MACROAZONITRILES FOR THE PREPARATION OF POLYMERS WITH CROWN ETHER UNITS

Ph. D. THESIS
Ömit TUNCA, M.S.

T. C.
Yükseköğretim Kurulu
Dokümantasyon Merkezi

Date of Submission : 18 APRIL 1989

Date of Approval : 1 JUNE 1989

Examination Commitee

Supervisor : Prof.Dr. Yusuf YAĞCI
Member : Prof.Dr. Çakıl ERK
Member : Prof.Dr. Selim KOSEFOĞLU

JUNE , 1989

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ACKNOWLEDGEMENTS

April 1989   Umit TUNCA

CONTENS

SUMMARY

The purpose of this work is to obtain the macroazonitriles containing crown ether moieties and various amounts of -N=N- units in the main chain. Macroazonitriles were prepared by low temperature solution polycondensation between cis-4,4'-diamino dibenzo-18-crown-6 (DADC) and adipoyl chloride or terephtaloylchloride (TPC) with the addition of 4,4'-azobis (4-cyanopentanoylchloride)(ACPC). The decomposition of the azo linkage present in the polyamides obtained by using DADC and ACPC-TPC were studied by DSC. The rate constants and activation energies for the decomposition of polyamides were determined from DSC thermograms. Small effect of terephtaloyl segments on the rate was observed. The kinetics of the polymerization of styrene initiated by the polyamide, obtained from ACPC and DADC was investigated in DMSO by using gravimetric method and kinetic parameters were evaluated.

ÖZET

TAÇ ETER BİRİMLERİ İÇEREN POLİMERLERİN HAZIRLANMASI İÇİN MAKROAZONİTRİLLERİN SENTEZİ

Halkalı polieter bileşiklerinin alkali ve toprak alkali metal tuzları ile oluşturduğu kararlı kompleks yapılar ilk kez Pedersen tarafından 1967 yılında ortaya çıkarılmıştır. Pedersen bu çalışmasında aromatik visinal diollerden başlayarak çeşitli halka büyüklüklerinde otuz üç polieter sentezlemiş ve genel olarak onlara yapılarından dolayı 'taç eter' adını vermiştir. Pedersen'in öncü çalışmasından sonra, bu konuda yapılan çalışmalar katlanarak artmış ; 1987 yılında kendisine Cram ve Lehn ile birlikte Nobel Kimya ödülü verilmiştir.

Bu alanda yapılan çalışmalardan birisi de taç eter içeren polimer sentezidir. 1971 yılında, Feigenbaum ve Michel, dibenzo-18-crown-6'nın nitrolanması ve oluşan ürünün indirgenmesi ile ele geçen cis/ trans-4,4'-diaminodibenzo-18-crown-6'nın çeşitli diasit klorürler ile tepkimeye sokularak poliamid eldesini gösterdiler. Diğer yandan, Smid ve çalışma grubu, asılı taç eter grupları içeren polimer eldesi için, 4'-vinil-benzocrown eterleri sentezlediler. Taç eter grupları taşıyan polimerlerin en önemli üstünlüğü, taç eter boşluğunun boyutlarından daha büyük çapta iyonları kuvvetle bağlayabilmesidir. Bu davranış polimer zincirindeki taç eterlerin katyonlarla kompleks oluşturmasında ortaklaşa etkileşmeleri sonucudur (sandviç tipi).

Yakın zamanlarda, düşük sıcaklık çözelti ve karıştırmalı yüzeylerarası polikondensasyon yöntemleri ile taç eterleri içeren polimerlerin eldesi için makroazo-başlatıcılar sentez ettik.

Düşük sıcaklık çözelti polikondensasyonu yöntemiyle trans-4,4'-diaminodibenzo-18-crown-6 ve 4,4'-azobis(4-siyanopentanoil klorür)'ü kullanarak poliamid yapısında bir makroazo-başlatıcı sentezlendi :

$$\text{HOOC-CH}_2\text{-CH}_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-N=N-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-CH}_2\text{-CH}_2\text{-COOH} \xrightarrow{PCl_5}$$

$$\text{Cl-}\overset{\overset{O}{||}}{C}\text{-CH}_2\text{-CH}_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-N=N-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-CH}_2\text{-CH}_2\text{-}\overset{\overset{O}{||}}{C}\text{-Cl}$$

$$+ \quad H_2N-\text{(crown ether)}-NH_2$$

$$\xrightarrow[\text{CH}_2\text{Cl}_2, \text{DMF}]{0°C \,(N_2)}$$

(chemical structure: crown ether with HN— ... —NH–C(=O)–CH$_2$–CH$_2$–C(CH$_3$)(CN)–N=N–C(CH$_3$)(CN)–CH$_2$–CH$_2$–C(=O)—)$_n$

$$\xrightarrow[-N_2]{70°C}$$

(chemical structure: alkyl–HN—crown ether—NH–C(=O)–CH$_2$–CH$_2$–C(CH$_3$)(CN))

| monomer ↓

(chemical structure: alkyl–HN—crown ether—NH–C(=O)–CH$_2$–CH$_2$–C(CH$_3$)(CN)–P$_n$) etc.
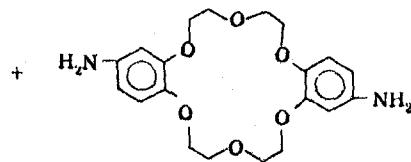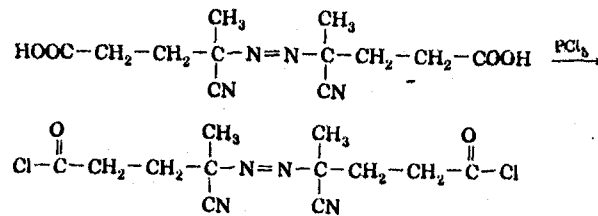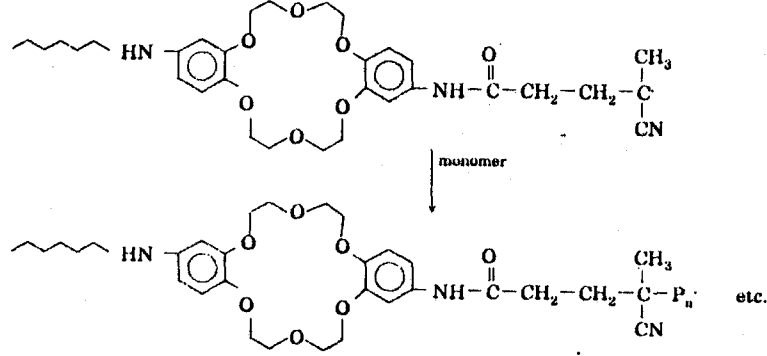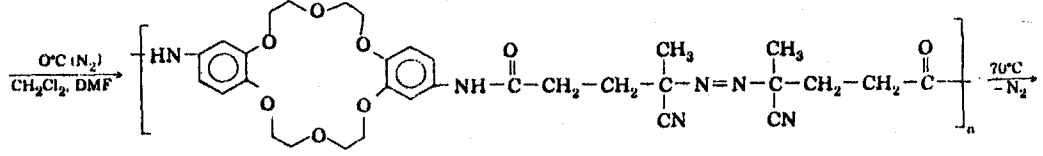
Karıştırmalı yüzeylerarası polikondensasyon yönteminde ise cis ya da trans-4,4'-diaminodibenzo-18-crown-6'nın KI'lü kompleksleri hazırlanarak su fazında çözülmüş, organik fazda çözülen 4,4'-azo-bis (4-siyanopentanoil klorür) ile yüksek hızlı bir karıştırıcı yardımıyla KI kompleksli makroazo-başlatıcılar elde edilmiştir(1).

Her iki yöntemde de elde edilen makroazo-başlatıcılar stiren ve metilmetakrilatın serbest radikal polimerleşmesinde başlatıcı olarak kullanılmış ve böylece taç eter gruplarını içeren polistiren, polimetilmetakrilat hazırlanmıştır.

Bu ön çalışmalardan sonra, düşük sıcaklık polikondensasyon yöntemi ile ana zincirde değişen oranlarda -N=N- birimleri ve taç eter grupları içeren makroazonitrillerin sentezi yapılmıştır. Bunun için, cis-4,4'-diaminodibenzo-18-crown-6, adipoil klorür ya da tereftaloil klorür ve değişen oranlarda 4,4'-azo-bis (4-siyanopentanoil klorür) ile tepkimeye sokulmuştur(2).

(chemical structure: crown ether complex with K$^+$I$^-$, labels b, c, d, a — [HN—crown ether—NH–C(=O)–CH$_2$–CH$_2$–C(CH$_3$)(CN)–N=N–C(CH$_3$)(CN)–CH$_2$–CH$_2$–C(=O)—]$_n$)   (1)

$$nxCl-\overset{\overset{O}{\parallel}}{C}-R_{\bar{1}}\overset{\overset{O}{\parallel}}{C}-Cl + nyCl-\overset{\overset{O}{\parallel}}{C}-R_{\bar{2}}\overset{\overset{O}{\parallel}}{C}-Cl + n(x+y)H_2N-R_{\bar{3}}NH_2 \qquad (2)$$

$$0\text{--}5\,°C\,\big\downarrow\,HMPA$$

$$\left[\left(\overset{\overset{O}{\parallel}}{C}-R_1-\overset{\overset{O}{\parallel}}{C}-NH-R_3-NH\right)_x\left(\overset{\overset{O}{\parallel}}{C}-R-\overset{\overset{O}{\parallel}}{C_2}-NH-R_3-NH\right)_y\right]_n$$

$$R_1 = (CH_2)_2\underset{CN}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-N=N-\underset{CN}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}(CH_2)_2$$

$$R_2 = \langle O \rangle \quad or \quad (CH_2)_4$$

$$R_3 =$$
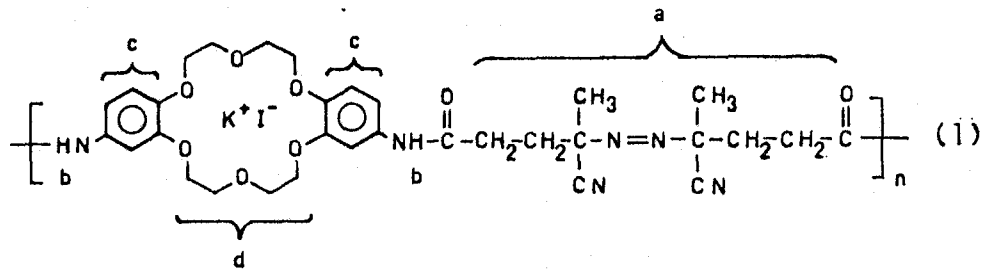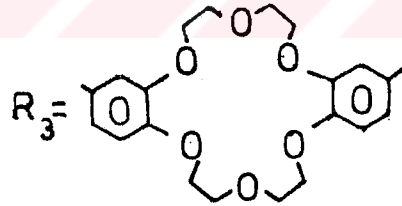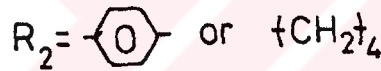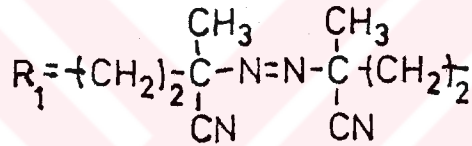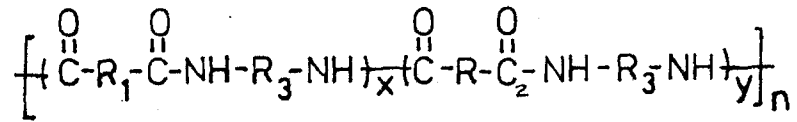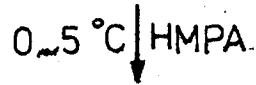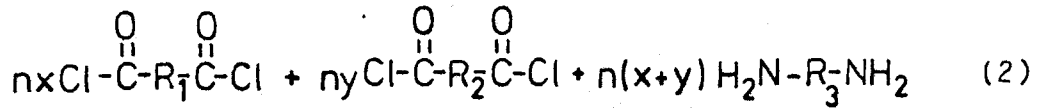
Tereftaloil klorür ile değişen oranlarda 4,4'-azo-bis(4-siyano-pentanoil klorür)'den elde edilen poliamidlerin DMSO ya da MeSO$_3$H'de-ki bozunma kinetikleri DSC ile incelenmiş ve elde edilen DSC termogram-larından bozunma hız sabitleriile aktivasyon enerjileri bulunmuştur. Kinetik verilerden bazıları aşağıdadır :

$10^3 k_d$ (Temp)	E_a
sec^{-1} ($^{\circ}$C)	(kJ/mole)

ACPA	$1.27(77)$; $2.12(82)$;$3.59(87)^a$	108
PA-1	$5.29(118)$; $6.85(121)$;$10.7(126)^b$	115

^{a}in $MeSO_3H$ ($\sim 5\,\mu L$)

^{a}in DMSO ($\sim 5\,\mu L$)

Tereftaloil gruplarının, makroazo-başlatıcıların bozunma kinetiği üzerinde etkisinin çok küçük olduğu gözlenmiştir.

Yukarda adı geçen çözelti polikondensasyonu yöntemi ile cis-4,4'-diaminodibenzo-18-crown-6 ile 4,4'-azo-bis (4-siyanopentanoil klorür)' den elde edilen poliamid (PA-1), stirenin 70°C de DMSO varlığında serbest radikal polimerleşmesinde başlatıcı olarak kullanılmıştır. 60,70 ve 80°C'de yapılan stiren polimerleşmesi sonucu elde edilen polimerleşmesi sonucu elde edilen polimerleşme hızlarının logaritmaları -mutlak polimerleşme sıcaklıklarının tersleri diyagramı (Arrhenius) nın eğimi, polimerleşme aktivasyon enerjisi olarak 87 kJ/mol vermiştir.

Log R_p - log [M] ya da log [I] diyagramlarının eğimlerinden

$$R_p = K [M]^{1.00} [I]^{0.43}$$

bulunmuştur.

Mayo denkleminden yararlanılarak ($1/\bar{P}_n$)-([II])/R_p) diyagramları, değişen [M] sabit [I] ve sabit [M] değişen [I] için çizilmiş ve bunların eğiminden fk_d'ler hesaplanarak sırasıyla 0.17 ve 0.13 değerleri bulunmuştur. Sabit başlatıcı konsantrasyonunda çizilen eğrinin doğrusallığı C_s'in sıfır olduğunu da göstermektedir.

($1/\bar{P}_n$)-($1/R_p$) diyagramı sabit başlatıcı konsantrasyonlarında doğrusal bir eğri verdi. Bunun kayımı, eğer $C_I = 0$ varsayılırsa, $C_s([S]/[M])$ = C_M olup, C_M'in ortalama literatür değeri $0.6.10^{-4}$ alınarak, C_s $0.1.10^{-4}$ olarak bulunmuştur. Bu değer C_s literatür değerleri,DMSO için, 0.54-$0.48.10^{-4}$ (50-60°C) ile uyumludur.

($1/\bar{P}_n$)-([II]/[M]) diyagramının başlangıçtaki doğrusal eğiminden bulunan C_I değeri 0.47 dir. Bu değer, azonitriller genellikle transfer tepkimesi göstermedikleri için yüksek gözükmektedir. Makroazobaşlatıcı (PA-1) da zincir boyunca yeralan amid gruplarının varlığı göreceli olarak daha yüksek C_I değerini doğurabilir. Ayrıca,poliamidlerin su ve dioksan ortamında potasyum pikrat tuzu tutuculuk özellikleri incelenmiştir.

	Ekstrakte Edilen Pikrat Tuzu (%)	
	Su	Dioxan
PA-1	60.5	36.3
PA-2	77.4	52.2
PA-3	17.6	17.2
PA-4	64.9	2.8
PA-5	11.2	14.0
PA-6	28.8	1.5
PA-7	51.6	43.4
PA-8	18.9	10.9
PA-9	71.9	38.1
PA-10	13.2	6.4
PA-11	29.4	40.4

1. THE OBJECTIVES OF THE WORK

The object of the work described in this thesis was to prepare the macroazo-nitriles having appropriate functionality for the synthesis of polymer with crown ether units.

Recently, there has been a significant growth of interest in the synthesis of polymers with ion binding abilities. This approach finds an application in purification of liquids and in ion exchange technology.

Thereby, it turned out that complexing property can be achieved by incorporation of crown ether groups into polymers. In order to combine crown ether structures with a polymer, most approaches have been made through the condensation reactions. In these reactions the derivatives of crown ethers were employed as two functional monomers. On the other hand, Smid and co-workers [52,53] synthesized 4'-vinyl benzo crown ether which may contribute to the formation of polymers having pendant crown ether groups. From the practical point of view, however, polymers with pendant crown ethers are more attractive than main chain crown ether containing polymers, because in the former case, pendant crown ethers can perform a cooperative action to bind ions.

It might be pointed out, in this connection, that till now there are various drawbacks which retarded quite often the practical application of polymers with pendant crown ether groups. These draw-backs include the difficulty of preparation and purification of the corresponding monomers. Thus, we have focused our studies on the preparation of polymers possessing crown ethers in the main chain.

Macroazo-nitriles prepared by means of condensation,cationic, and anionic insertion polymerization are useful the synthesis of block copolymers with desired properties.

It seemed reasonable therefore to synthesize appropriate macroazo-
nitrile and employ to initiate the polymerization of radical susceptib-
le monomers.

In addition, mechanistic and kinetic details of individual steps
were to be studied.

2. INTRODUCTION

2.1. Polymerization Systems

Carothers [1] classified polymers as addition and condensation types and the processes as addition polymerization and condensation polymerization.

