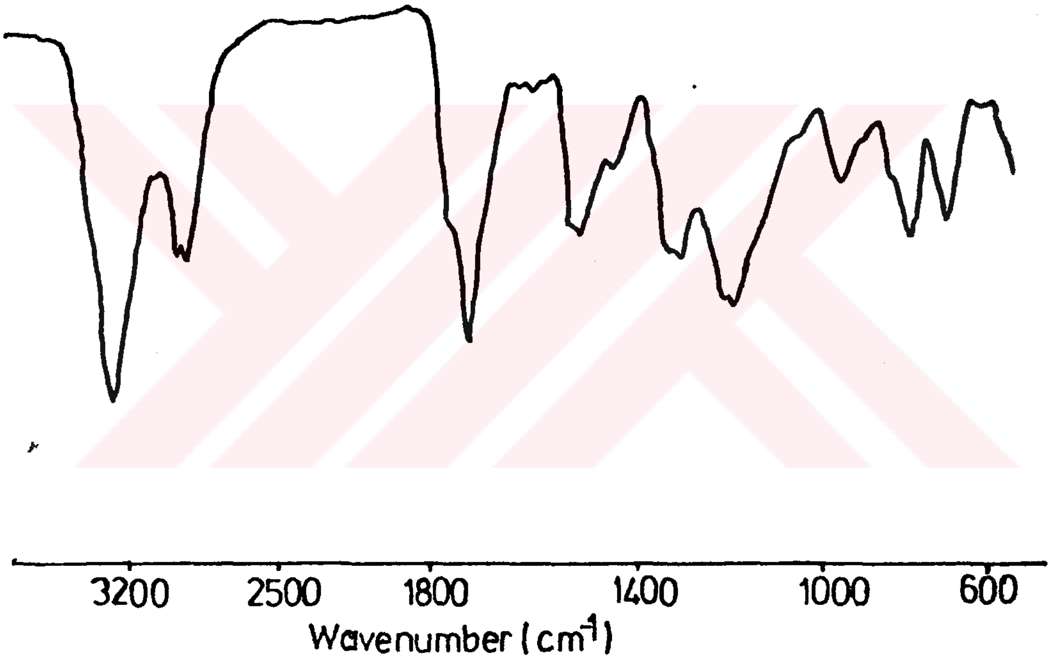


Figure 4.10 Infrared Spectrum of Styrene-Methylmethacrylate Block Copolymer.

The NMR spectra of block copolymers display signals at 0.8-1 ppm ($-CH_3$), 1.4-2.0 ppm ($-CH_2$), 3.6 ppm ($-OCH_3$), and 7,05 ppm ($-C_6H_5$). The ratio of the aromatic protons to methoxy protons varies according to the composition of block copolymer. Furthermore, the sequence length of the second monomer in the block increased with increasing reaction time of polymerization. It is shown in Figure 4.11.