2.1.1. Condensation Polymerization

Many simple organic reactions are known in which two molecules become joined, typical examples being the condensation of an acid with an alcohol to yield an ester and the similar reaction of an acid with an amine to yield an amide. Reactions of this type may be adapted to the formation of polymers by using molecules which are functionally capable of coupling indefinitely by condensation reactions may be achieved by using a single monomer bearing two different functions as for example in the polymerization of an amino acid to a polyamide,

$$n \quad H_2N-(CH_2)_x-COOH \longrightarrow H \Big[NH-(CH_2)_x-\overset{\overset{O}{\|}}{C} \Big]_n OH + (n-1)H_2O \qquad (2.1)$$
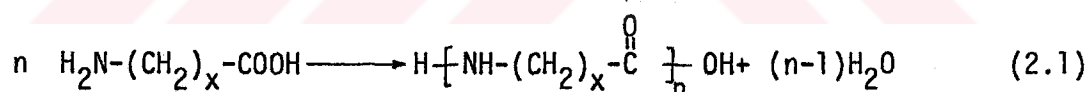
or different molecules having the two functional groups as for example in the reaction of a diacid with a diamine to yield a linear polyamide.

$$n \quad HOOC-(CH_2)_4-COOH \quad + \quad H_2N-(CH_2)_6-NH_2 \longrightarrow$$

$$H-O \Big[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N} \Big]_n H + (n-1)H_2O \qquad (2.2)$$
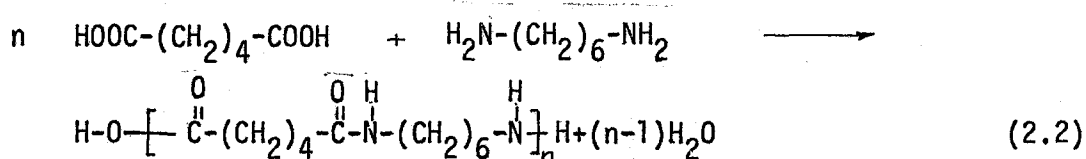
2.1.1.1. High Temperature Polycondensation Methods

Carothers was first to apply high-temperature procedure to polyamides which led to the commercial production of 6-6 Nylon [2,3]. This technique is still the basic melt condensation process for many polyamides with some simplifications and variations. The melt method

requires high pure and heat stable intermediates. A characteristic
feature of the reactions employed in high-temperature polycondensations
is that they are slow [4]. Rates of high-temperature polycondensation
reactions are increased by increases in temperature, changes in solvent
polarity, and the presence of catalysts.

2.1.1.2. Low Temperature Polycondensation Methods

The best known and most widely used of these reactions is that
of an acid chloride with a compound containing an active hydrogen in
the functional group such as an amine, phenol, or thiol etc.

Condensation polymers are formed if the complementary compounds
are bifunctional as in eq. (2.3)

$$H_2N-R-NH_2 + Cl-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{NaOH} H \left[\overset{H}{\overset{\|}{N}}-R-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}} \right]_n Cl + NaCl \qquad (2.3)$$
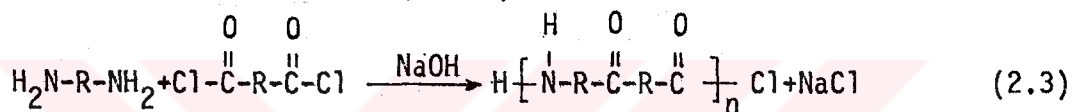
The low-temperature methods employ reactions which proceed at
high rates and which are capable of giving quantitative yields at ordi-
nary temperatures.

The two principal low-temperature polycondensation methods are
interfacial polycondensation and solution polycondensation.

2.1.1.2.1. Interfacial Polycondensation

In this [5], the two fast-reacting intermediates are dissolved
in a pair of immiscible liquids, one of which is preferably water.
The water phase contains the diamine or diol and any added alkali.
The other phase which is called organic phase consists of   diacid
chlorides and an organic solvent such as carbon tetrachloride dichlo-
romethane, xylene or hexane. The polymerization takes place at or near
the liquid interface.

2.1.1.2.1.1. Unstirred Interfacial Polycondensation

When the two phases for an interfacial polycondensation are
brought together without stirring and if the organic solvent is a
non solvent for the polymer a thin film of polymer will be formed

at once at the interface Fig.1.1 . This polymer precipitate is tough and has high molecular weight if the film is grasped and pulled from the area of the interface, more polymer forms at once and a collapsed sheet or tube of polymer may be with-drawn continuously.

Water Phase }	Diamine + Inorganic Base
Interphase Organic Phase }	Diacid Chloride
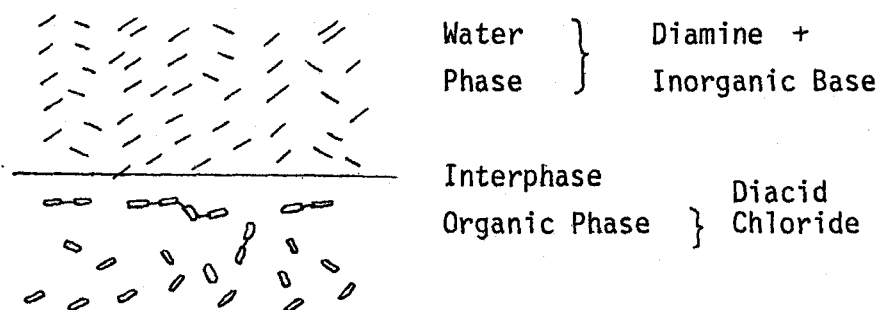
Fig.1.1 : Diagram of reactants in interfacial
amidation systems.

Exact stoichiometry of reactants is not so important as it is in melt polycondensations, presumably because of the extremely rapid rate of interfacial polycondensation. In fact, enough excess diamine as well as the inorganic base to act as the acid acceptor may be used in some cases without seriously reducing the molecular weight of the product. This is taken as evidence for a reaction site in the organic phase close to the interface, but apart from the excess diamine. Acid chloride enters the aqueous phase very little, thus avoiding hydrolysis. Reaction is so rapid that lack of precise equivalency of reactants in the solution does not prevent the formation of high molecular weight products at the surface contact of the two liquids.

Probably the simplest example of unstirred interfacial polycondensation is the preparation of 6-6 or 6-10 nylon by the beaker method of Morgan and Kwolek which is called The Nylon Rope Trick [6,7]. Their process contains a carefully pouring an aqueous solution of excess hexamethylenediamine onto a carbon tetrachloride solution of adipoly or sebacoyl chloride, then steadily pulling away a coherent film of

polyamide from the interface.

2.1.1.2.1.2. Stirred Interfacial Polycondensation

The interfacial polycondensation with stirring uses the same chemical reactions and media as the process without stirring but differs in a number of important ways.

Stirred systems do not require any coherence or strength in the film. The product may be granular, powdery, plasticized, or even dissolved. Since there is no need to consider film quality, the number of useful solvents and the range of polymers which may be prepared in stirred systems are greater than for the unstirred systems [8-10].

The method with stirring requires fast-reacting intermediates but the rate range is considerabely greater than for the method without stirring. The faster reactions have been estimated to have rate constants of the order of 10^2-10^6 l/mole-sec.

Most interfacial polycondensations are carried out at ambient temperature, and the mixture is allowed to warm up from the heat of reaction and heat of stirring. But, raising the temperature will change the solubility of the intermediates and the polymer and accelerate side reactions.

Stirring is a critical variable in the production of polymers by low-temperature polycondensation process , yet it is the most difficult to control and cannot be readily fully described.

The systems are divided into three general cases based on polymer behavior : (1) The polymer precipitates rapidly in a swollen state ; (2) the polymer is extremely solvent-insensitive and forms nonswollen precipitates ; (3) the polymer remains in solution until after polymerization is complete.

The encounter of diacid chloride and diamine can take place under several different sets of circumstances relative to the supply of intermediates in progression of polycondensation. The least complex

condition would be a dispersion of acid chloride solution droplets so small that the critical film formation would completely use up all the acid chloride. Polymerization would proceed to the center of the drop and occlude all the solvent. The more likely situation is that droplet or interface area would be large in relation to film thickness. Under the ideal conditions, fast stirring would provide fresh interface so rapidly that there would be little time for formation of low polymer inside a film-coated solvent drop and both reactants within the film structure would be used in completing high polymer formation.

Some polyamides which are very insoluble and therefore , precipitate very rapidly are best prepared in highly dilute solutions such that polymerization takes place in a thin layer approaching a mono-layer.

Another factor in the technique of interfacial polycondensation is the manner of addition of the second reactant. Possibly the best method would be to use a high-speed low-volume mixer into and through which both solutions would pass simultaneously . In the batch process, rapid addition of the diacid chloride solution to the highly stirred diamine solution has given the best results. The strong bases such as triethylamine, sodium hydroxide and sodium carbonate are the best acid acceptors for producing 6-10 polyamides. In the absence of an added acceptor, diamine becomes the acceptor. When there is no excess of diamine the polymer yield drops because only half the diamine will be reacted with the diacid chloride to form polyamide.

Hydrolysis of acid chlorides is definetely the principal inter-fering side reaction in interfacial polycondensation processes. For many polymer preparations it provides no problem, for a few it is a major difficulty. The rates of hydrolysis parallel general reactivity but, since hydrolysis occurs almost wholly in the aqueous phase, the solubility of the acid chloride in the aq.phase is a principal factor in losses by hydrolysis.

Short-chain diacid chlorides, that is, those from about C_7 down, are hydrolyzed very rapidly even at pH values as low as 4. On the

other hand the less water-soluble sebacyl chloride and the less reactive aromatic acid chlorides are hydrolyzed rather slowly at high pH values.

The majority of reactions suitable for interfacial polycondensation are sufficiently rapid so that the reaction is complete 1-5 minutes. This provides time for thorough mixing in a high-speed mixer. Reaction rates so slow that the polycondensation is incomplete at 20 min or more rarely yield polymers with high molecular weight.

Interfacial polycondensation can be carried out in a nonaqueous two phase system [8]. These are few such systems and none appears to possess any advantages over aqueous systems. The advantages of water are that is inexpensive, has low miscibility with many organic liquids, is a good solvent for many diamines, bisphenoxides and alkalies and is a good solvent for by product salt.

2.1.1.2.2. The Low Temperature Solution Polycondensation

The method involves bringing together fast reacting intermediates in an inert solvent medium and providing for the removal of any acidic by-products by means of acid acceptors. The method is designated broadly solution polycondensation, although the process encompasses both systems in which the polymer and reactants stay dissolved as well as systems in which the reactants are not all dissolved at the start and great many from which the polymer precipitates. Solution polycondensation can be used to prepare many classes of polymers polyurethanes, and polyphenyl esters. Any difficulty with acid chloride hydrolysis, encountered in the aqueous two phase system, is avoided, and the number of useful reaction media is extended to include many polar solvents.

Reactions leading to formation of condensation polymers by the solution method can be divided into three groups which involve varying degrees of complexity.

The most complex type of polycondensation system is the reaction between a diacid chloride and a diamine, with or without an acid acceptor.

In this polymerization system, one of the intermediates, the diamine, is a base and as such it can react with by-product acid and compete with added acid acceptor. In this pointof view, the stoichiometric balance of the intermediates may be disturbed, since the diamines are not acylated as salts or in the ionic state.

The less complicated polymerization is between a diacid chloride and a diol. The equivalent strong base or an excess of weak base is needed in the low temperature process to accelerate the reaction and to accept the by-product acid. There is no competition between intermediates acceptor for by-product acid as in the first case.

The simplest type of solution polymerization in which neither by-products are eliminated nor acid acceptors are needed is not a condensation reaction but a step-addition reaction resulting in a condensation polymer as in the reaction of a diisocyanate with diamine or diol.

The main goal in performing a solution polycondensation is to produce a polymer in high yield and with high molecular weight. Both physical and chemical effects which may lead to the formation of a polymer with lower molecular weight than is considered possible because of a previously demonstrated high quality in the intermediates.

Low temperature solution polycondensation reactions are suprisingly tolerant of impurities, but this tolerance varies considerably with the circumstances. The purity of the reactants and solvents must be higher than for the interfacial polycondensation method.

Nonreactive impurities in the solvent are harmless except insofar as they may depress the solubility of the polymer. Reactive impurities in solvents are substances such as water, alcohols, acids, and phosgene.

The solvent should not react with amines or acid chlorides during the time necessary to carry out the polymerization.

Contact between a tertiary amine acceptor and the acid chloride or certain solvents must be avoided to prevent several possible side reactions. In the usual preparative method wherein acid chloride is added to a solution of diamine and strongly basic acceptor, no difficulty is experienced if the polycondensation reaction is fast. As the polycondensation reaction becomes slower, then there is a greater interference from side reactions. The base strength of acid acceptor must be equal or exceed the base strength of the monoacylated diamine or of the diamine group at the end of an oligomer or polymer.

Solution polycondensations between diamines and diacid chlorides produce polymers with the highest molecular weights when carried out at room temperature or below.

The sensitivity to the concentration of the reactant in the solution polycondensations is not clear. The preferred concentration range has shown many variations, i.e., for the synthesis of polyamides.

The by-product hydrogen chloride in the case of reactions between diamine and diacid chloride at low temperature polycondensations must be removed from the reaction site, for amine salts do not react. Thus, the acid acceptors must be employed to retain by-product acid.

Recently developed the N-silylated diamine method has several advantages over the conventional diamine-acid chloride route [11]. Both N-silylated aromatic diamines are more reactive to the diacid chlorides than the corresponding unsubstituted diamines and polycondensation goes on under almost neutral reaction conditions with elimination of alkyl silyl chloride, whereas that by the conventional diamine-diacid chloride system proceeds with evolving of hydrogen chloride [12].
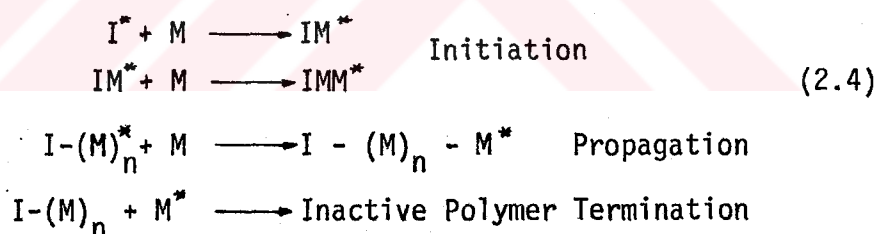
Many activating agents are also employed for the synthesis of polyamides from diacid and diamine at low temperature to overcome the difficulties concerning with the acid acceptors and handling problems of diacid chlorides [13,14].

2.1.2. Addition Polymerization

Many compounds of the general formula $_C M_\rangle$ are able to behave as difunctional monomers by the opening of multiple bonds or strained rings and ignoring end-groups, the resulting polymers may be described by the general formula $(M)_n$ [15] .

These polymers have a repeat unit which is identical in composition to the monomer and they are formed without the loss of any portion of the monomer molecules. Polymers of this type are commonly named as addition polymers and the reactions which form them are referred to as addition or chain-growth polymerization.

Addition polymerization invariably proceeds by a chain reaction mechanism, chain initiation being achieved by addition of an active initiator which reacts with the monomers to produce an active centre. Addition of further monomers to the resulting active centres proceeds in a series of rapid propagation steps, until termination occurs, either by a chemical reaction of the centre or by exhaustion of the monomer supply

$$
\begin{array}{ll}
I^* + M \longrightarrow IM^* & \text{Initiation} \\
IM^* + M \longrightarrow IMM^* &
\end{array} \tag{2.4}
$$

$$
I\text{-}(M)_n^* + M \longrightarrow I - (M)_n - M^* \quad \text{Propagation}
$$

$$
I\text{-}(M)_n + M^* \longrightarrow \text{Inactive Polymer Termination}
$$

where denotes the active centres which may be free radicals, anions, cations or a varietly of complex co-ordination compounds.

The types of unsaturated molecule readily undergoing chain reaction polymerization include olefins, conjugated dienes, acetylenes and carbonyl compounds with the first two types being of most importance.

The tendency of a ring compound to polymerize depends upon the extent of ring strain and the availability of suitable mechanism for the ring opening process [16] . Ring strain is a thermodynamic property which is caused by either forcing the bonds between ring atoms into angular distortion or by steric interaction of substituents on the ring

atoms.

Addition polymerization is classified into free radical and ionic polymerization according to the structure of active growing species which may be either a radical or an ion.

2.1.2.1. Free Radical Polymerization

The chain mechanism of the addition of free radicals to double bonds was applied quantitatively to the chain growth polymerization of olefin monomers by Flory in 1937 [17]. Flory showed that a free radical polymerization, like other radical processes, was a typical chain reaction requiring three distinct steps : initiation, propagation, and termination.

The initiation step is considered to involve two reactions. The first is the production of free radicals by anyone of a number of reactions. The usual case is the homolytic dissociation of an initiator or catalyst species I to yield a pair of radicals R.

$$I \xrightarrow{k_d} 2R. \qquad (2.5)$$

where k_d is the rate constant for the initiator dissociation. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce the chain initiating species M_1.

$$R. + M \xrightarrow{k_i} M_1. \qquad (2.6)$$

where M represents monomer molecule and k_i is the rate constant of the initiation step.

Propagation contains the growth of M_1. by the successive of large numbers of monomers. Each addition creates a new radical which has the same identity as the one previously, except that it is larger by one monomer unit. In general terms

$$M_n. + M \xrightarrow{k_p} M_{n+1}. \qquad (2.7)$$

where k_p is the rate constant of propagation. Propagation takes place very rapidly. The value of k_p for most monomers is in the range of $10^2 - 10^4$ liter/mole-sec.

The propagating polymer chain stops growing and terminates. Two radicals react with each other by combination

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tc}} M_{n+m} \quad \text{(Dead polymer)} \qquad (2.8)$$
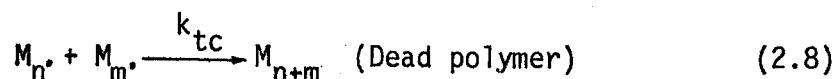
or, more rarely, by disproportionation in which a hydrogen radical that is beta to one radical center is transferred to another radical center. This results in the formation of two polymer molecules : one saturated and one unsaturated

$$M_n\cdot + M_m\cdot \xrightarrow{k_{td}} M_n + M_m \quad \text{(Dead polymer)} \qquad (2.9)$$
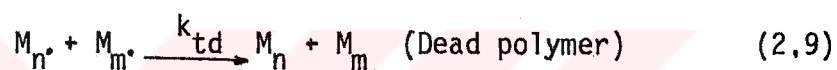
where k_{tc} and k_{td} are the rate constants of termination by coupling and disproportionation, respectively. Typical termination rate constants are in the range of $10^6 - 10^8$ liter/mole-sec or orders of magnitude greater than the propagation rate constants. The much greater value of k_t compared to k_p does not prevent propagation because the radical species are present in very low concentrations and because the polymerization rate is dependent on only the one-half power of k_t (This subject will be discussed later) .

2.1.2.2. Kinetics of Radical Polymerization

The initiation process is a two-step sequence, both steps of which enter into the overall rate equation. The first of the two steps is the dissociation of the initiator, I, to generate two radical fragments, and the second step is the addition of one of these fragments to a monomer molecule, M, to start the growth of a polymer chain. The second step may have a much higher rate constant than the first, but it still must be taken into consideration in kinetic treatments because not every free radical formed by dissociation of the initiator lives long enough to add to a monomer. Some radical fragments from the initiator are lost through recombination within the original solvent cage (cage effect) and some are lost by reaction

with another initiator radical or a polymer radical after escaping from the cage.

The mole fraction of initiator radicals formed which successfully add to monomers to initiate polymer chains is named the efficiency, f.

The rate of initiation, R_i, is then a composite of the dissociation and the initial addition reactions, but a general approximation made in deriving kinetic expressions for radical polymerization is that these two reactions have equal rates.

$$R_i = 2fk_d \ [I] = k_i \ [I.] \ [M] \qquad (2.10)$$

This approximation is based on the steady-state assumption which implies and requires that the concentration of free radicals is effectively constant throughout the course of a chain-growth polymerization reaction.

The propagation step involves only one type reaction the addition reaction, the rate of this reaction may vary considerably at the start of the polymerization reaction with the size of the polymer chain radical. Still, it is usually assumed that the rate constant for propagation is invariant after the initial addition reaction, so that the kinetic expression for the rate of propagation, R_p

$$R_p = k_p \ [M.] \ [M] \qquad (2.11)$$

includes one rate constant.

The termination state can be either a combination or disproportionation reaction, and both reactions must be included in the kinetic expression for the rate of termination, R_t

$$R_t = 2(k_{tc} + k_{td}) \ [M.]^2 \qquad (2.12)$$

The overall rate of polymerization, R_o, is the rate of disappearance of monomer, which is removed both in the first initiator radical-addition reaction and in the propagation step. The overall

rate expression should contain both of these terms, but because there are hundreds or thousands of propagation steps

$$R_0 = k_i [I.] [M] + k_p [M.] [M] \qquad (2.13)$$

for every initiation step in the production of high molecular weight polymer. The overall rate of polymerization is assumed to be idential to the rate of propagation.

$$R_0 = R_p = k_p [M.] [M] \qquad (2.14)$$

This rate equation, although adequately representative of the rate of polymerization in most cases, is not very useful because it contains the quantity M. , which is the concentration of free-radical endgroups. The steady-state assumption is invoked to eliminate this difficulty. In order to achieve a steady-state with constancy of radical concentration, the rate of initiation, R_i, is assumed to be equal to the rate of termination, R_t, and equating these two expressions yield an equation for [M] .

$$R_i = R_t$$

$$2fk_d [I] = 2(k_{tc}+k_{td}) [M.]^2 \qquad (2.15)$$

$$[M.] = [fk_d/(k_{tc}+k_{td})]^{1/2} [I]^{1/2} \qquad (2.16)$$

and finally,

$$R_p = k_p [M.] [M] = k_p [M] [fk_d/(k_{tc}+k_{td})]^{1/2}[I]^{1/2} \qquad (2.17)$$

and,

$$K = k_p [fk_d/(k_{tc}+k_{td})]^{1/2} \qquad (2.18)$$

$$R_p = K [I]^{1/2} [M] \qquad (2.19)$$

The rate equation, predicts that the rate of polymerization should be dependent on the first power of the monomer concentration, and on the square root of the initiator concentration.

These rate expressions can be adapted further to indicate the effect of different reaction variables on the degree of polymerization of the polymeric products. If no side reactions such as chain transfer, occur during the polymerization reaction, then each polymer chain should contain one or two initiator fragments as endgroups, depending upon whether termination occurs by disproportionation occurs exclusively, the degree of polymerization should equal the kinetic chain length, v, while for termination by combination, the degree of polymerization should be twice the kinetic chain length

$$v = \frac{R_p}{R_i} = \frac{R_p}{R_t} \qquad (2.20)$$
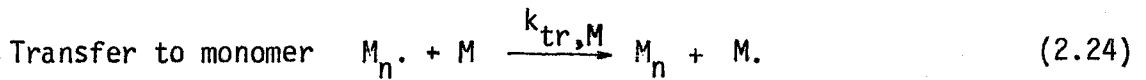
Consequently, the average degree of polymerization, $\bar{P}_n$, is either equal to or twice this rate ratio for a clean chain-growth reaction

$$\bar{P}_n = k_p^2 \ [M]^2/2(k_{tc}+k_{td})R_p \qquad (2.21)$$

This last relationship reveals that the average degree of polymerization in a polymerization reaction is inversely proportional to the rate of polymerization. However, the inverse relationship is not strictly correct because R_p can be increased by increasing the monomer concentration which would also increase $\bar{P}_n$. Instead, this relationship applies only to an increase in R_p brought on by an increase in the rate of formation of radicals, and consequently by an increase in [M]. The important factor is that an increase in [M] causes a considerable increase in R_t which increases with [M], and therefore, a decrease in $\bar{P}_n$ occurs because of the inverse relationship of $\bar{P}_n$ and R_t.

Effective chain transfer is the physical termination of a polymer chain without destruction of the kinetic chain. The new radical formed in the chain-transfer reaction, which terminates the growing polymer chain, is reactive enough to initiate a new polymer chain more or less within the same period of time required for the addition of a monomer molecule to a growing chain endgroup in the normal propagation step.

As a result, there is no detectable decrease in the overall rate of polymerization, only a decrease in the average molecular weight of the polymer produced compared to that from a polymerization reaction in which chain transfer does not occur. Therefore the equation used to express quantitatively the result of effective chain transfer is one based on $\bar{P}_n$. There are many chain-transfer reactions being termination reactions.

Transfer to initiator $M_n\cdot + I_2 \xrightarrow{k_{tr,I}} M_n I + I.$ (2.22)

Transfer to solvent $M_n\cdot + SH \xrightarrow{k_{tr,S}} M_n + S.$ (2.23)

Transfer to monomer $M_n\cdot + M \xrightarrow{k_{tr,M}} M_n + M.$ (2.24)
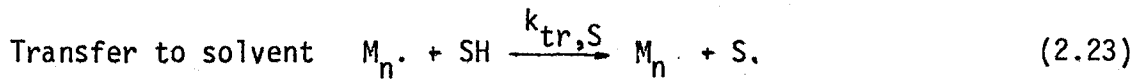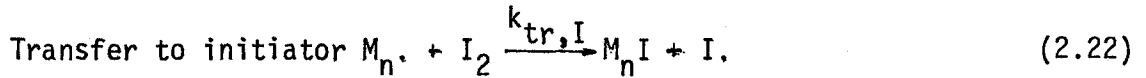
where $M_n\cdot$ represents the growing polymer chain, and SH represents the solvent containing labile group such as hydrogen or halogen atom. $k_{tr,I}$, $k_{tr,S}$ and $k_{tr,M}$ are the rate constants of the chain transfer reactions. In the case of combination termination occurs

$$\bar{P}_n = \frac{R_p}{(R_t/2) + k_{tr,M}[M\cdot][M] + k_{tr,s}[M\cdot][S] + k_{tr,I}[M\cdot][I]} \quad (2.25)$$

$$\frac{1}{\bar{P}_n} = \frac{R_t/2}{R_p} - \frac{k_{tr,M}[M\cdot][M]}{k_p[M][M]} + \frac{k_{tr,s}[M\cdot][S]}{k_p[M][M]} + \frac{k_{tr,I}[M\cdot][I]}{k_p[M\cdot][M]} \quad (2.26)$$

$$\frac{1}{\bar{P}_n} = \frac{k_t[M\cdot]}{k_p[M]} + \frac{k_{tr,M}}{k_p} + \frac{k_{tr,s}[S]}{k_p[M]} + \frac{k_{tr,I}[I]}{k_p[M]} \quad (2.27)$$

The transfer constants are defined by

$$C_M = \frac{k_{tr,M}}{k_p} \quad ; \quad C_S = \frac{k_{tr,s}}{k_p} \quad ; \quad C_I = \frac{k_{tr,I}}{k_p} \quad (2.28)$$

The initiator concentration may be eliminited in favor of rate of polymerization by eq. (2.27). The last form of equation is called as Mayo eq.[18].

$$\frac{1}{\bar{P}_n} = \frac{k_t R_p}{k_p^2 [M]^2} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{k_t R_p^2}{k_p^2 f k_d [M]} \qquad (2.29)$$

In the absence of solvent(bulk polymerization) the third term of eq.(2.29) vanishes. Also, by the choice of an initiator such as an aliphatic azonitrile which is not susceptible to chain transfer, the last term in eq.(2.26) is rendered negligible.

Upon substituting Arrhenius expressions for each of the rate constants occurring in this eq.(2.30), we obtain

$$\ln (R_p/[M][I]^{1/2}) = \ln [A_p (fA_d)^{1/2}/A_t^{1/2}] - [E_p - (E_d-E_t)/2]/RT \qquad (2.30)$$

where f is assumed independent of temperature. Hence the apparent activation energy E_a obtained from the slope of a plot of the logarithm of the rate against $1/T$ will be related to the individual activation as follows

$$E_a = E_d/2 + E_p - E_t/2 \qquad (2.31)$$

2.1.2.3. Initiators for Free Radical Polymerization

Compounds that generate radicals by homolytic scission when heated or irradiated or by any other means, may initiate free radical polymerizations under certain conditions. The free radical initiators may be classified in several groups of which, most important are as follows,

   i. Organic or inorganic peroxides

  ii. Hydroperoxides

 iii. Peresters

  iv. Azo compounds

2.1.2.3.1. Thermal Decomposition of Azo Compounds

The question of whether the azo compounds lose nitrogen by simultaneous breakage of both C-N bonds (concerted mechanism) (1)

or whether they proceed via adiazenyl radical (step wise mechanism) (2) was discussed as early as 1929 [19].

$$R - N = N - R \xrightarrow{\quad (1) \quad} \begin{matrix} R \\ \diagdown \\ N \equiv N \\ \diagup \\ R \end{matrix} \longrightarrow \begin{matrix} R \cdot \\ N \equiv N \quad \cdot R \end{matrix} \qquad (2.32)$$

$$\downarrow (2)$$

$$\begin{matrix} R \\ \diagdown \\ N = N. \\ \cdot R \end{matrix}$$
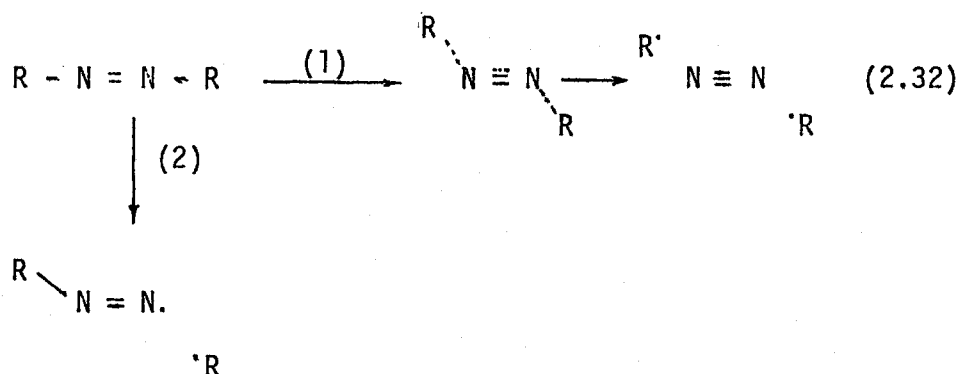
Route 1 seems preferable for several reasons. For one, in no case has an azo compound of the type which would result from reactions of the intermediate radical RN_2. been detected in such decompositions. For another, for statistical reasons the rate of decomposition of a mixed azo compound, $R-N_2-R'$, should be approximately one-half that of the more reactive symmetrical azo compound if the step-wise mechanism operates eq.(2.33).

$$R - N = N - R' \longrightarrow R - N = N. + R! \qquad (2.33)$$

but the rate should be approximately equal to the geometric mean of the decomposition rates of the two symmetrical azo compounds if the concerted mechanism operates ; the latter was found to be true [20]. Lastly, the energy gained from the electron pairing in the formation of stable N_2 molecule during the concerted reaction would be expected to greatly decrease the activation energy for the overall homolytic decomposition; and this factor probably accounts for the low activation energies observed for many of these reactions. The activation energies for the decomposition of several azo compounds are collected in Table 2.1.

The azo nitriles are effective initiators for free radical polymerization reactions because of their favorable rates of thermal dissociation in the temperature range of $40-60^{\circ}C$, their resistance to induced decomposition, and their ease of synthesis.

Table 2.1. Decomposition Rate Parameters for Azonitriles of the Type :
$R_1R_2R_3C-N= N-CR_1R_2R_3$

R_1,R_2,R_3	E_a,kJ mole^{-1}	logA	Solvent	Ref
Me$_2$, CN	128.5	15.0	C_6H_6	21
Et,Me,CN	138.17±1.25	16.31±0.18	PhEt	22
n-C$_3$H$_7$,Me,CN	135.6	16.25	PhMe	23
n-C$_4$Hg,Me,CN	$k=1.58.10^{-4}s^{-1}$at 80.2^{o}C		PhMe	23
HOOC(CH$_2$)$_3$,Me,CN	133.5	-	DMAc	24

The cage recombination reactions can occur with these compounds, with the formation of an inactive product, so that the new product, no longer contains a labile covalent bond susceptible to thermal dissociation owing to restrictions on the motion of molecules in the liquid state, a pair of radicals formed in solution may execute many oscillations in their respective cages consisting of surrounding molecules before they diffuse apart [25]. These wasteful reactions reduce the efficiency, f, of initiators in free radical polymerization.

2.1.2.3.2. Poly-functional Azo Initiators

Compounds which consist of at least two non-equivalent azo functions are stepwise radical generators and useful azo initiators for free radical polymerization to obtain homopolymers and graft and block copolymers, as crosslinking agents for elastomers, as additives for resin gelification and hardening [26].
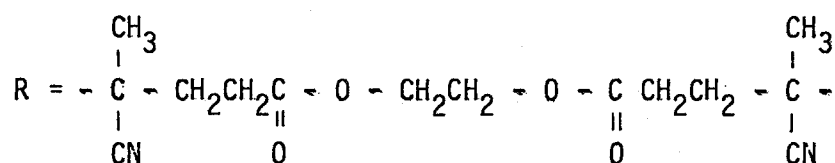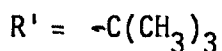
Polyazo compounds can be obtained by 'coupling' through a chemical reaction, two or more mono azo derivatives [27]. In order to perform it, one of the components contains an acylating function, the order one a reactive group (alcohol, thiol, amine) that allows the fragment bonding by formation amides, esters, thio esters, etc.

A classification of polyazo compounds based on chemical structures is very difficult to achieve. Generally, they are differentiated two types of polyazo compounds :

    i. Alkyl azo compounds, eg the diazo esters with a symmetrical structure have the following formula [28].

$$R' - N=N - R - N=N - R' \qquad (2.34)$$

where

$$R' = -C(CH_3)_3$$

$$R = - \underset{\underset{CN}{|}}{C} - CH_2CH_2\underset{\underset{O}{\|}}{C} - O - CH_2CH_2 - O - \underset{\underset{O}{\|}}{C} CH_2CH_2 - \underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} -$$

Also, polymeric azo initiators, eg polyazoesters having the form

$$\left[R - N = N \right]_n \qquad (2.35)$$

where R might be

$$- \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{O}{\|}}{C} - O - R' - O - \underset{\underset{O}{\|}}{C} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} -$$
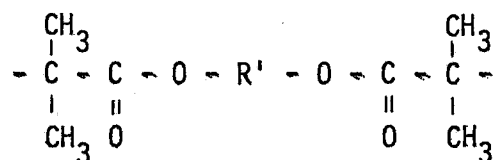
are involved in this type [29].

    ii. Alkyl carbonyl azo compounds, the bis azo derivatives of this type contain two species of azo groups, one of them linked to the carbonyl group of an ester, amide, etc.