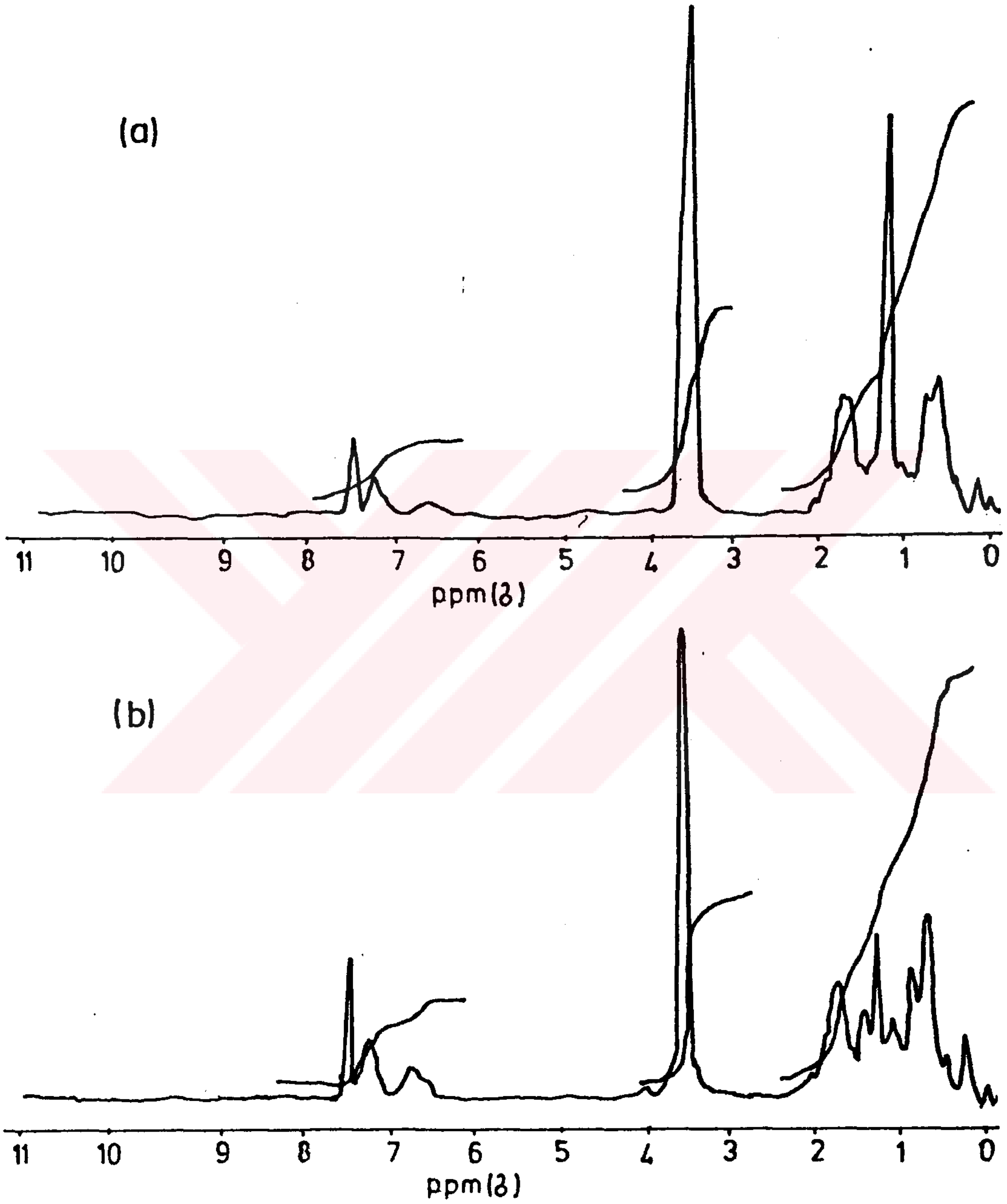


Figure 4.11 ^{1}H-NMR Specta of block copolymers obtained from (a) Run 7, (b) Run 8.

A different monomer sequences of the same procedure may also be used to prepare block copolymers Table 4.6 shows the results of block copolymerization experiments using polymethylmethacrylate prepolymer, which was polymerized with PA-2, to initiate the polymerization of styrene in a manner similar to that of previously described. The formation of homo polystyrene increased with increasing reaction time whereas formation of homo polymethylmethacrylate decreased. In both cases, the amount of the second monomer in the composition of block copolymer increased with increasing reaction time. Similar NMR spectra are recorded for these block copolymers as shown in Figure 4.12 and 4.13.

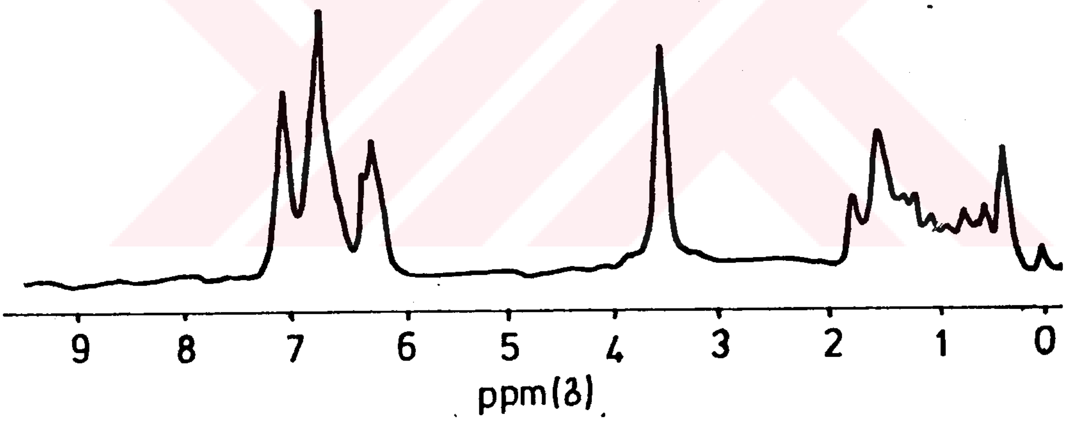


Figure 4.12 ^{1}H-NMR spectrum of the block copolymer obtained from Run 9.

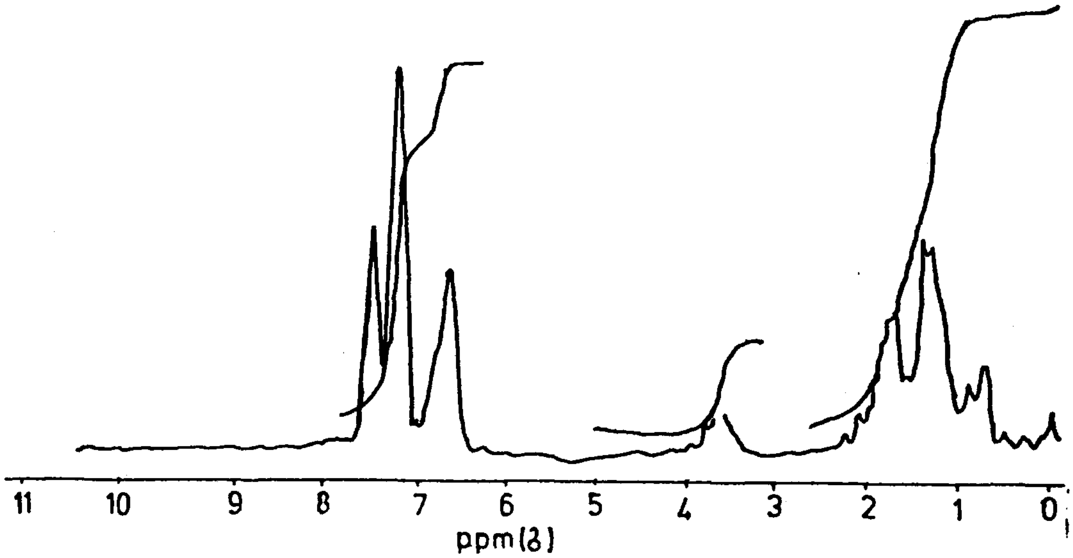
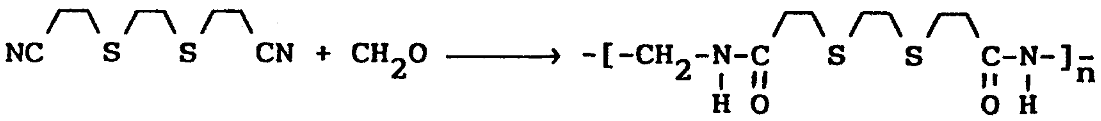


Figure 4.13 ^{1}H-NMR spectrum of the block copolymer obtained from Run 10.

IV.4. Synthesis and Chelating Properties of Sulfur-containig Poly(amidethioether) (PATE).