    The terms have been described by Sheppard et al [27,28]. with the following general formulae

$$R' - \underset{\underset{O}{\|}}{C} - N=N - R -N=N - R' \text{ or } R' - N=N - \underset{\underset{O}{\|}}{C} - N=N - R' \qquad (2.36)$$
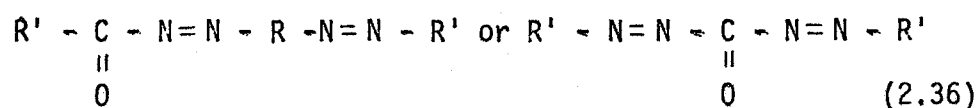
2.1.2.3.2.1. Polymeric Azo Initiators

The azo group can take place either on the polymeric backbone or as pendant groups along the main skeleton [30]. Polymers in which the azo group is part of the terminal segment might be considered as a special case of those polymers having azo groups on their main chain.
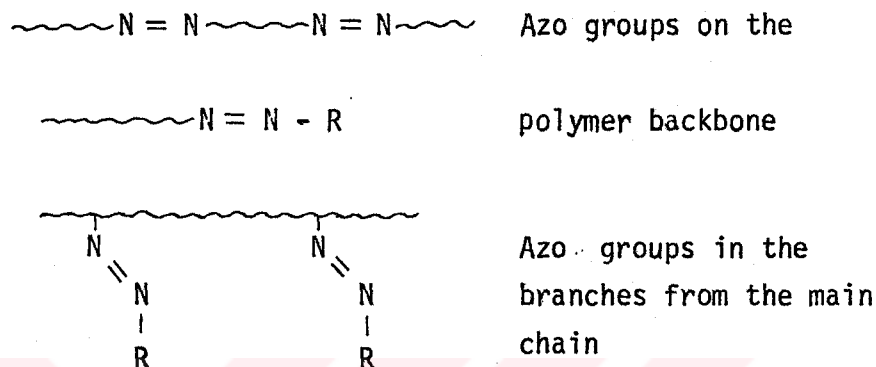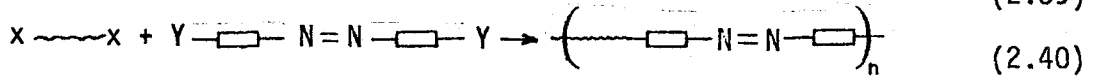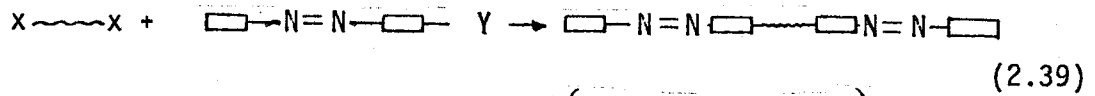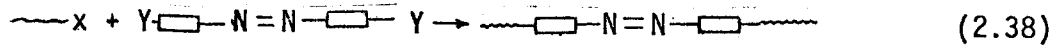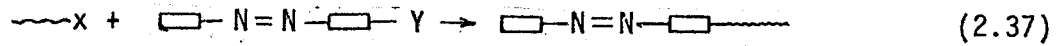
~~~~N = N~~~~~N = N~~~~ Azo groups on the

~~~~~~N = N - R polymer backbone

Azo groups in the
branches from the main
chain

Where the azo groups form part of the polymer backbone their decomposition leads to a simultaneous fragmentation of the polymer. In the presence of a suitable monomer, the radical terminated polymer fragments can initiate a polymerization and become part of a block copolymer. Thermolysis of azo functions which is terminal group of polymer also lead to block copolymers, but in this case no fragmentation of the azo-containing polymer occurs.

Graft copolymers can be obtained when the azo functions are pendant groups of the main polymer backbone. The decomposition of such azo groups forms radicals along the chain which can then behave as grafting centres. The synthesis of polymers containing azo groups as branches along their backbone can be obtained from polymer analogue reactions [31], copolymerization [32], and copolycondensation [33].

The prepolymers containing azo groups can be snythesized by three routes [30].

i. Reaction of low-molecular weight azo compounds having additional suitable functional groups

i a. with functional polymers :

$$\sim\!\!\sim\!\! x \; + \; \square\!\!-\!N=N\!-\!\square\!\!-Y \;\rightarrow\; \square\!\!-\!N=N\!-\!\square\!\!-\!\sim\!\!\sim \tag{2.37}$$

$$\sim\!\!\sim\!\! x \; + \; Y\!\!-\!\square\!\!-\!N=N\!-\!\square\!\!-Y \;\rightarrow\; \sim\!\!-\!\square\!\!-\!N=N\!-\!\square\!\!-\!\sim\!\!\sim \tag{2.38}$$

$$x\!\!\sim\!\!\sim\!\! x \; + \; \square\!\!-\!N=N\!-\!\square\!\!-\; Y \;\rightarrow\; \square\!\!-\!N=N\,\square\!\!-\!\!\sim\!\!\sim\!\!-\square N=N\!-\!\square$$
$$\tag{2.39}$$

$$x\!\!\sim\!\!\sim\!\! x \; + \; Y\!\!-\!\square\!\!-\; N=N\!-\!\square\!\!-Y \;\rightarrow\; \left(\!\!\sim\!\!\sim\!\!-\!\square\!\!-\!N=N\!-\!\square\!\!-\!\right)_{\!n} \tag{2.40}$$

x,Y = Reactive groups

i b. with monomers :

$$Y\!\!-\!\square\!\!-\; N=N\!-\!\square\!\!-\; Y \; + \; (n\!+\!m)M \;\longrightarrow\; (M)_n\!-\!\square\!\!-\; N=N\; \square\!\!-(M)_m \tag{2.41}$$
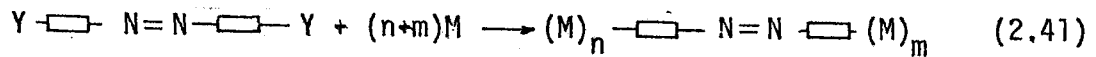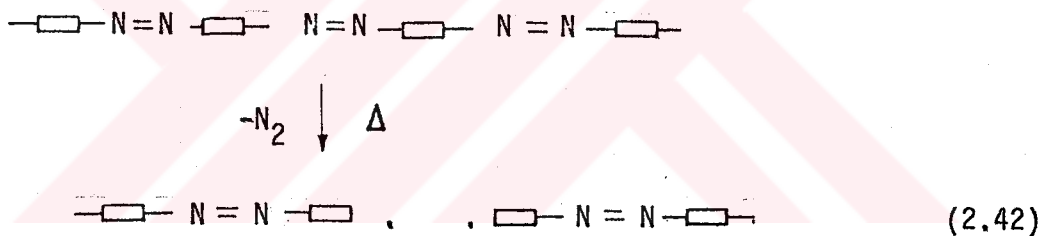
   ii. Condensation of α,ω-bifunctional small molecules
ii a. Partial degradation of polymeric azo compounds :

$$-\square\!\!-\!N=N\; \square\!\!-\; N=N\!-\!\square\!\!-\; N=N\!-\!\square\!\!-$$

$$-N_2 \;\downarrow\; \Delta$$

$$-\square\!\!-\; N=N\!-\!\square \quad,\quad\; \square\!\!-\; N=N\!-\!\square\!\!- \tag{2.42}$$

$$\downarrow \; (n\!+\!m)M_1 \quad \text{radical disproportionation}$$

$$-\square\!\!-\; N=N\!-\!\square\!\!-(M)_n \; + \; (M)_m\!-\!\square\!\!-\; N=N\!-\!\square\!\!-$$

   Decomposition of the remaining azo groups with another monomer
causes a block copolymerization.

ii b. Cocondensation method

$$n(a\; Y\!\!-\!\blacksquare\!\!-\; Y \; + \; b\; Y\!\!-\!\square\!\!-\; N=N\!-\!\square\!\!-\; Y) \; + \; n(a\!+\!b)x\!\!-\!\!\diagup\!\!\!\!\diagup\!\!-\; x$$

$$\downarrow \tag{2.43}$$

$$\left(\!\left(\!-\blacksquare\!\!-\!\diagup\!\!\!\!\diagup\!\!-\right)_{\!a}\!\left(\!-\square\!\!-N=N\; \square\!\!-\!\diagup\!\!\!\!\diagup\!\!-\right)_{\!b}\!\right)_{\!n}$$

The average concentration of azo groups per polymer chain and the length of the segments depends on the ratio a:b.

iii. Polymer analogue reactions such as

$$\sim\sim NH - (CH_2)_5 - CO - NH - (CH_2)_5 - CO\sim\sim + NOCl$$

$$\downarrow -HCl$$

$$\sim\sim NH - (CH_2)_5 - CO - N (NO) - (CH_2)_5 - CO\sim\sim \qquad (2.44)$$

$$\downarrow \text{rearrangement}$$

$$\sim\sim NH - (CH_2)_5 - CO - O - N=N - (CH_2)_5 - CO\sim\sim$$

Only one azo group which takes place along a polymer backbone is cleaved to yield a polymeric monoradical. In the presence of another monomer, it initiates a block copolymerization as follows

$$\sim\sim\sim\sim\sim N = N \sim\sim\sim\sim\sim$$

$$\Delta \downarrow -N_2$$

$$\sim\sim\sim\cdot \quad \cdot\sim\sim\sim \qquad (2.45)$$

$$\downarrow + (n+m)M$$

$$\swarrow \qquad \searrow$$

$$\sim\sim\sim(M)_n + (M)_m\sim\sim\sim \qquad \qquad \sim\sim\sim(M)_{\overline{n+m}}\sim\sim\sim$$

radical disproportionation   radical combination

When prepolymer backbone carries many azo groups as follows, there are many possibilities

$$\{ \sim\sim\sim N = N \}_n \sim\sim\sim\sim N = N - R$$

$$\downarrow \quad \text{decomposition}$$

$$\cdot\sim\sim\sim\sim\cdot \quad + \cdot R \qquad\qquad (2.46)$$

$$\downarrow \quad M$$

disproportionation   combination

$(M)_a \sim\sim\sim (M)_b +$ $\{\sim(M)_d\}_n + R \{M_{c+c}\}R$

$\quad R-(M)_c$

$\qquad\qquad\qquad +R-(M)_c\{\sim(M)_d\}_n-(M)_c-R$

Azo groups at the ends of prepolymer backbone lead to radicals producing both block copolymer and homopolymer

$$\sim\sim\sim\sim N = N - R$$

$$\downarrow \Delta$$

$$\sim\sim\sim\sim\cdot + N_2 + R\cdot$$

$$\downarrow \quad M$$

$$\sim\sim\sim(M)_n\cdot + R-(M)_m\cdot \qquad\qquad (2.47)$$

$$\swarrow \text{combination} \searrow$$

$\sim\sim\sim(M)_{n+n}$ $R-(M)_{m+m}-R$

$\sim\sim\sim(M)_{n+m}$

Block copolymer   Homopolymer

Hill first showed the synthesis of polymeric azonitriles via a synthesis analogous to that for AIBN itself [34].

$$\left[\begin{array}{c} \underset{|}{\overset{CH_3}{C}} - (CH_2)_n - \underset{|}{\overset{CH_3}{C}} - N=N \\ CN \qquad\qquad CN \end{array}\right]_x \qquad (4 \leq n \leq 12) \qquad (2.48)$$
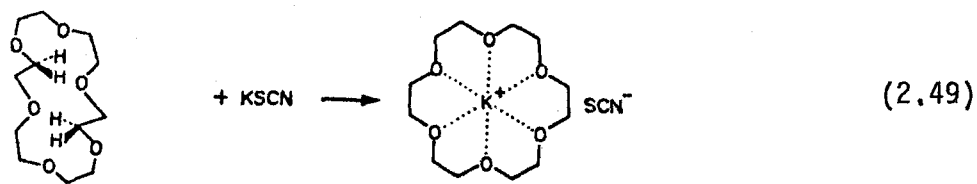
Polymeric azonitrile

The other examples are the reaction of AIBN or AIBN derivatives such as 4,4'-azobis (4-cyano valeryl chloride) with 1,2-ethylene diamine [35], 1,6-hexa methylene diamine [35-37], cis/trans-diamino dibenzo-18-crown-6 [38,39], bisphenol A [40].
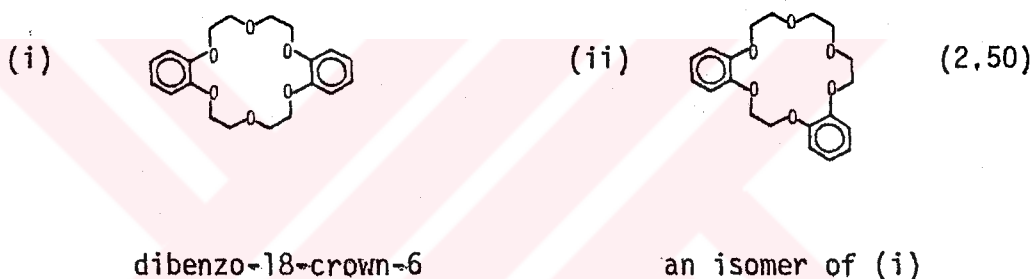
2.2. Crown Ethers

There are many developments which predate Pedersen's first papers on crown ether chemistry [41,42]. Luttringhaus had made early preparations of crown ether compounds [43]. Moreover, the nitrogen macrocycles had been studied for decades prior to 1967 [44] and macrocyclic polyethers had been obtained years before from the cyclooligomerization of ethylene oxide [45]. At about the same time, cation complexation by naturally occurring polyoxygen containing species was established [46] and the 'self solvating bases' described by Ugelstad [47] bear a striking resemblance to what it is called 'crown complexation'. But, nevertheless, the beginning of crown ether chemistry is generally dated from Pedersen's first disclosures in 1967 because many examples of these compounds were prepared and their potential as complexing agents was recognized by Pedersen.

The 'crown ether' term was first suggested by Pedersen and has been widely used [42]. It generally refers to macrocyclic polyethers having the ethyleneoxy unit as the basic repeating structure. When every third atom is oxygen, binding is obviously higher than when more carbons separate the hetero atoms. In addition, the unfavorable conformational interactions are reduced relative to the carbon analogs.

$$+ \text{ KSCN} \longrightarrow \qquad (2.49)$$

The nomenclature convention suggested by Pedersen [42] for the simplecompounds involves two numbers. The first of these indicates the total number of atoms in the macrocycle. The second number indicates how many hetero atoms are present in the ring.
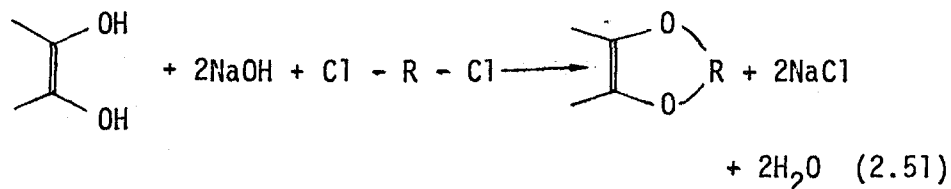
(i)   (ii)   (2.50)

dibenzo-18-crown-6   an isomer of (i)

Compound (ii), above, is essentially 18-crown-6 into which two benzene rings have been fused. Pedersen suggested the name 'dibenzo-18-crown-6' to describe it. But, the name dibenzo does not adequately describe the relative positions of the benzene rings. Naturally, systematic names may be used for these compounds but such names have generally proved cumbersome. The systematic name for dibenzo-18-crown-6 is 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxa-cyclooctadeca-2,11-diene.
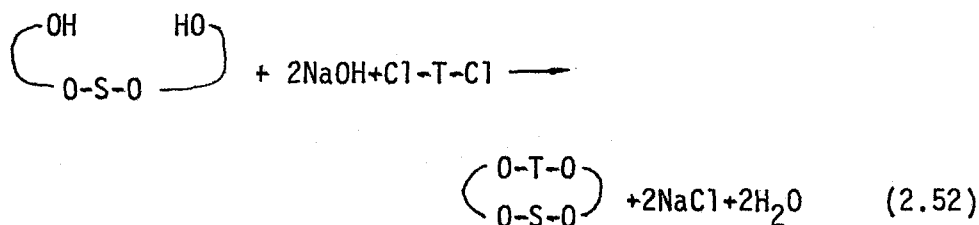
2.2.1. Synthesis of Crown Ethers

In Pedersen's first paper on the synthesis of macrocylic polyethers [41], he generalized the synthetic approaches. The four principal methods, for example, are V , W , X , and Y .

Method 'V' is shown in eq.(2.51). This corresponds to the so-called 'one plus one' synthesis of crowns. The notion is that a single diol unit is allowed to react

$$\text{(structure)} + 2NaOH + Cl - R - Cl \longrightarrow \text{(structure)} R + 2NaCl$$

$$+ 2H_2O \quad (2.51)$$

with a single polyethylene glycol having leaving groups at each end. An example of this would be the synthesis of benzo-15-crown-5 from catechol and tetraethylene glycol dichloride. In addition, bases other than sodium hydroxide may be used and in many cases are preferred. For aliphatic alcohols, potassium-t-butoxide has been used often, but NaH has been the base of choice. Although Pedersen succesfully utilized chlorides as leaving groups in a number of syntheses, the most common choice of leaving group appears to be tosylate or methanesulfonate.
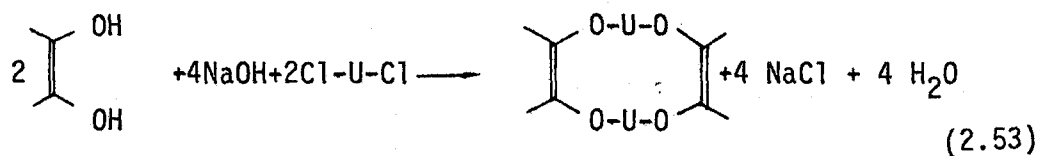
The second generally approach outlined by Pedersen is the so-called 'method W' in which the two hydroxyl groups are separated by a portion of the crown chain. A good example of this is the assembly of 18-crown-6 from triethylene glycol and triethylene glycol dichloride.

$$\text{(OH HO / O-S-O structure)} + 2NaOH+Cl-T-Cl \longrightarrow$$

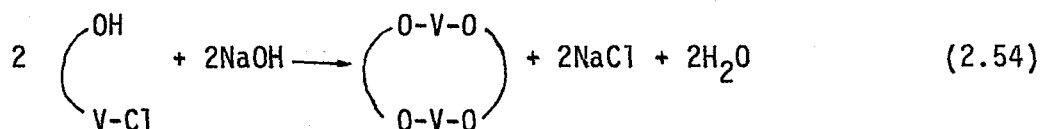$$\text{(O-T-O / O-S-O structure)} +2NaCl+2H_2O \quad (2.52)$$

This method would be especially important when the two halves of the crown unit are different.

Method X is almost a corollary to method V since the stoichiometry is identical. In fact, it is not intention, but the size of crown which will determine the outcome of the reaction. For example, the synthesis of dibenzo-18-crown-6 is carried out by treating two equivalents of catechol with two equivalents of diethylene glycol dichloride in the

presence of four equivalents of sodium hydroxide.

$$2 \underset{\text{OH}}{\overset{\text{OH}}{\bigg|}} + 4\text{NaOH} + 2\text{Cl-U-Cl} \longrightarrow \underset{\text{O-U-O}}{\overset{\text{O-U-O}}{\bigg|}} + 4 \text{ NaCl} + 4 \text{ H}_2\text{O}$$

$$(2.53)$$

The fourth of Pedersen's general methods is expressed as method Y. In this approach, a single unit may be both nucleophile and electrophile and react with the corresponding portions of its counterpart to yield a macrocycle.

$$2 \left(\underset{\text{V-Cl}}{\overset{\text{OH}}{}} + 2\text{NaOH} \longrightarrow \left(\underset{\text{O-V-O}}{\overset{\text{O-V-O}}{}} \right) + 2\text{NaCl} + 2\text{H}_2\text{O} \qquad (2.54)$$
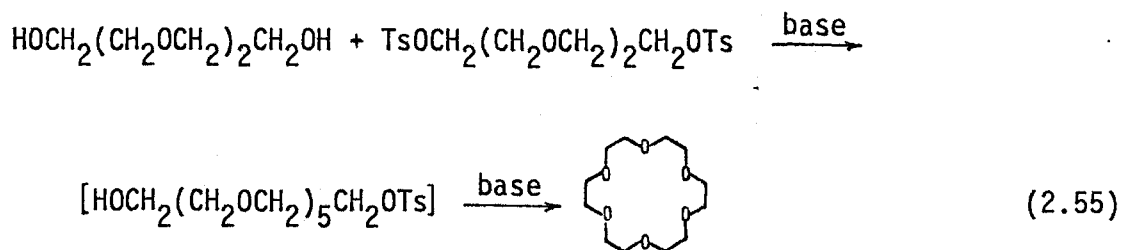
There are really two possibilities here. The first of these is that two units will react as illustrated, cyclize to afford a crown of half the size. It is precisely this approach which Pedersen used in the first synthesis of 18-crown-6.
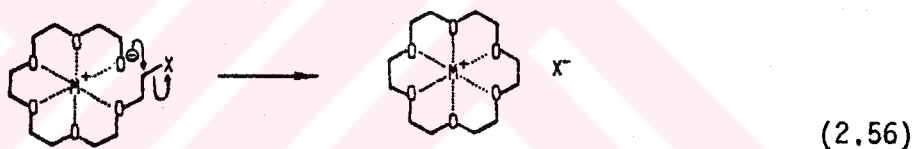
These four methods suggested by Pedersen serve as a useful starting point for the consideration of other approaches and should certainly not be considered an overview of existing methodology.

2.2.2. Template Effect and Mechanism of Complexation

Many of the crown ether syntheses are one form or another of the Williamson ether synthesis. Although the symplest example of such a reaction would involve an W-haloethylene glycol oligomer which undergoes intramolecular cyclization, it is more common for two new bonds to be formed in crown synthesis. An early example of the formation of a crown by a double-Williamson can be found in Dale's synthesis of 18-crown-6 [48]. The rather obvious chemical steps are shown in eq. (2. 55).

$$HOCH_2(CH_2OCH_2)_2CH_2OH + TsOCH_2(CH_2OCH_2)_2CH_2OTs \xrightarrow{\text{base}}$$

$$[HOCH_2(CH_2OCH_2)_5CH_2OTs] \xrightarrow{\text{base}} \qquad (2.55)$$

The first C-O bond formation is probably not influenced strongly by the presence of a templating cation. Since it is not crucial for one end of the chain to meet the other rather than reacting with a different molecule, it is not necessary to superimpose either a template or dilution condition on the reaction to prejudice the statistics. In the second step, however, such a prejudicial condition is required. This is available in the form of an alkali metal cation for which the long ethyleneoxy chain has a certain affinity. Presumably, the cation is ion-paired with the alkoxide anion and the remainder of the chain wraps around it. Note that such a picture corresponds to Ugelstad's 'self-solvating' bases [47]. The wrapping is illustrated in eq.(2.56) below

$$(2.56)$$

It is not clear exactly when association illustrated above actually takes place. It is certainly involved by the final ring closure stage, but it seems reasonable to assume that there is some cation-glyme type interaction taking place from the instant of solution. The fact that wrapping occurs in such a way that the two ends of the molecule are held in proximity, allows the reaction to be conducted at much higher concentrations than might otherwise be practical.

The first suggestion of a' template effect' which was ofered in the literature was made by Greene in 1972 [49]. The illustration of this concept is approximately that shown in eq.(2.56)above.

The optimization of template effects is probably achieved when the diameter of the cation corresponds most closely to the cavity
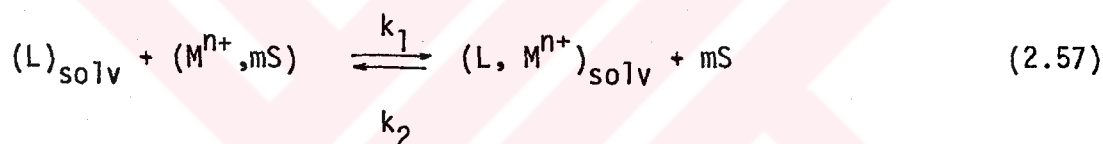
diameter of the macrocycle being formed. Thus, for simple crown ethers, Li^+, Na^+, and K^+ ions are clearly suited to templating the syntheses of 12-crown-4,15-crown-5 and 18-crown-6, respectively [50].

The formation of a 'complex' by association of two or more chemical units is one of the most basic molecular processes and of utmost importance in chemistry, physics and biology.

A host-guest complex, unlike covalent bonds, arises mostly through weak bond interactions (hydrogen bonding, metal-to-ligand bonding, pole-dipole binding forces, dipole-dipole binding forces, hydrophobic bindings etc).

The complexation process between a ligand, L, and a cation, M^{n+}, in solvent S may be represented by the general equation, where k_1, k_2 are defined as the rate

$$(L)_{solv} + (M^{n+}, mS) \xrightleftharpoons[k_2]{k_1} (L, M^{n+})_{solv} + mS \qquad (2.57)$$

constants of formation and dissociation of a complex. The quotient of k_1/k_2 gives the stability constant, K_s. The thermodynamic stability constant K_{th} can be given by equation, where f_c, f_L and f_m are the activity coefficients of the three

$$K_{th} = \frac{f_c [L, M^{n+}]}{f_L [L] f_m [M^{n+}]} \qquad (2.58)$$

species present (complex, ligand, cation) since these coefficients are generally unknown, however, the stability constants K_s, based on the concentrations, are usually employed. K_s is an average stability constant for the system in
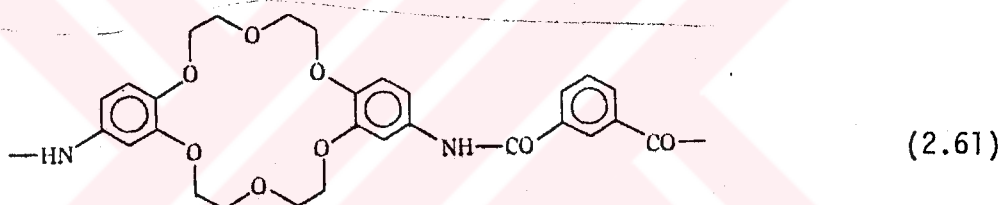
$$K_s = K_{th} \cdot \frac{f_L f_M}{f_c} = \frac{[L, M^{n+}]}{[L][M^{n+}]} \qquad (2.59)$$

thermodynamic equilibrium on the basis of ligand conformation and complexation. The relationship between K_s and the free enthalpy of formation ΔG^0 of a complex is given by the following equation

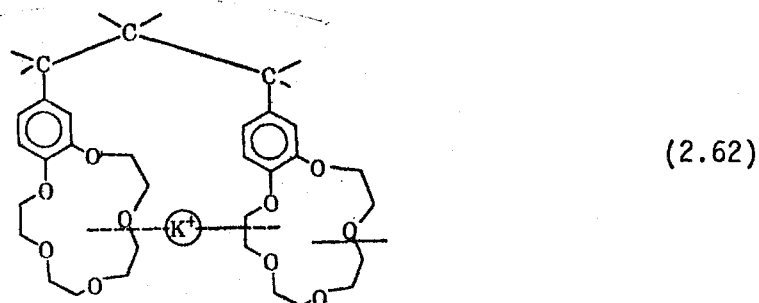$$\Delta G^0 = -RT \ln K_s \qquad (2.60)$$

2.2.3. Polymers Having Crown Ether Moieties

A macrocyclis polyether-polyamide was first synthesized by Feigenbaum and Michel [51]. It was a pioneer work on the incorporation of complexing properties of crown ethers into the polymeric backbone. The dibenzo-18-crown-6 was converted to two isomeric diamines by using corresponding dinitro derivatives. The polyamides were prepared by condensation of the diamines with aromatic diacid chlorides.

$$(2.61)$$

The polyamide film form maximum complexing with K^+ similar to the monomeric analogue, dibenzo-18-crown-6, but demonstrates much greater selectivity. Despite dibenzo-18-crown-6 itself forms strong complexes with Ca^{2+}, Ba^{2+}, and Cs^+, the polyamide film does not.

Smid et al synthesized the 4'-vinyl derivatives of monobenzo-15-crown-5, of monobenzo-18-crown-6 and of dibenzo-18-crown-6 [52,53]. The monomers may be polymerized to high molecular weight polymers by radical or anionic initiators.

$$(2.62)$$

Polyvinyl macrocyclic polyethers are more efficient in complexing cations than their monomeric analogues, especially in those cases where the diameter of the polyether ring is smaller than that of the cation. For example, log K_s for formation of the $K^{\pm}$ poly (4'-vinly) benzo-15-crown-5 complex is found to be > 5, whereas that for the corresponding monomer benzo-15-crown-5-K^+ complex is 3.7. This can be explained by cooperative coordination effects, where two neighbouring crown ether rings combine with a single cation (sandwich type).
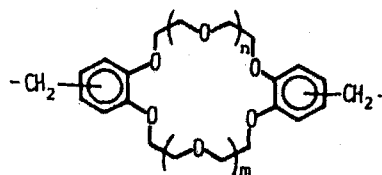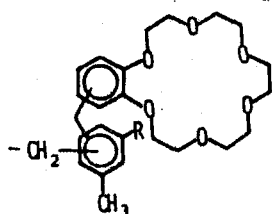
Patchornik et al prepared the polymeric pseudo crown ethers by the reaction between chloro-methylated styrene divinylbenzene copolymers and polyoxyalkylene [54].

$$n = 2\text{-}14 \qquad (2.63)$$

where $\textcircled{P}$ represents polymeric backbone. The polymeric pseudo crown ethers coordinate MX_4^- - or MX_4^{2-} - complexes ($M = Au, Fe, Zn; X = Cl, Br, I$).
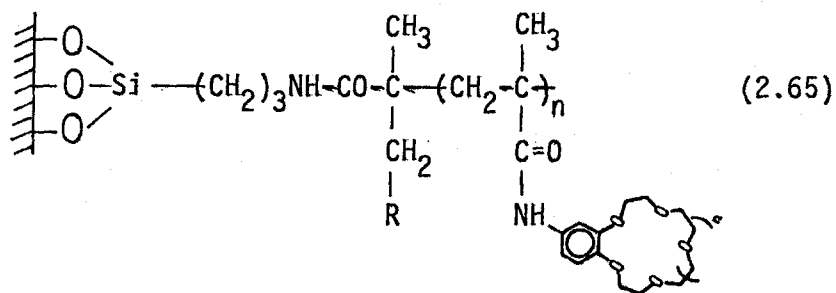
Blasius et al incorporated cyclic polyethers with various ring diameters into a polymer matrix to prepare special exchangers [55].

$$(2.64)$$

The exchangers have wide application in analytical chemistry, such as in separations of cations with a common anion (eg.alkaline and alkaline earth metals, heavy and precious metals), anions with a common cation (eg.halides and pseudo halides) and organic compounds, trace enrichment and the determination of water.

Some crown compounds are immobilized on silica gel to produce the stationary phases for high-performance liquid chromatography [56].
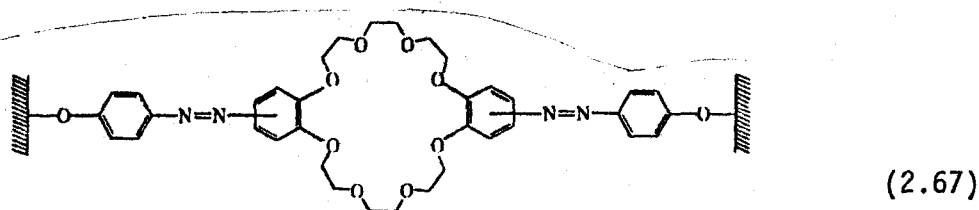
$$ (2.65) $$

Cinquini et al reported the preparation of polymers and their use as catalysts in the reaction

$$ (2.66) $$

of cyanide and iodide with 1-bromo octane [57]. Polymers were synthesized by reaction of the appropriate amine form of the crown ether with a chloromethylated polystyrene resin.

Shinkai et al have reported that a photoresponsive crown ether combines within a molecule both a crown ether and a photoresponsible cromophore changes its conformation in response to photoirradiation, resulting in a change in the complexation ability [58]. The polymer beads

$$ (2.67) $$

adsorbed Cs^+ in the dark while they rapidly released Cs^+ into the solution under UV-light irradiation and the photoresponsive complexation occurred reversibly.

3. EXPERIMENTAL

3.1. Purification of Materials

3.1.1. Styrene

Washed with aq. 5 % NaOH remove inhibitors, then water, dried for several hours with $MgSO_4$ and distilled under reduced pressure (50°C/25 mm Hg). Middle fraction is collected and immediately used.

3.1.2. Methyl methacrylate

Washed twice with aq. 5 % NaOH to remove inhibitors and twice with water. Dried with $CaCl_2$ and then distilled at reduced pressure (46°C/100 mm Hg) and middle fraction is collected and immediately used.

3.1.3. Dimethyl sulphoxide

Dried with CaH_2 and fractionally distilled under reduced pressure (75.6-75.8°C/12 mm Hg).

3.1.4. N,N-Dimethyl formamide

Dried with $CaSO_4$ or Linde type 4A molecular sieves, followed by distillation under reduced pressure (76°C/39 mm Hg).

3.1.5. Methanesulphonic Acid

Stirred with P_2O_5 at 100°C for 1/2 hr, then distilled under vacuo (135°C/3 mm Hg). 70 % technical grade was used as received.

3.1.6. Hexamethylphosphoric Triamide

Distilled under vacuo at nitrogen atmosphere from CaH_2 (68-70°C/1 mm Hg). The middle fraction was collected. Kept in the

dark, in nitrogen atmosphere.

3.1.7. Benzene

It can be purified sufficiently by shaking with concentrated H_2SO_4 until free from thiophen, the with water, dilute NaOH, and water, followed by drying with sodium, and distilling (80.1°C/760 mm Hg).

3.1.8. Chloroform

Can be shaken with several portions of conc. H_2SO_4, washed thoroughly with water, and dried with water, and dried with $CaCl_2$ before filtering and distilling (61°C/760 mm Hg).

3.1.9. Terephtaloyl Chloride

It was recrystallized from dry n-hexane (mp :80°C) and kept in dessicator.

3.1.10. Adipoyl Chloride

It was used as received and kept in dessicator.

3.2. Preparation of Materials

3.2.1. Dibenzo-18-crown-6 (DB18C6)

This was prepared by Pedersen method [42]. A mixture of 330 g (3 moles) of catechol, 2000 mL of n-butanol, and 122 g (3 moles) of sodium hydroxide pellets was refluxed under nitrogen for 30 min to ensure complete dissolution of sodium hydroxide (temperature about 115°C). A solution of 222 g (1.55 moles) of bis (2-chloroethyl) ether diluted with 150 ml of n-butanol was added dropwise over 2 hr and the mixture was refluxed for 1 hr. The temperature was lowered to 90°C, and 122 g of sodium hydroxide pellets was added. Refluxing was continued for 30 min, and 222 g of bis (2-chloroethyl) ether diluted with 150 mL of n-butanol was added dropwise over 2 hr. Refluxing was continued for 16 hr.

Concentrated hydrochloric acid (21 mL) was slowly added, and then 700 mL of solvent was rapidly removed by distillation. The distillation was continued but the volume in the flask was kept constant by the steady addition of water until vapor temperature reached $100^{o}C$, then for 10 minutes more.

The mixture was filtered, washed with 2000 mL of water, and sucked dry. The solids were dispersed in 1500 mL of acetone,stirred for 30 min, filtered, washed with 500 mL of acetone, and dried in an oven at $100^{o}C$. The dry product was recrystallized from chloroform-hexane. Pure product melts at $161^{o}C$ (lit.[42] $164^{o}C$). IR spectra of the dibenzo-18-crown-6 is shown in Fig.(3.1).

El.An.Calc.: C% 66.66 ; H % 6.66
    Found : C %65.09 ; H % 6.64

3.2.2. Cis-4,4'-Dinitrodibenzo-18-crown-6

It was prepared by nitration of dibenzo-18-crown-6 [51,59]. Into a 2-liter flask equipped with a magnetic stirrer, water condenser, and dropping funnel was placed 20 g(0.052 mole) of DB18C6 and 400 mL of chloroform. After dissolution of the DB18C6 by stirring 300 mL of glacial acetic acid was added, followed by a nitrating solution of 14.5 mL of conc, nitric acid (d=1.42) in 40 mL of acetic acid. The latter was added dropwise over 30 minutes. The reaction was stirred without heating for an hour, during which it successively turned, green, blue, and yellow. After refluxing for 3hours, the reaction was filtered, giving trans-dinitro derivative. The filtrate was concentrated and poured into the water to obtain a crude cis-dinitro derivative. The crude product (10g) was refluxed with 400 mL of ethylene glycol monomethylether, and hot solution was filtered from insoluble trans isomer and recrystallized from this solvent. The cis isomer had a mp. $198^{o}C$ (lit.[59] $200-201^{o}C$). IR spectra of the cis-4,4'-dinitrodibenzo-18-crown-6 is shown in Fig(3.2).