A new poly(amidethioether) (PATE) was synthesized from the reaction between β,β′(ethylenedithiol)-dipropionitrile (EDP) and trioxane in sulfiric acide as shown below.



$$NC\frown S\frown S\frown CN + CH_2O \longrightarrow -[-CH_2-\underset{H}{N}-\underset{O}{\overset{}{C}}\frown S\frown S\frown \underset{O}{C}-\underset{H}{N}-]_n$$

(4.11)

The results of polyamidation for various molar ratios of sulfuric acid are summarized in the Table 4.6.

Table 4.6 Polymerization of EDP with Trioxane in $H_2SO_4^a$.

Code	H_2SO_4/EDP (mol/mol)	Trioxane ($mol.10^{-4}$)	Conversion (%)	$\eta_{sp/c}^{b}$ (dl/g)
PATE-1	10	3.3	69.56	0.32
PATE-2	15	3.3	80.04	0.33
PATE-3	20	3.3	45.96	0.30
PATE-4	30	3.3	74.6	0.03

a: Reaction temperature 0 °C, 90 min.

b: Measured at 30 °C in N-methylpyyrolidone.

It is interesting to note that viscosity of polymer solutions decreases with decreasing concentration of dinitrile compound present in the solution.

The structure of the polyamide containing thioether was confirmed by elementel analysis as well as spectroscopic investigations. The results of elemental analysis are collected in Table 4.7. The infrared spectrum of typical poly(amidethioether) is shown in Fig.4.14. Polyamide structure can be characterized by the strong -NH and -C=O streching bands appearing 3300 and 1650 cm^{-1} respectively. In addition to these characteristic peaks, 1440-1415 cm^{-1} C-S-C deformation band can also be seen. The nitrile peak at 2200 cm^{-1} disappeared after the polymerization as observed with previous dinitriles (vide ante).

Table 4.7. Elementel Analysis of EDP and PATE

		C (%)	H (%)	N (%)	S (%)
EDP	Calculated	57.15	7.14	16.66	19.04
	Found	56.32	8.34	12.82	20.92
PATE	Calculated	43.54	6.45	11.29	25.8
	Found	44.81	6.24	8.66	—

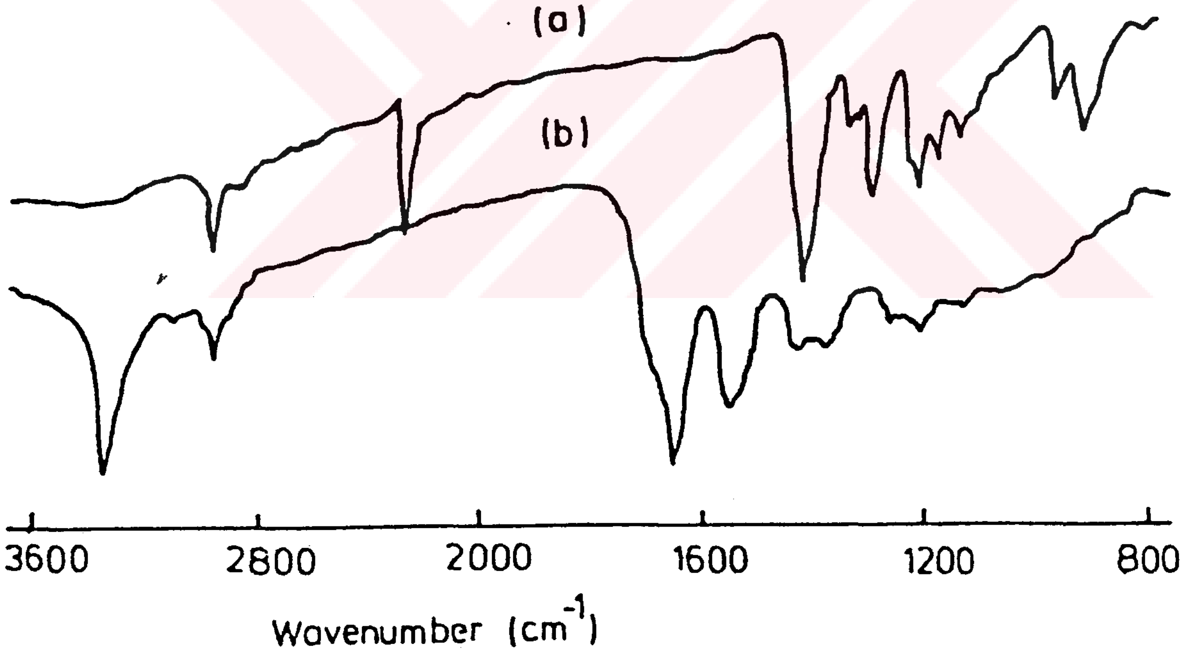


Figure 4.14 Infrared Spectra of (a) EDP and (b) PATE obtained from EDP.

Monomer EDP is soluble in common organic solvents methanol, acetone, chloroform etc.. Solubility properties completely changed after polymerization and it became soluble only in N-methylpyyrolidone (NMP).

The melting point of EDP is measured with DSC and found to be 92 °C. The DSC chromatogram of EDP and PATE are shown in Fig. 4.15. It appears that the polymer begins to fuse at about 271 °C with broad exoterm which may be due to the decomposition.

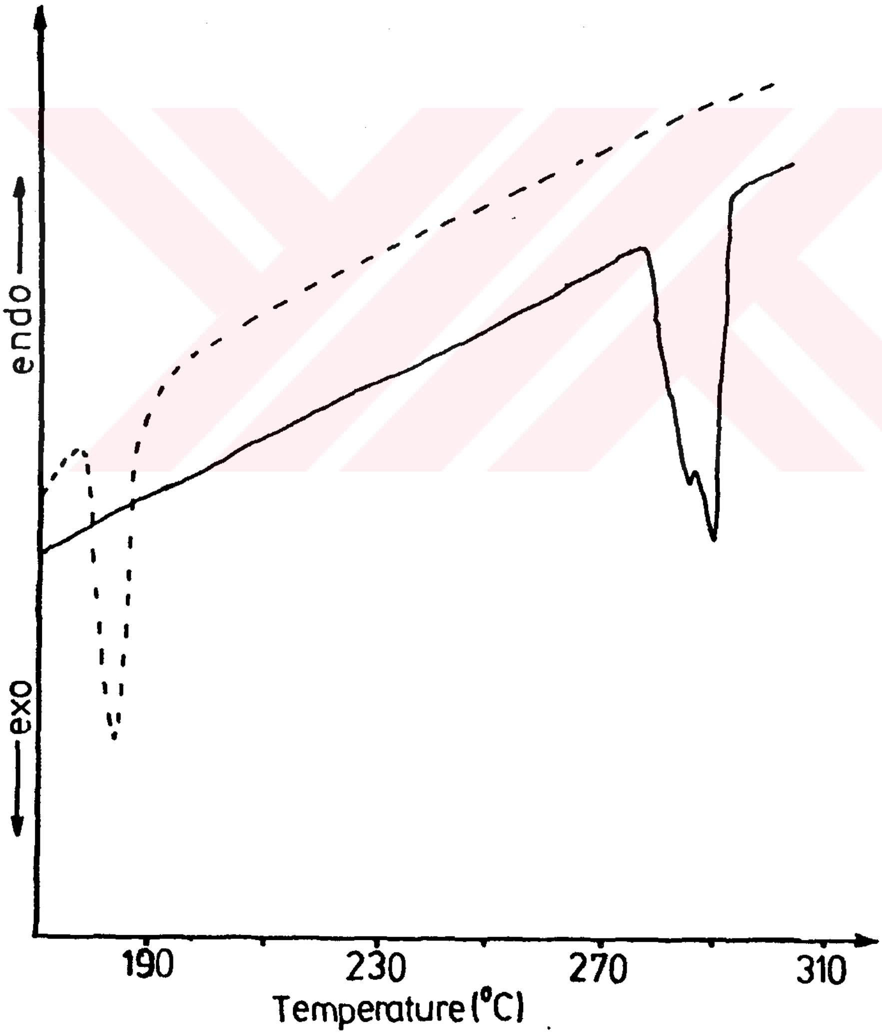
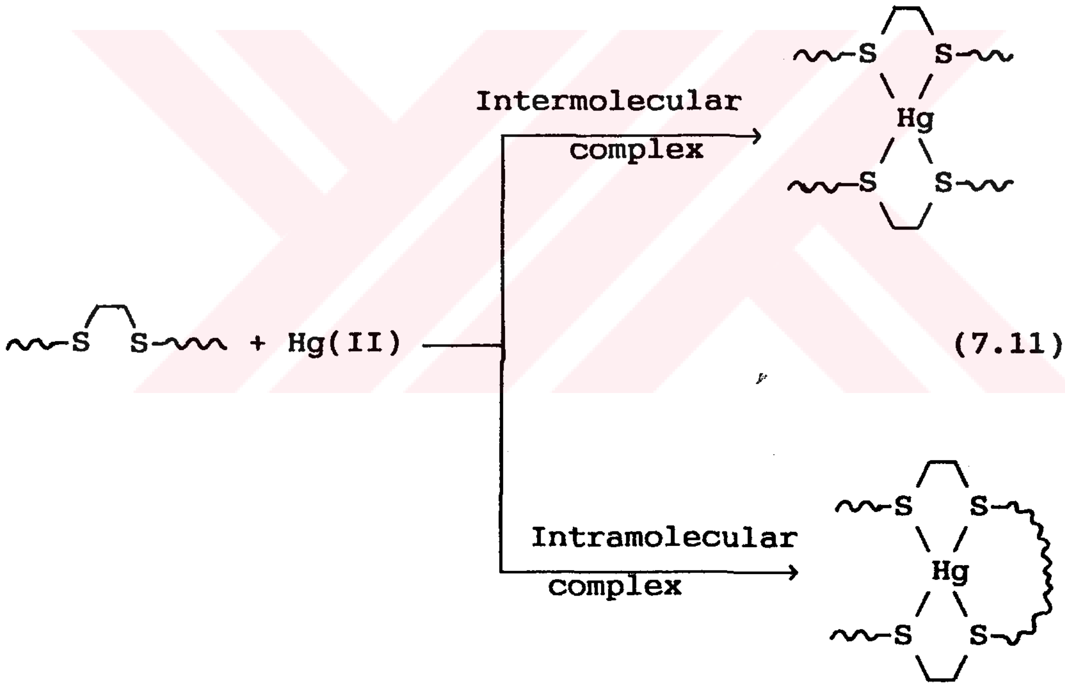


Figure 4.15. DSC trace for EDP (----) and PATE (——).

PATEs were subjected to interact with metal ions to examine ion binding properties. In these experiments, polymer solutions, which were prepared in NMP, were chaleted with acetate salts of Zn(II), Cd(II), and Hg(II) by addition of equimolar quantities at about 70 °C. In the case of mercury the mixture turned to clear solution due to the precipitation of yellow coloured polymer which indicates complex formation. The reaction probably proceeds via complexation of mercury with sulfur atom situated on the same or different chains as depicted below.



(7.11)

In the case of interaction with Zn(II), Cd(II), only a small amount of metal was bound to the polymer. The overall results are summarized in Table 7.8. UV measurements were used to determine the concentration of Hg(II). The UV spectrum is shown in Fig.4.16.

Table 4.8. Chelating Properties of PATE

	Zn(Ac)$_2^a$	%^{b}	Cd(Ac)$_2^a$	%^{b}	Hg(Ac)$_2^a$	%^{b}
Standart	0.5	-	0.5	-	0.08	-
PATE 1	0.465	7	0.417	3.8	0.06	25
PATE 2	0.462	7.6	0.481	3.8	0.048	40
PATE 3	0.465	7	0.477	4.6	0.069	42
PATE 4	0.469	7.6	0.481	3.8	0.048	40

a : Free ion concentration in solution.

b : Percentage of the free ion extracted by PATE.