El.An.Calc.: C % 53.33 ; H % 4.88 ; N % 6.22
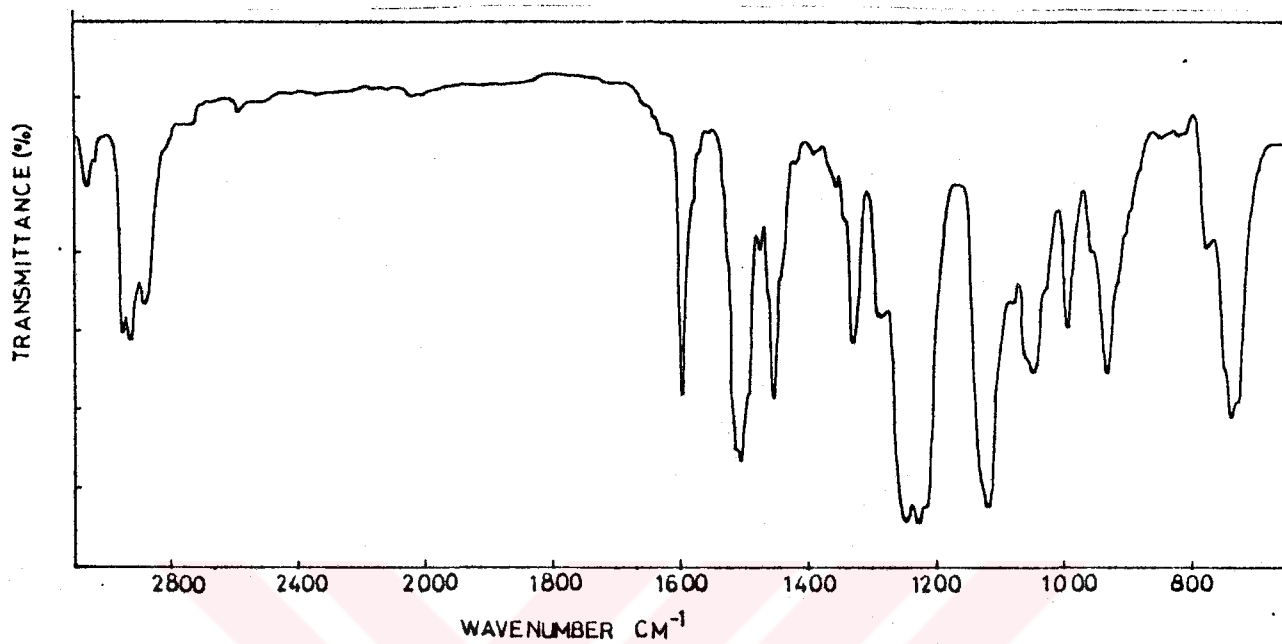   Found : C % 53.26 ; H % 4.87 ; N % 6.10

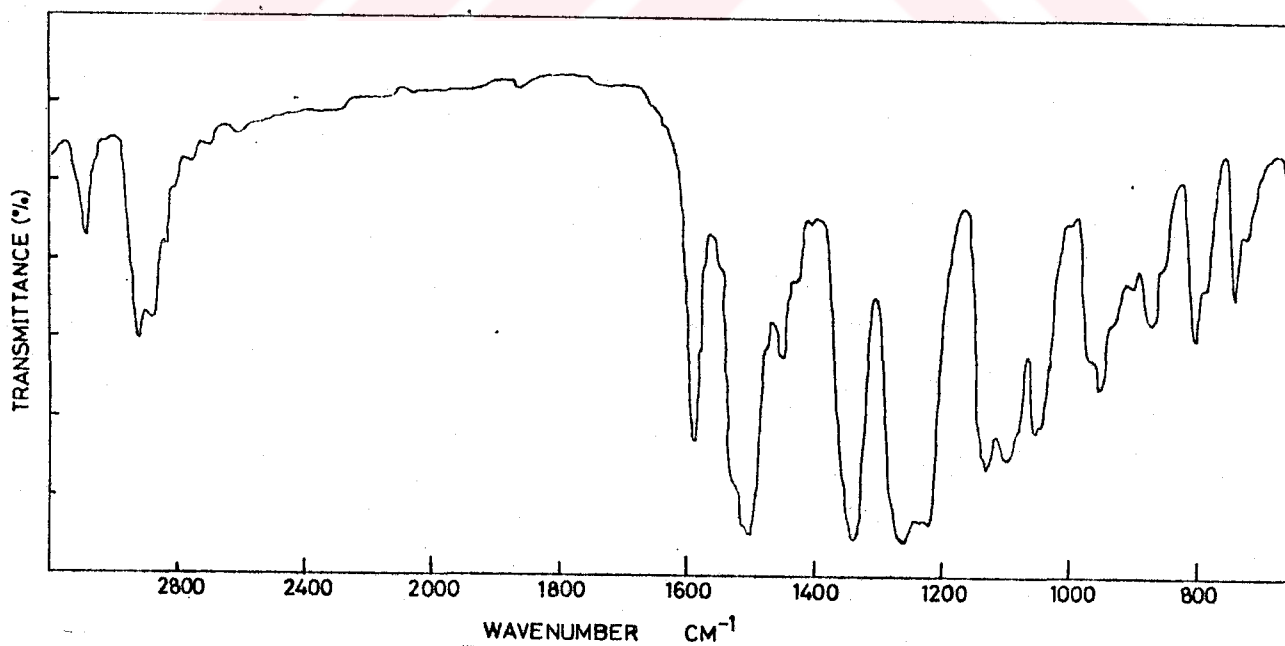Fig 3.1. IR Spectra of dibenzo-18-crown-6 on KBr disc.

Fig 3.2. IR Spectra of cis-4,4'-dinitrodibenzo-18-Crown-6 on KBr disc.

3.2.3. Trans-4,4'- Dinitrodibenzo-18-crown-6

Trans product was obtained as described previously. It was recrystallized from DMF to give yellow crystals, mp.248°C(lit. [51] 247-252°C).

El.An. Calc.: C % 53.33 ; H % 4.88 ; N % 6.22
        Found   : C % 53.21 ; H % 4.80 ; N % 6.14

3.2.4. Cis-4,4'-Diaminodibenzo-18-crown-6(DADC)

It was prepared by reduction of the corresponding dinitro derivative [59]. Ethylene glycol monomethylether (300 mL) was mixed with 5.2 g of cis-dinitro derivative. The reduction was started upon addition of 1.2 g of 5% Pd/c catalyst followed by the addition of hydrazine hydrate. After 30 min of reflux the reaction mixture was filtered and evaporated. The pure product obtained after recrystallization from ethanol had mp.183°C (lit.[59] 177-178°C). IR spectra of cis-DADC is shown in Fig (3.3).

El.An.Calc : C % 61.53 ; H % 6.66 ; N % 7.18
        Found   : C % 60.51 ; H % 6.74 ; N % 7.02

3.2.5. Trans-4,4'-Diaminodibenzo-18-crown-6 (DADC)

The same procedure was applied as in the synthesis of cis-diamino derivative only changing the solvent to n-propanol [59].

3.2.6. 4,4'-Azo-Bis (4-cyanopentanoyl chloride) (ACPC)

4,4'-Azo-bis (4-cyanopentanoic acid) (ACPA) was converted into its acid chloride by the modified Smith [35] and Simionescu [60] procedure. 10 g of ACPA was suspended in 100 mL of anhydrous benzene and stirred until dissolution. 20 g of phosphorus pentachloride was added to the solution in portions within 30 minutes under cooling with ice-water. The stirring was continued for another 1.5-2h at 0°C. The reaction mixtures must be kept out of the light. After filtering the clear solution was distilled under vacuum and nitrogen not exceeding 30°C for removal of benzene and phosphorus oxychloride. The resulting
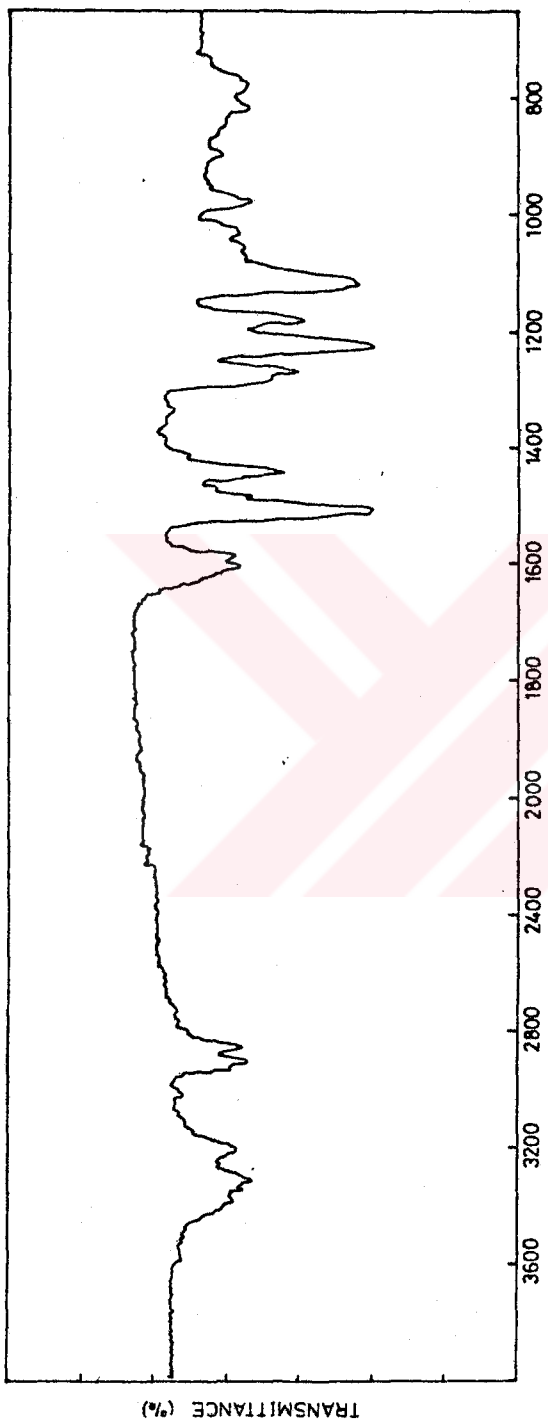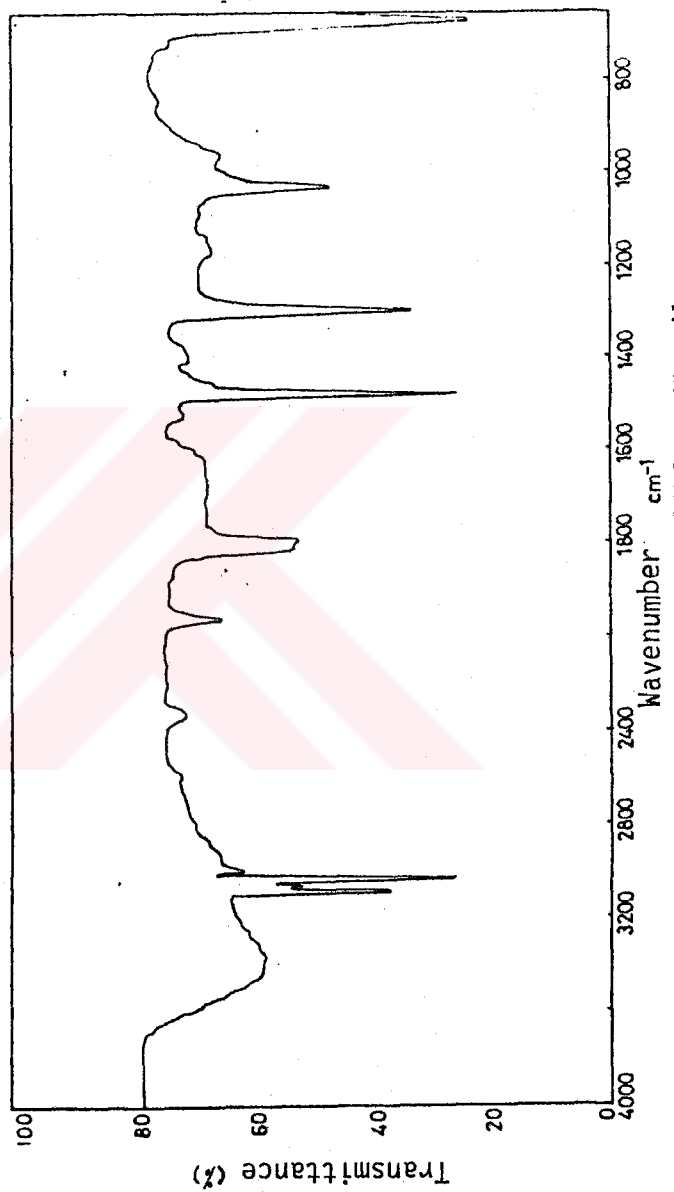
Fig 3.3. IR Spectra of cis-DADC on KBr disc.

Fig 3.4. IR Spectra of ACPC on KBr disc.

yellow solid was dissolved in 10 mL of CH_2Cl_2 under nitrogen followed
by the addition of a cooled non polar solvent 30 mL of hexane until the
appearance of turbidity. After keeping at low temperature, solvent
was removed by syringe and the acid chloride was dried and stored under
nitrogen in frig. mp : 94-96.5°C(dec.). IR spectra of ACPC is shown
in Fig (3.4).

3.2.7. Potassium Picrate

Potassium picrate was obtained by neutralizing picric acid with
the KOH in aqueous MeOH, recrystallization of the salt from this solvent
mixture, and drying the crystalline compound for several days under
vacuum at about 140°C.

3.3. Techniques and Apparatus

3.3.1. Condensation Polymerization

Two types of polycondensation methods were utilized to obtain
polyamides :
   i. The stirred interfacial polycondensation
  ii. The low temperature solution polycondensation

3.3.1.1. The Stirred Interfacial Polycondensation

The stirred interfacial polycondensation was carried out at
room temperature. A two-necked flask provided with an Ultra-Turrax
stirrer (20 000 rpm) and a separatory funnel was charged with aqueous
solution of KI complex salt of cis or trans-4,4'-diaminodibenzo-18-
crown-6 (DADC) which were prepared by Pedersen's method [42] and K_2CO_3.
A methylene chloride solution of 4,4'-Azo-bis (4-cyanopentanoyl chloride)
(ACPC) which was synthesized from the corresponding acid [35,60] was
placed in separatory funnel. The stirrer was turned on to its maximum
speed and the contents of the separatory funnel were added in one
portion. Stirring continued for ca.8 minutes. The polymer which
spontaneously formed was removed by filtration. The product was washed
successively with water, ethanol, and ether, and dried in vacuum oven
at room temperature.

3.3.1.2. The Low Temperature Solution Polycondensation

The low temperature solution polycondensation method was used to obtain polyamides containing different concentration of azo groups in main chain which was adjusted by the mole ratio of ACPC/ACPC+TPC or ACPC/ACPC+AC.

The ACPC was placed in a Schlenk tube of which the air was evacuated followed by nitrogen inlet. The stirring and externally ice-water cooling to maintain the temperature at $0-5^{\circ}C$ was continued. The cis-DADC was dissolved in HMPA with continous stirring under nitrogen atmosphere and added to the Schlenk tube by syringe. The reaction was then continued overninght under nitrogen. The reaction solution was poured into a chilled MeOH. Vigorous stirring produced yellow precipitates that were filtered off, washed with ether and dried at room temperature in a vacuum oven.

In the case of acid chloride mixtures, eg ACPC+TPC or ACPC+AC, the appropriate solutions of acid chloride mixtures were prepared in addition of HMPA so as to obtain homogeneous solution in a Schlenk tube. The other details are the same.

3.3.2. Free Radical Polymerization

Polymerization of styrene and methylmethacrylate using polyamide, which was obtained from DADC and ACPC, as macroazo-initiator was studied.

Polymerization tubes with standart socket joints are charged with certain amount of macroazo-initiator and with polar aprotic solvent such as DMSO, or DMF so as to dissolve the initiator. The required volume of freshly distilled styrene or methylmethacrylate is pipetted into the tubes. The tubes are fitted to high vacuum apparatus by means of manifold with standart sockets (Fig.3.5).

Polymerization tubes are now placed in a Dewar flask containing liquid nitrogen and after their contents are frozen, are degassed. After thawing, they are frozen once more. This freeze-thaw technique
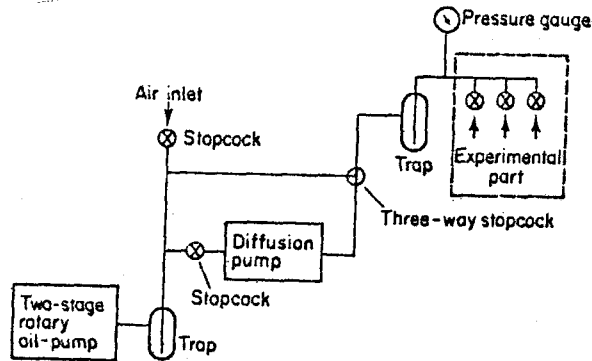
Fig 3.5. Schematic representation of a high vacuum system

is repeated three times before sealing the tubes. These samples are
polymerized at constant temperature by placing them in water bath.
After required time, the tubes are quickly cooled off by dipping into
the cold water and are opened. The contents of samples are poured
into the excess amount of methanol to precipitate the polymer. The
precipitates are filtered off and dried in a vacuum and weighed.