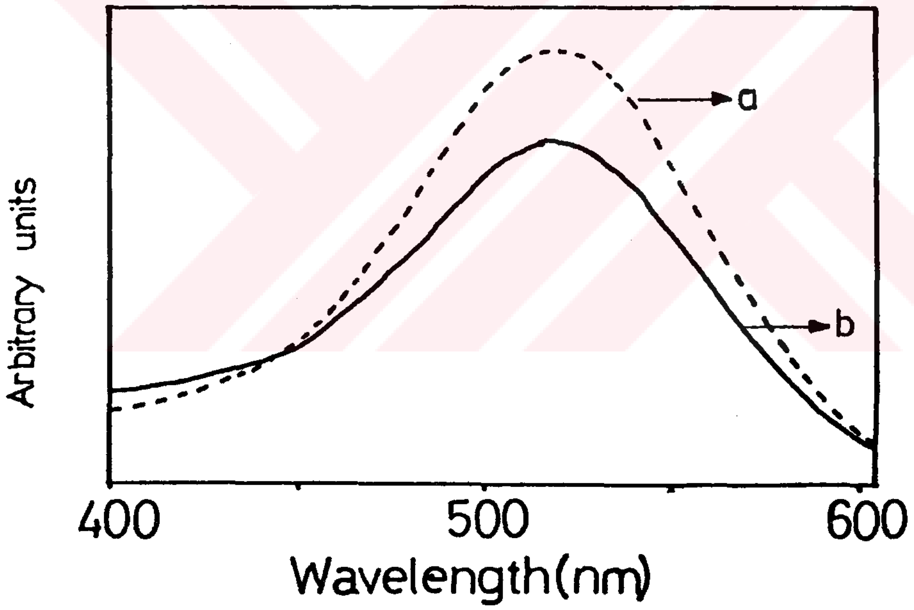


Figure 4.16 UV Spectrum of (a) before complexation.
(b) after complexation.

The percentage of free ion extracted by PATE is calculated from the equation below.

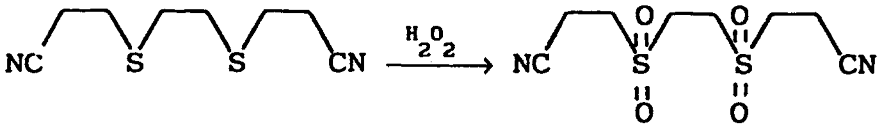
$$\text{Ion capture (\%)} = \frac{\text{(Standart solution)} - \text{(After extraction)}}{\text{(Standart solution)}} \times 100 \qquad (4.12)$$

PATE chaletes selectively with Hg(II). According to Jones et.al [53]. This selectivity can be attributed to favourable interaction of soft acid Hg(II) with soft base thioether. This result is in agreement with Pearson's principle. Pearson suggested that hard acids prefer to bind hard bases and whereas soft acids prefer to bind soft bases. Zn(II) and Cd(II) are softer than Hg(II) therefore these metal ions do not interact with sulfur atom along the chain.

Some chemical and physical properties of PATE is changed after complexation. Chelated PATE is insoluble in common organic solvents. Thermal behaviour of mercury binded PATE was investigated with DSC. It is observed that thermal stability of the chaleted polymer much better than the initial PATE. It doesn't decompose or melt up to 400 °C. The IR spectra of chelated polymers are similar but characteristic bands are broadened because of complexation with mercury.

IV.5 Synthesis and Properties of Polyamide Sülfon (PAS)

The synthesis of sulfone dinitrile compound, as illustrated in scheme 1, was performed using general sulfonation process ÆrefÅ.



(4.13)

The structure of EDSP was confirmed by spectroscopic investigation. The IR spectrum contains characteristic C-H and C N bands at 2950 cm^{-1},2250 cm^{-1}

respectively and O=S=O groups 1425,1175 and 1125 cm^{-1} (Fig.4.17). The ^1H-NMR spectrum recorded in DMSO-d_6 evidenced resonance signals of the CH_2 groups between 3-3.5 ppm (Fig.4.18).

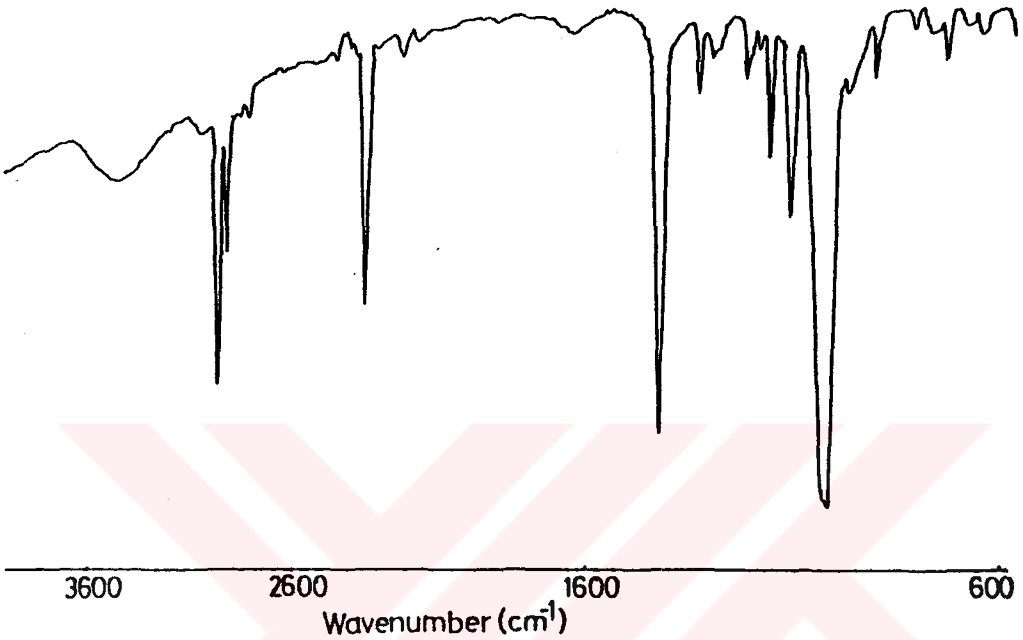


Figure 4.17 IR spectrum of EDSP

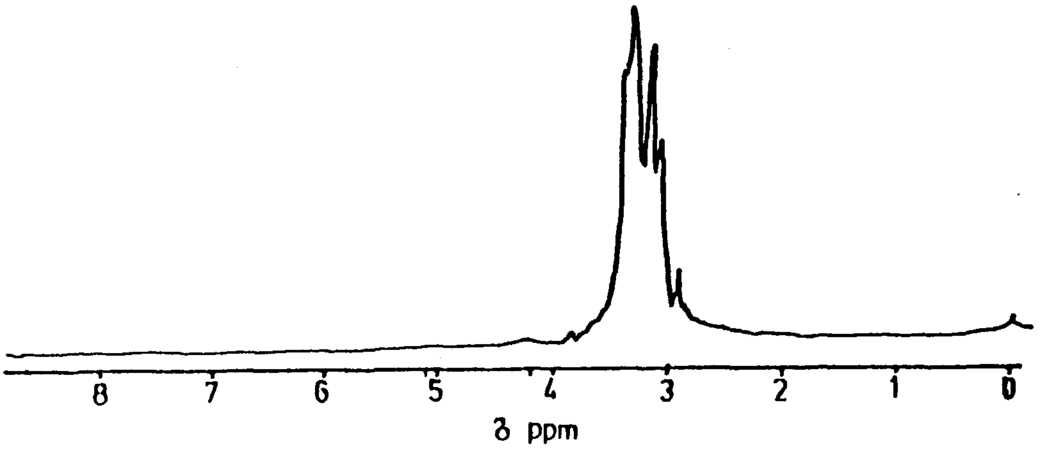


Figure 4.18. ^1H-NMR Spectrum of EDSP.

For preparing polyamidesulfones (PAS), a procedure developed earlier for poly(amidethioether) was followed; thereby pure PASs could be obtained in 30-50% yields. The synthesis is a one pot reaction of the dinitrile compound and trioxane in strong acid such as sulphiric acid at low temperature. Typical polymerization reaction for various molar ratios of sulfuric acid are shown in Table 4.9.

Table 4.9

Polymerization of EDSP with Trioxane in Sulfuric Acid[a]

EDSP/H_2SO_4	H_2SO_4	[Trioxane]10^4M	[EDSP]10^4M	Yield (%)
1/10	3.78	1.2	3.78	27.81
1/20	7.56	1.2	3.78	31.45
1/30	11.34	1.2	3.78	43.18
1/40	15.12	1.2	3.78	53.91

a:Reaction temperature 0°C, 90 min.

To investigate the effect of partial replacement of EDSP with adipoyldinitrile, polyamide sulfone copolymers (co-PAS) containing 20-50-80 mol% of EPSP and 80-50-20 mol% of adipoyldinitrile were synthesized. All of the polymers were obtained in similar yields (Table 4.10).

Table 4.10 Polymerization of EDSP and Adipoyldinitrile (AD) with Trioxane in Sulfuric Acid [a].

Code	EDSP+AD/H_2SO_4 (mol/mol)	Trioxane	AD	EDSP	Yield (%)
PAA	1/20	0.7	2.1	-	22.3
PAAS1	1/20	0.7	1.68	0.43	14.87
PAAS2	1/20	0.7	1.05	1.05	11.48
PAAS3	1/20	0.7	0.43	1.68	9.19
PAS	1/20	0.7	-	2.1	5.72

a: Reaction temperature 0°C, 90 min.

PASs and co-PASs obtained were characterized by IR and ^{1}H-NMR spectra. The IR spectra of all polymers showed characteristic IR absorption at 2950 cm^{-1} (aliphatic CH strectching), 3300-3250 cm^{-1} (-NH stretching), 1650 cm^{-1} (amide I, C=O stretching), 1550 cm^{-1} (amide II, interaction of -NH- bending and C-N stertching of C-N-H) and at 1380 and 1160 cm^{-1} (O=S=O stretching) (Figure 4.19a). Incorporation of adipoyl segments into PAS does not bring additional bands in the IR spectra of polymers since CH groups are already present in the structure (Figure 4.19b). ^{1}H-NMR spectrum of a typical DMSO soluble co-PAS possesses bands of CH_2 protons at 3.3 ppm range, -NH protons were detected as a weak signal at 7 ppm because of intermolecular exchange and hydrogen bonding [9]. Exchange with D_2O results in the disappearance of this signal at 7 ppm (Figure 4.20).

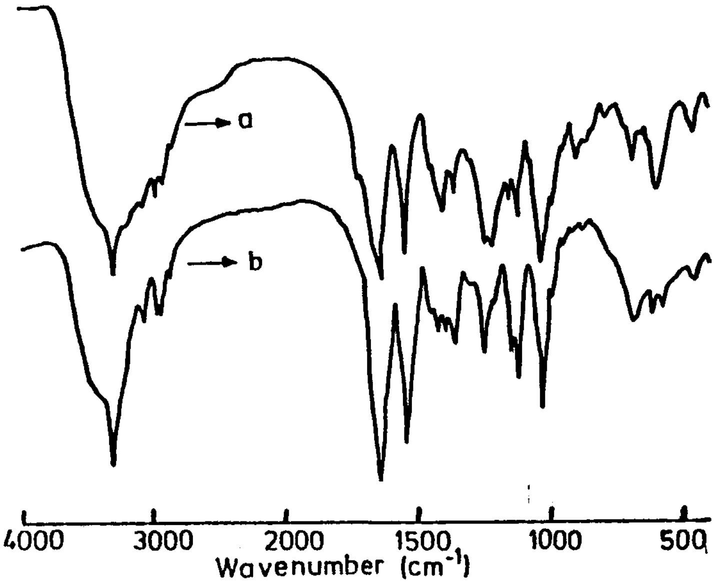


Figure 4.19 Infrared spectra of (a) PAS.
(b) co-PAS (PAAS2).