It can be shown that the conversion % is given by

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

Rate of polymerization (R_p) is calculated from

$$R_p = \frac{(\text{Conversion \%}) \times M}{\text{Time (sec)}} \qquad (3.2)$$

Where M is molar concentration of monomer which is derived from

$$[M] = \frac{\text{Initial amount of monomer (g)}}{\text{Molecular weight} \quad \times \quad \text{Volume of solution}} \atop \text{of monomer(g/mol)} \quad \text{at } t^{o}C \text{ (L)}} \tag{3.3}$$

and

$$\text{Volume of Solution at } t^{o}C = \frac{\text{Weight of Solution (g)}}{\text{Density of solution at } t^{o}C \times 1000 \atop (g/mL)} \tag{3.4}$$

3.3.3. Thermolysis of Azo Compounds

A differential scanning calorimeter (DSC) has been used to determine thermal and kinetic data of azo compounds.

Barret first investigated first-order decomposition of azobisisobutyronitrile (AIBN) in di-n-butyl phthalete as solvent by using a DSC [61]. Nuyken et al applied this technique to polymeric azo-initiators [62].

Since the rate of heat change due to decomposition is directly related to the rate of decomposition at a given temperature, suitable analysis of the differential thermal curve can yield the Arrhenius parameters of a reaction from a single run.

The heat change involved in a reaction can be measured directly with DSC. The rate of heat evolution (dH/dt) with respect to time (or temperature) is recorded directly. Figure 3.6 shows a typical DSC trace from the decomposition of an azo-containing compound.

The total area under the curve, A (kJ/mole), corresponds to the total heat of reaction, H, and the area, a (kJ/mole), to the heat evolved up to any time, t. If it is assumed that the amount of heat

$\frac{dH}{dt}$ ($\frac{kJ}{mole.s}$)

Temperature
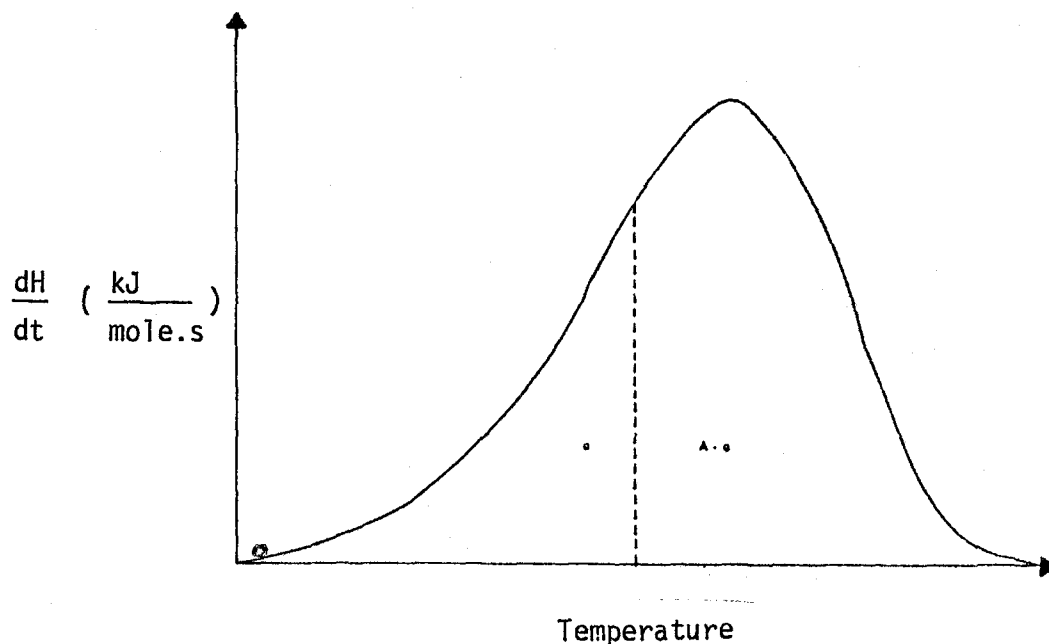
Fig 3.6. A DSC trace for the decomposition of an azo compound.

evolved is proportional to the number of moles reacted, n,

$$\frac{a}{A} = \frac{n}{n_0} \qquad (3.5)$$

also,

$$- \frac{dn}{dt} = \frac{n_0}{A} \cdot \frac{dH}{dt} \qquad (3.6)$$

where n_0 is the number of moles of reactant present initially. Assuming the validity of the general formula for the reaction rate

$$- \frac{1}{V} \cdot \frac{dn}{dt} = k \left(\frac{n}{V} \right)^x \qquad (3.7)$$

where, V reaction volume, k the rate constant for the reaction and x the order of reaction then, with $n = n_0 \cdot (1 - \frac{a}{A})$, the rate constant k can be calculated from

$$k = \frac{\left(\frac{Av}{n_0} \right) \frac{dH}{dt}}{(A-a)^x} \qquad (3.8)$$

For a first-order reaction, $x = 1$, the expression can be simplified to :

$$k = (dH/dt)(A-a) \hspace{3cm} (3.9)$$

From Eq (3.9) it is possible to obtain the rate constant of decomposition of the azo compound being studied at a range of temperatures with a single measurement, by DSC. It is possible to confirm that the azo compound being studied decomposes according to first-order kinetics, and to obtain its activation energy, by a plot of lnk vs the reciprocal of the absolute temperature with a reasonable degree of accuracy.

A Perkin-Elmer differential scanning calorimeter, model DSC-IB, was used for thermal determinations. The standard aluminum sample pans with lids were used. Due to some "solvent creep" at higher temperatures it was necessary to crimp the top of aluminum pan tightly to retain the initiator solution. Mixtures of initiator ($\sim$1mg) and $MeSO_3H$ or DMSO($\sim$15μL) were put directly into the aluminum pan. An aluminum sample pan containing the sample weight of solvent was used as a reference. A slow current of nitrogen passed over the sample holders during the determination.

Typical differential enthalpy curves obtained for the decomposition of ACPA and macroazo-initiators derived from cis-DADC and ACPC or ACPC-TPC in $MeSO_3H$ or DMSO at different heating rates (4,8,16^{o}C/min) and ranges.

All melting points of starting materials were obtained from DSC thermagrams from the sharp endothermic peaks as deflection point of them.

3.3.4. ^{1}H-NMR Spectroscopy

^{1}H-NMR spectra were recorded on a JNM-FX-1000 Fourier Transform NMR (125 MHz) in DMSO-d_6+ DMF-d_7(1/1) with tetramethylsilane as internal standart to elucidate the construction of polymers.

3.3.5. IR Spectroscopy

IR spectra were recorded on a Shimadzu IR-400 using KBr discs.

3.3.6. Measurement of Cation Binding Properties of Macroazo-Initiators Containing Crown Ethers

A considerable amount of work has been reported on the properties of polymers containing the cation-chelating crown ethers as part of the polymer backbone or anchored to the chain as pendant ligands [63]. The use of insoluble supports such as polymeric networks, glass beads, or gels led to the applications of these ligands as chromatographic stationary phases for separation of both ionic and neutral solutes and as heterogenous anion-activating catalysts [55,64,65]. Quantitative information on the binding of ionic solutes to crown ether containing network polymers as a function of cation, counterion, solvent, ligand structure or content and the spacing between polymer backbone and ligand was first reported by Smid et al [65,67]. They have delt with the quantitative measurement of binding constants of alkali picrates to network with pendant benzo-15-crown-5 or benzo-18-crown-6 ligands.

A small quantity of polyamide containing crown ether moieties as ligand (usually ~10 mg) and 10 mL of potassium picrate solution in water or dioxane were placed in a 100 mL flask. The system was thermostated at $25^\circ C$ and gently shaken for 24 hours so as to reach equilibrium. The solution was filtered off and the spectrum of unbound picrate anion recorded on a Hewlet Packard Diode Array 8452 A Spectrophotometer. The picrate anion in water or dioxane has its main absorption maximum at 356 nm ; $\varepsilon = 1.51.10^4$ L mol^{-1}cm^{-1} and at 350 nm ; $\varepsilon = 1.46.10^4$ L mol^{-1} cm^{-1}, respectively.

The concentration of unbound picrate anion is calculated from Lambert-Beer equation
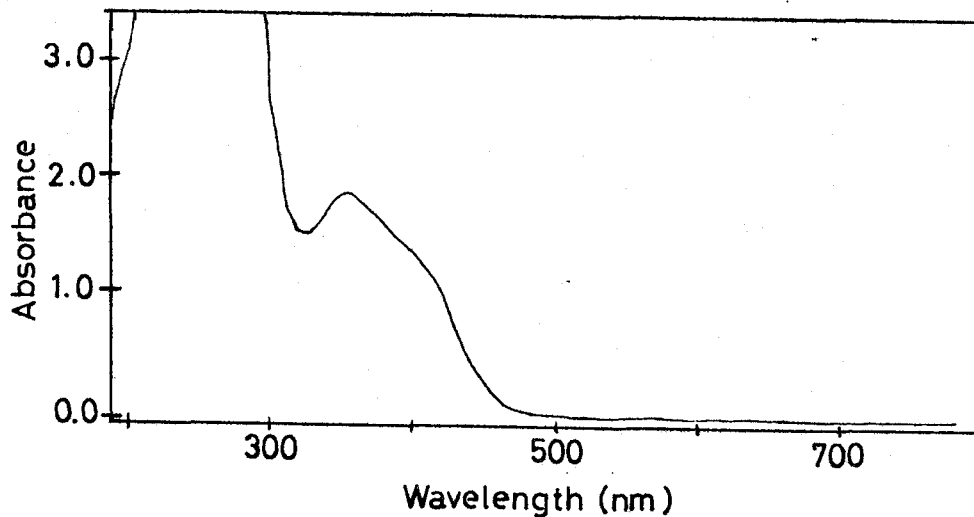
$$\text{Absorbance} = \varepsilon . C . L \qquad (3.10)$$

Fig 3.6. UV spectrum of picrate anion in water

where ε : molar extinction coefficient (L mol^{-1} cm^{-1})
       C : Concentration (mol L^{-1})
       L : Cell path (cm)

3.3.7. Viscosity Measurements

The viscosity numbers of various polyamides were measured in polar solvents such as DMF or $MeSO_3H$ at two different temperatures (25 or 30°C).

The viscosity measurements of polystyrene were measured in toluene at 30°C. The molecular weight of polystyrene was calculated from eq.(3.11)[68].

$$[\eta] = 1.1.10^{-4} \ M^{0.725} \quad (Toluene, 30°C) \tag{3.11}$$
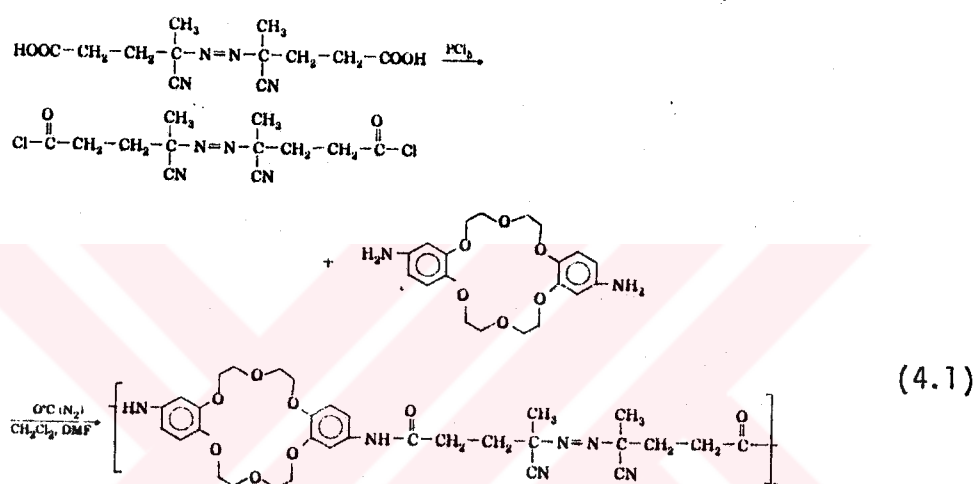
The Ostwald viscometer was used in all measurements.

3.3.8. Elemental Analysis

Elemental analysis of various compounds was carried out with a Yanaco CHN Corder MT-3.

4. RESULTS AND DISCUSSION

4.1. Preliminary Results

4.1.1. Synthesis of Macroazo-initiator by Solution Condensation

$$(4.1)$$

Equimolar solution of trans-4,4'-diaminodibenzo-18-crown-6
(0.03 mole/liter) in DMF was placed in a flask under nitrogen atmosphere.
Equimolar solution of 4,4'-azobis (4-cyanopentanoyl chloride)(0.03
mole/liter) in CH_2Cl_2 was added to the chilled solution. The reaction
was continued overnight at room temperature under nitrogen atmosphere.
Polymerization was accompanied by darkening of the solution and
formation of dimethyl formamide hydrochloride crystals. The polymer
was precipitated by pouring the polymerization mixture into rapidly
stirred crushed ice-water. After it had dried, brownish polyamide
eq(4 .1), was obtained (42 %) having solution viscosity [?]= 0.15
in DMF at $25^{\circ}C$. Although this oligomeric product started decomposing
at lower temperatures, its melting point was observed to be above
$350^{\circ}C$. As a crude demonstration, the macroazo-initiator became fibrous
on heating. The infrared spectrum of the macroazo-initiator is given
in Figure (4.1). The polyamide structure was easily distinguished

from the starting acid chloride by the strong band at 1670 cm^{-1}(CONH).

Fig 4.1. Infrared spectra of the macroazo-initiator on KBr disc.

4.1.2. Synthesis of Macroazo-initiator by Interfacial Polycondensation

(4.2)

Conventional condensation polymerization is more sensitive to the monomer purity and stoichiometry than interfacial polymerization although it proceeds at appreciable rates. We employed mainly this method to obtain the complexed crown ether moieties before the polymer is synthesized and to prevent some difficulties arising from solution polycondensation. The stirred interfacial polycondensation between cis and trans derivatives of DADC and ACPC resulted in good yields as summarized in Table 4.1. The rather high viscosity of the cis product might be ascribed to better solubility of the corresponding starting diamine and higher diamine/acid chloride mole ratio.

The infrared spectrum of the polyamide showed similar bands to the uncomplexed polyamide (Fig 4.1). The ^{1}H-NMR spectrum of cis polyamide is shown in Figure 4.2.

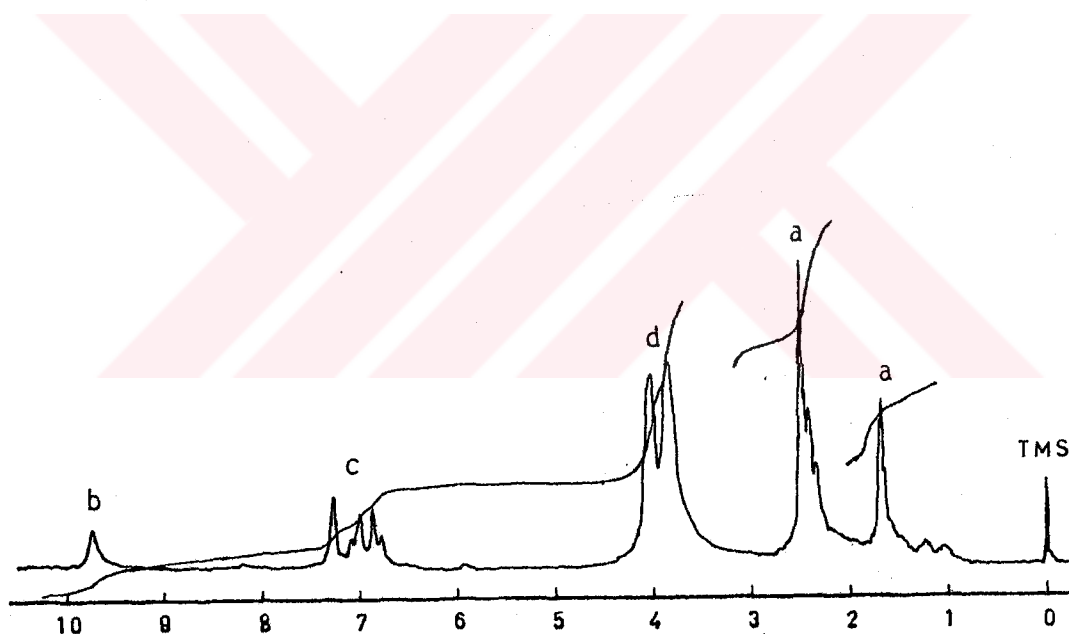Fig 4.2. ^{1}H-NMR spectrum of KI complexed cis-macroazo-initiator in DMSO-d$_6$+DMF-d$_7$(1/1),δ 1.2-2.7(a ,14H), 9.7 (b,12H),6.5-7.5 (c,6H), 3.9(d,16H).
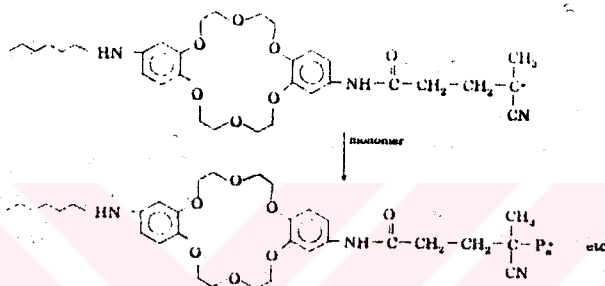
Table 4.1

Stirred Interfacial Polymerization of KI Complexed Salt of DADC and ACPC at Room Temperature

Run No.	Organic Phase		Aqueous Phase			Product			
	ACPC (mg)	Methylene Chloride (ml)	KI comp. salt of DADC (mg)	K_2CO_3 (mg)	H_2O (ml)	Yield (mg)	(%)	$[\eta]^a$ (dL/g)	N (%)	ACPunit (mol fraction)[b]
1	158	40	400 (cis)	138	50	285	43	0.38	10.3	0.98
2	158	40	200 (Trans)	138	50	169	52	0.23	9.9	0.94

[a]30°C in DMF.
[b]Calculation of composition based on the N content of the polyamide, N = 10.5% being 1 mol fraction of ACP unit.