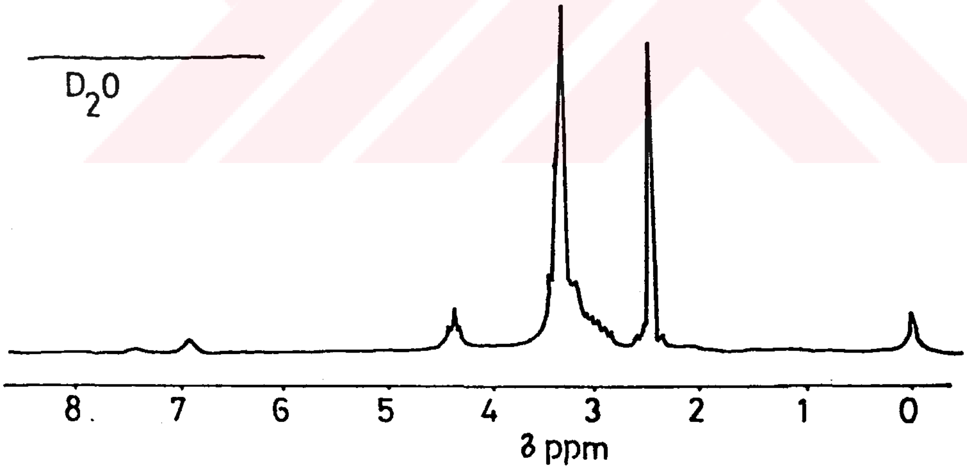


Figure 4.20 ^{1}H-NMR Spectrum of co-PAS (PAAS2).

PASs are insoluble in all organic solvents. Incorporation of adipoyl segments (co-PAS) improved solubility to some extend (Table 4.11).

Table 4.11

Solubilities of copolyamides,obtained from EDSP and AD.

Solvent	PAA	PAAS1	PAAS2	PAAS3	PAS
DMSO	SS	S	S	S	I
DMA	I	I	I	I	I
NMP	I	I	I	I	I
Formic acid	SS	SS	SS	SS	SS
Sulfuric acid	SS	SS	SS	SS	SS
m-Cresol	S	S	S	S	S
THF	I	I	I	I	I
DMF	I	I	I	I	I
NMP/ Pyridine	I	I	I	I	I

SS:Soluble at room temperature S:Soluble on heating
I:Insoluble

The polyamides possessing adipoyl segments namely PAAS1 and PAAS3, exhibit partial crystalline pattern whereas PAS were found to be amorphous (Fig.4.21). From this result it can be concluded that adipoyl segments increases the crystallinity of the polyamide.

The thermal stability of PAS's was studied by thermogravimetric analysis (TGA). The polymers began to decompose around 175^{o}C with a 78.4% weight loss occuring 175-375 ^{o}C (Fig.4.21). Two distinct plateaus observed may be atributted to the decomposition of sulfone and adipoyl segments. It is clear that PASs do not show good thermal stabilities as aromatic polyamidesulfones where rigidity is achived by phenyl groups

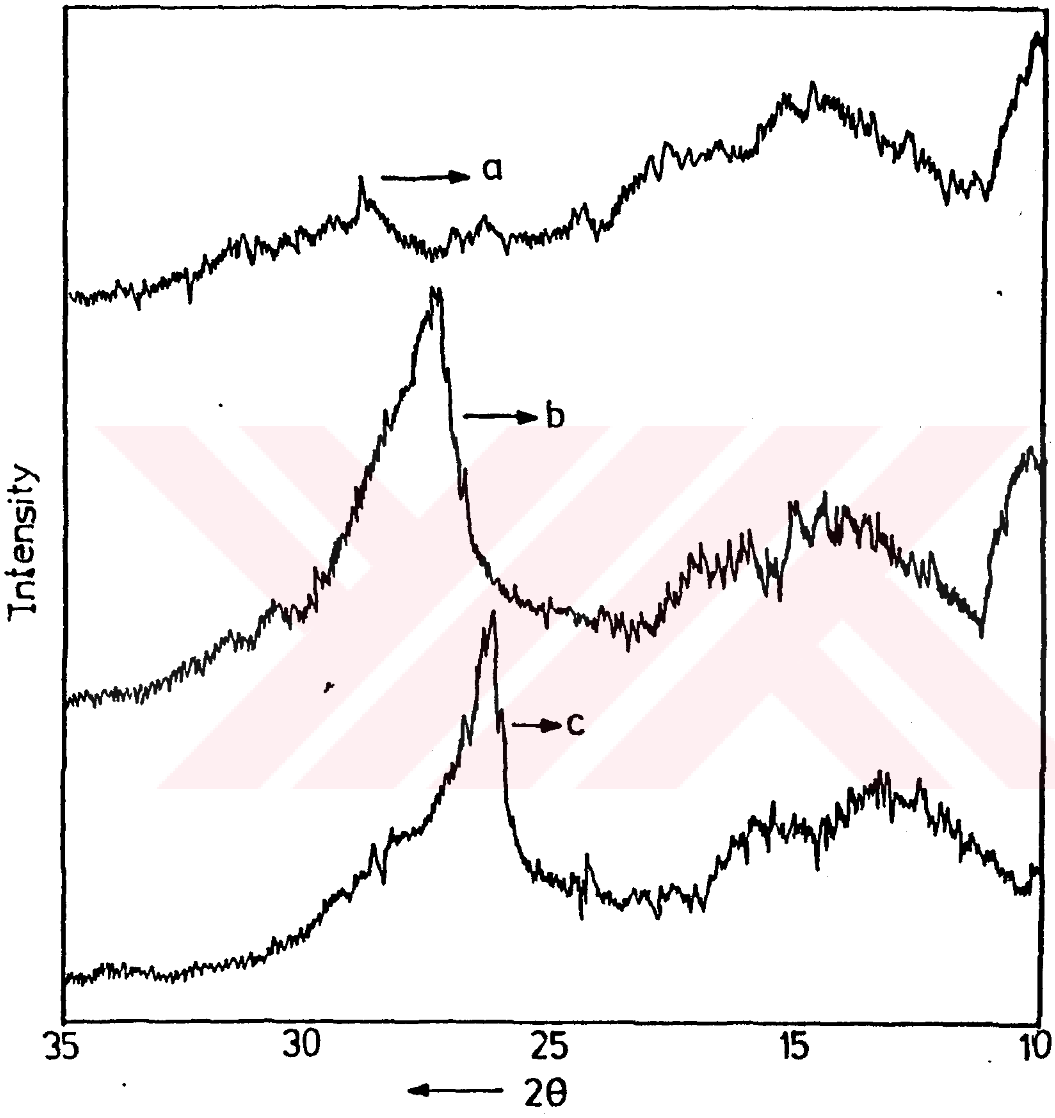


Figure 4.21 X-ray diffraction of polyamides (a) PAS. (b) PAAS3 (c) PAAS1.

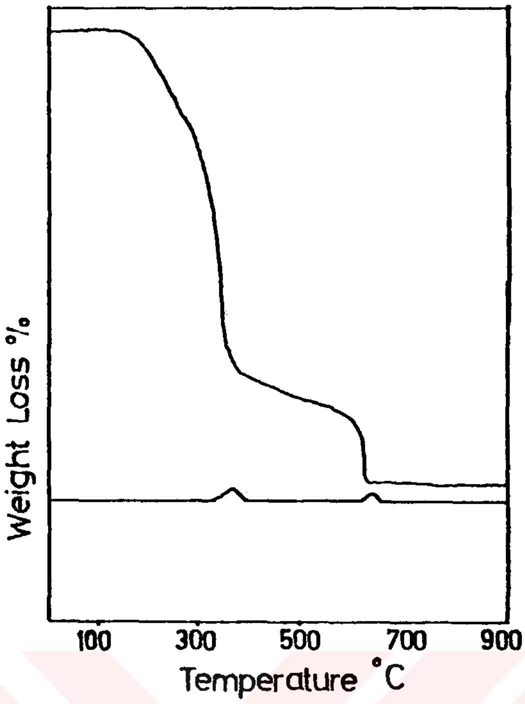


Figure 4.21 TG curve of polyamide PAAS2.

It is interesting to note that U.V. irradiation of co-PAS in DMSO at 306 nm resulted in the increase of the viscosity and absorption. Moreover, the absorption maxima of the polymers shifted to longer wavelength. This may be due to the interaction of macroradicals formed upon irradiations with the other chains. This process would lead to an increase of the viscosity. UV spectrum of polysulfone is shown in Figure 4.22.

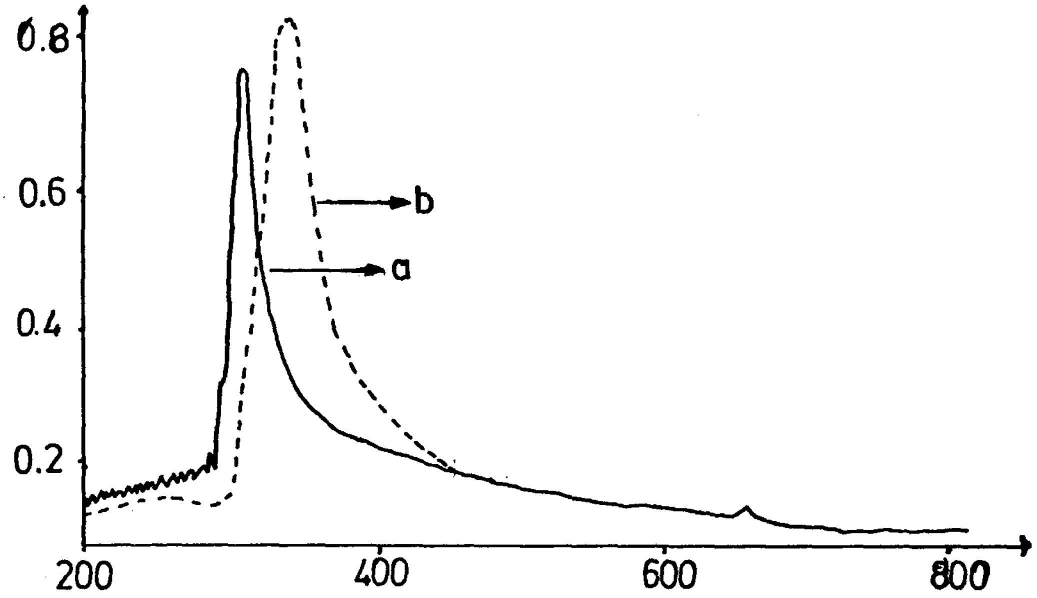


Figure 4.22 UV spectra of polysulfone (a) Before Irradiation (b) After Irradiation.

V.CONCLUSIONS

These results suggest that functional polyamides can be prepared by reacting suitably selected dinitriles with formaldehyde. Block copolymerization of vinyl monomers using polyamides pertains to the sequential decomposition of azo groups incorporated in polyamides. Block copolymer efficiency is limited. However, this efficiency may be rationalized in terms of a design of the polyamide initiator and duration of polymerization of vinyl monomers.

Ion binding experiments clearly demonstrate polyamides containing thioether groups show high selectivity towards Mercury (II).

Polyamidation reaction is a versatile procedure to obtain crystalline polyamidesulfones which may find application in high energy radiation resist technology.

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