UV absorbance of $(-N=N-)(\lambda_{max}=345$ nm, $\varepsilon=20.9)$ [69] was hidden by the broad absorbance of diamino dibenzo-18-crown-6 $(\lambda_{max}=338$ nm, $\varepsilon=14000)$ [51].

4.1.3. Polymerization of styrene Initiated by Macroazo-initiator

$$(4.3)$$

Styrene was used as a representative monomer to test the efficiency of macroazo-initiator for free radical polymerization. Macroazo-initiator may be decomposed on heating to give polymeric radicals (eq 4.3). Smith [35] postulated that the diffusion of radicals out of the solvent 'cage' is effected by rigidity of the chain. It may be assumed that intrachain species, like crown ether, prevent diffusion until combination takes place.

A typical polymerization of bulk styrene at $70^{\circ}C$ with 50 g/L macroazo-initiator and a sufficient amount of DMF to facilitate dissolution produced a yield of 8.3% of polystyrene after 1hr. A control experiment without macroazo-initiator produced very little polymer after the same reaction time. The infrared spectrum of the obtained polymer exhibits bands at 3400 (N-H stretching), 1650(C= 0 stretching), 1600 (N-H bending) and 1130 cm^{-1}(C-O stretching) in addition to usual the absorption bands of polystyrene.

4.1.4. Polymerization of Styrene and Methylmethacrylate initiated by KI Complexed Macroazo-initiator

Styrene and methylmethacrylate were subjected to the KI complexed macroazo-initiator initiated polymerization. As can be seen from Table 4.2, using cis-macroazo-initiator yielded higher molecular weight polymers, probably due to a Trommsdorf effect since the viscosities of cis-initiated systems were higher than those of the trans-initiated systems. Composition of the obtained polymer backbone arises from both specific mechanism of termination and the number of -N=N- linkages in the main chain of the initiator.

Table 4.2

Polymerization of Styrene and MMA in DMF Initiated by KI Complexed Macroazo-initiator at 70°C

Monomer (M)	KI Complexed Macroazo-initiator (g/L)		Reaction Time (Min)	Conversion (%)	$[\eta]^a$ (dL/g)
St (6.43)	Cis	(3.70)	120	7	1.11
St (6.43)	Trans	(3.70)	120	8	0.46
St (4.34)	Cis	(5.00)	120	8	0.78
St (4.34)	Trans	(5.00)	120	9	0.26
St (4.34)	Cis	(12.50)	120	12	0.38
St (4.34)	Trans	(12.50)	120	13	0.36
MMA (4.70)	Cis	(12.50)	120	37	0.54
MMA (4.70)	Trans	(12.50)	120	44	0.37

^{a}30°C in DMF.

Crown units are expected to be part of the block copolymer. However, the segment length of the polyamide is small, because further decomposition in block copolymer occurs through azo linkages present in the backbone. This consideration would be supported by ^{1}H-NMR spectrum of the obtained polystyrene (Fig 4.3). Inspection of the intensity of signals suggested that each block copolymer chain contains approximately 70 styrene units per crown ether unit.
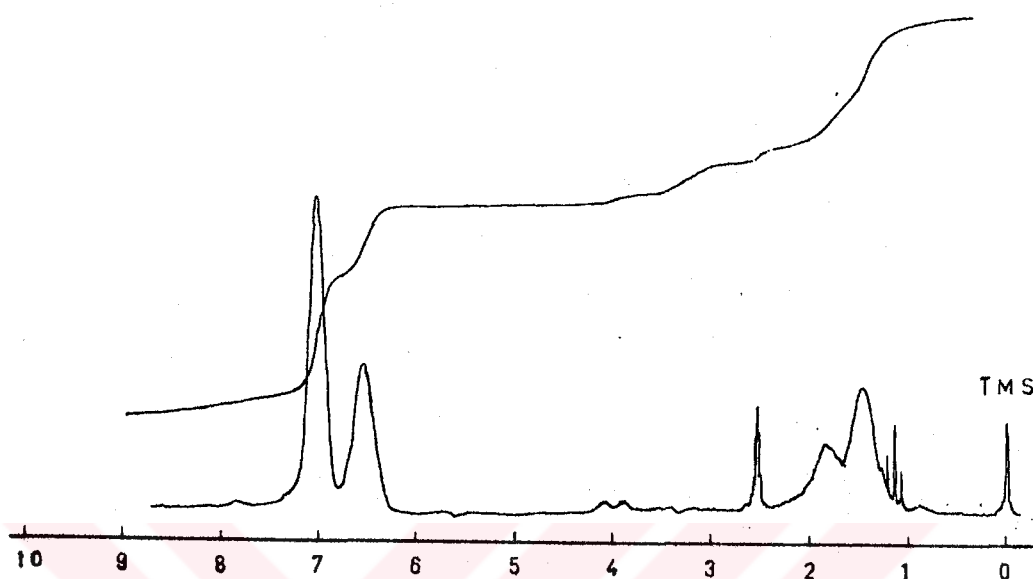
Fig 4.3. ^{1}H-NMR spectrum of polystyrene obtained with KI complexed cis-macroazo-initiator in DMSO-d_6+DMF-d_7(1/1), δ = 6.5-7.5 (Ar-H), 4.0 (aliph.-H in crown ether), 2.45 (aliph.-H in ACP), 1.2-2.0 (aliph.-H in styrene).

4.1.5. Complexation of Polystyrene with Potassium Picrate Salt

Samples of polystyrene are obtained by initiation with eq.(4.3) subjected to cationic complexing using potassium picrate. The solution of polystyrene in benzene became yellow in color as a result of complex formation of the crown ether portion of the polymer with K^+. The UV spectrum of the solution showed absorption in the 350 nm region, indicating picrate units.

4.1.6. Potassium Contents of The Products Obtained from KI Complexed DADC

On the other hand, complexation of the DADC derivatives, before the polymerization step yielded polymers with K^+ ions. Potassium

contents of the related reaction products at various stages are given in Table 4.3.

Table 4.3

The K Contents[a] of The Products at Various Stages

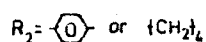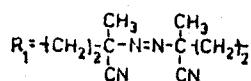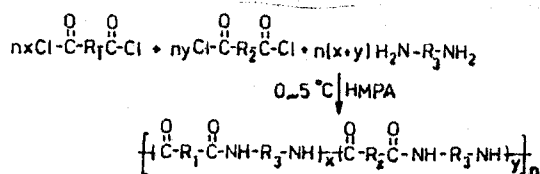| Product	Calculated K (%)	Found K (%)
KI Complexed Salt of Trans-4,4'-diaminodibenzo-18-crown-6	7.01	6.93
KI Complexed Macroazo-initiator	4.87[b]	2.22
Polystyrene	—	0.35

[a] Measured by flame photometry (Eppendorf).
[b] End groups are neglected.

The low potassium content of the macroazo-initiator may be attributed to the tendency of the complexed crown ether to release its salt to the aqueous solution.

4.2. Synthesis of Macroazonitriles Having Various Amount of -N=N- Linkage in The Main Chain.

Polycondensation of cis-DADC and diacid chlorides according to equation (4.4) over a wide range of feed compositions resulted in good yield as summarized in Tables 4.4 and 4.5.

$$nxCl-\overset{O}{\overset{||}{C}}-R_1\overset{O}{\overset{||}{C}}-Cl + nyCl-\overset{O}{\overset{||}{C}}-R_2\overset{O}{\overset{||}{C}}-Cl + n(x+y) H_2N-R_3-NH_2$$

$$\Big\downarrow 0\_5\,^{\circ}C \Big| HMPA$$

$$\Big\{ \Big[\overset{O}{\overset{||}{C}}-R_1-\overset{O}{\overset{||}{C}}-NH-R_3-NH \Big]_x \Big[\overset{O}{\overset{||}{C}}-R_2\overset{O}{\overset{||}{C}}-NH-R_3-NH \Big]_y \Big\}_n$$

$$R_1 = (CH_2)_2\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}(CH_2)_2$$

$$R_2 = \langle O \rangle \text{ or } (CH_2)_4$$

$$R_3 = $$

(4.4)

TABLE 4.4

The Stirred Low Temperature Poycondensation of cis-DADC and ACPC/TPC

Code No	ACPC (mg)	TPC (mg)	(ACPC) / (ACPC+TPC) (Mole ratio)	HMPA (ml)	DADC (mg)	Yield (mg)	Yield (%)	$\eta sp/C^a$ (dL/g)	C/N (%) (calc.)	C/N (%) (Found)
PA-1	396	-	1	6.25	488	551	70	0.14	4.57	4.99
PA-2	317	507	0.8	6.25	488	539	71	0.06	5.14	5.55
PA-3	238	102	0.6	6.25	488	650	88	0.09	5.92	6.31
PA-4	159	152	0.4	6.25	488	698	99	-	7.05	6.30
PA-5	79	203	0.2	6.25	488	678	100	-	8.82	9.78
PA-6	-	254	0	6.25	488	650	100	-	12.00	11.85

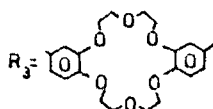[a] Measured in $MeSO_3H$ (70%) ; C = 0.12 g/dL ; [Crown Ether Unit]/ [K Picrate] = 1/1

TABLE 4.5.

The Stirred Low Temperature Polycondensation of cis-DADC and ACPC/AC

Code No	ACPC (mg)	AC (mg)	(ACPC)/(ACPC+AC) (mol ratio)	HMPA (ml)	DADC (mg)	YIELD (mg)	YIELD (%)	η_{sp}/C^a (dl/g)	C/N (%) (Calc.)	C/N (%) (Found)
PA-7	317	46	0.8	6.25	488	321	42	0.04	5.08	5.06
PA-8	238	91	0.6	6.25	488	515	71	0.14	5.77	5.83
PA-9	159	137	0.4	6.25	488	382	55	0.06	6.76	9.52
PA-10	79	183	0.2	6.25	488	605	92	-	8.33	9.43
PA-11	-	229	0	6.25	488	496	79	-	11.14	12.37

[a]Measured in $MeSO_3H$ (70%) ; C = 0.12 g/dl ;   [Crown Ether Unit] / [Picrate] = 1/1
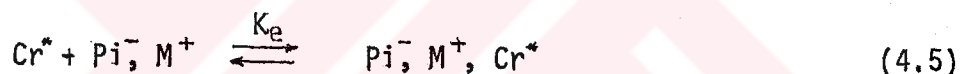
The yield of copolyamide increased in the TPC feed as can be seen from Table 4.4 whereas the results summarized in Table 4.5 do not indicate the dependency of yield and η_{sp}/C value on the feed composition in DADC/ACPC+AC system.

Similar behavior was observed by Ueda et al [69] who also prepared copolyamide containing scissile azo linkages in the main chain. In both cases the solubility of the copolyamide decreased by increasing TPC or AC content in feed composition.

4.3. Potassium Picrate Complexing Properties of The Macroazonitriles

The percentage of potassium picrate bounded by crown ethers moiety in polyamides and the intrinsic binding constant, K_e, in water and dioxane are shown in Tables 4.6 and 4.7, respectively.

Potassium picrate binding to the crown ether containing polyamides may be described in term of the reaction [70].

$$Cr^* + Pi^-, M^+ \; \underset{\longleftarrow}{\overset{K_e}{\rightleftharpoons}} \; Pi^-, M^+, Cr^* \tag{4.5}$$

where Cr^*, Pi^-, and M^+ refer to crown ether, picrate anion and metal cation, respectively. An asterisk denotes polyamide bounded species.

The concentration of the unbound picrate is measured spectrophotometrically (UV). If Cr_0^*, is total concentration of moiety and $1/n$, the number of ligands in the alkali picrate complex, Dibenzo-18-crown-6 units with K^+ favor the 1:1 complexes in the polyamide backbone, thus $1/n$ is equal to the one, then $Cr^* = Cr_0^* - [Pi^-,M^+,Cr^*] \;/n$ becomes $Cr^* = Cr_0^* - [Pi^-, M^+, Cr^*]$. The bound picrate concentration is calculated by subtracting $[Pi^-, M^+]$ from the total picrate concentration both expressed in equivalents. The intrinsic binding constant, K_e, can be calculated according to the following equation (4.6).

$$K_e = \frac{[Pi^-, M^+, Cr^*]}{[Cr^*][Pi^-, M^+]} \tag{4.6}$$

TABLE 4.6

Measurements of Potassium Picrate Salt Binding In Aqueous Solution By Polyamides

Polyamide[a]	% Picrate Salt Extracted[b]	K_e (M^{-1})
PA-1	60.5	1131.4
PA-2	77.4	2726.9
PA-3	17.6	143.4
PA-4	64.9	1371.7
PA-5	11.2	84.0
PA-6	28.8	410.2
PA-7	51.6	767.4
PA-8	18.9	156.0
PA-9	71.9	1931.5
PA-10	13.2	101.0
PA-11	29.4	422.3

a   [Picrate] / [Crown]=1/5

b   Extractability $\% = \dfrac{C_o - C}{C_o} .100$; C_o : Before, C : After extraction of potassium picrate salt.

TABLE 4.7

Measurements of Potassium Picrate Salt Binding In Dioxane By Polyamides

Polyamide	% Picrate Salt Extracted	K_e (M^{-1})
PA-1	36.3	1494.7
PA-2	52.2	2958.1
PA-3	17.2	523.0
PA-4	2.8	71.1
PA-5	14.0	407.1
PA-6	1.5	36.9
PA-7	43.4	2039.6
PA-8	10.9	302.5
PA-9	38.1	1617.9
PA-10	6.4	166.9
PA-11	40.4	1790.3

[a] [Picrate] / [Crown]=1/5

As can be seen from Tables 4.6 and 4.7, there is no dependency between the feed composition and the picrate binding properties of polyamides. This behavior may be attributed to the microenvironment of polymer since intramolecular cooperation involving ligands in the same.chain segment or other neighbouring chemical groups can modify the binding constants even in stable 1:1 crown cation complexes [67].

K_e values are in the range of the same order of magnitude for the water and dioxane which are chosen as polar and apolar solvents for the reaction medium, respectively. The binding constants are generally affected by the solvents having different dielectric constants, but the difference depends also on the nature of the cation.

4.4. Decomposition of Macroazonitriles.

Decomposition of the azo linkages was studied by DSC. This method can efficiently be used, since there is no secondary reaction beside the decomposition of the azo function as was shown for a great number of symmetrical and unsymetrical azo compounds. The rate constants for the decomposition of the macroazo-initiators were determined in DMSO and $MeSO_3H$. Typical DSC curves of ACPA and PA-1 are shown in Figures 4.4 and 4.5. All of the azo compounds exhibited first order kinetics, as can be seen from the Arrhenius plots in Figure 4.6.

The thermal and kinetic data obtained from the individual runs of decomposition of the azo compounds are summarized in Table 4.8. A small effect of terephtaloyl segment was seen, i.e, as the tereptaloyl segment increased in the main chain, the rate of decomposition decreased. For the experimental convinience, the temperature range of the analysis was kept higher as the azo-content of the polyamide decreased. In general, the temperature range can be varied by appropriate choice of heating rate and sample size. The larger sample sizes would allow the lower heating rates and consequently the lower temperature range to be examined, but suffers from a higher order of the reaction than first order [61].
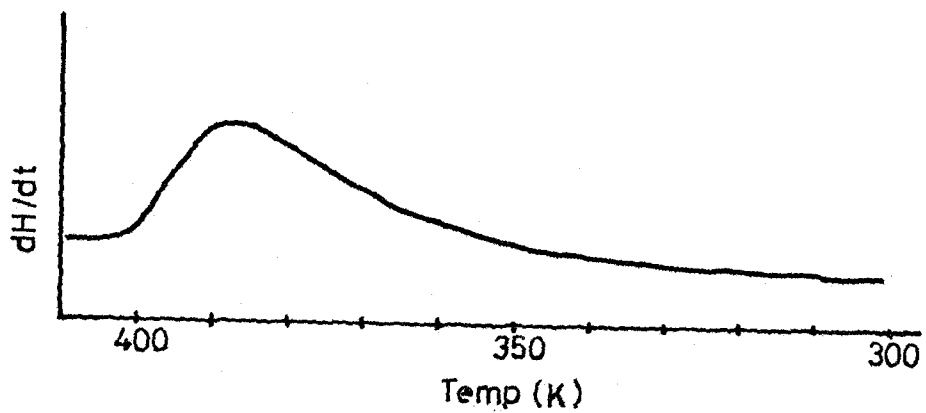
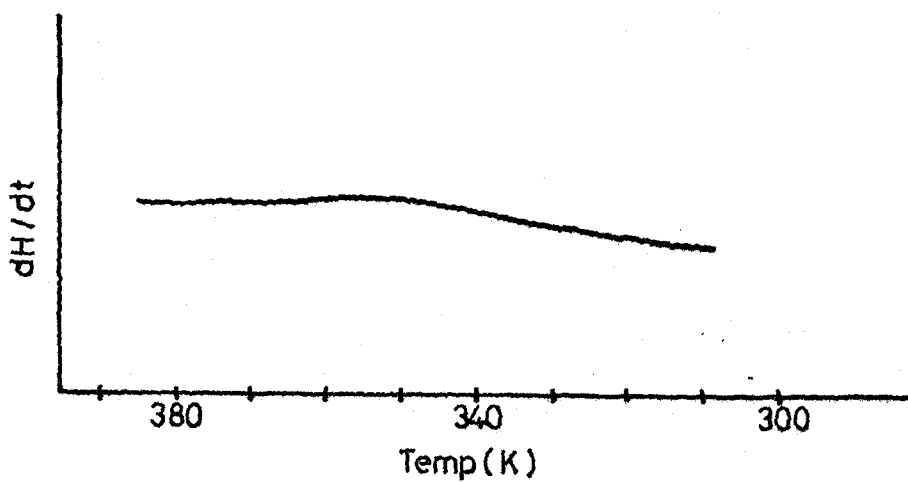Fig 4.4. DSC thermogram of ACPA in DMSO at a heating rate of 8°C/mi

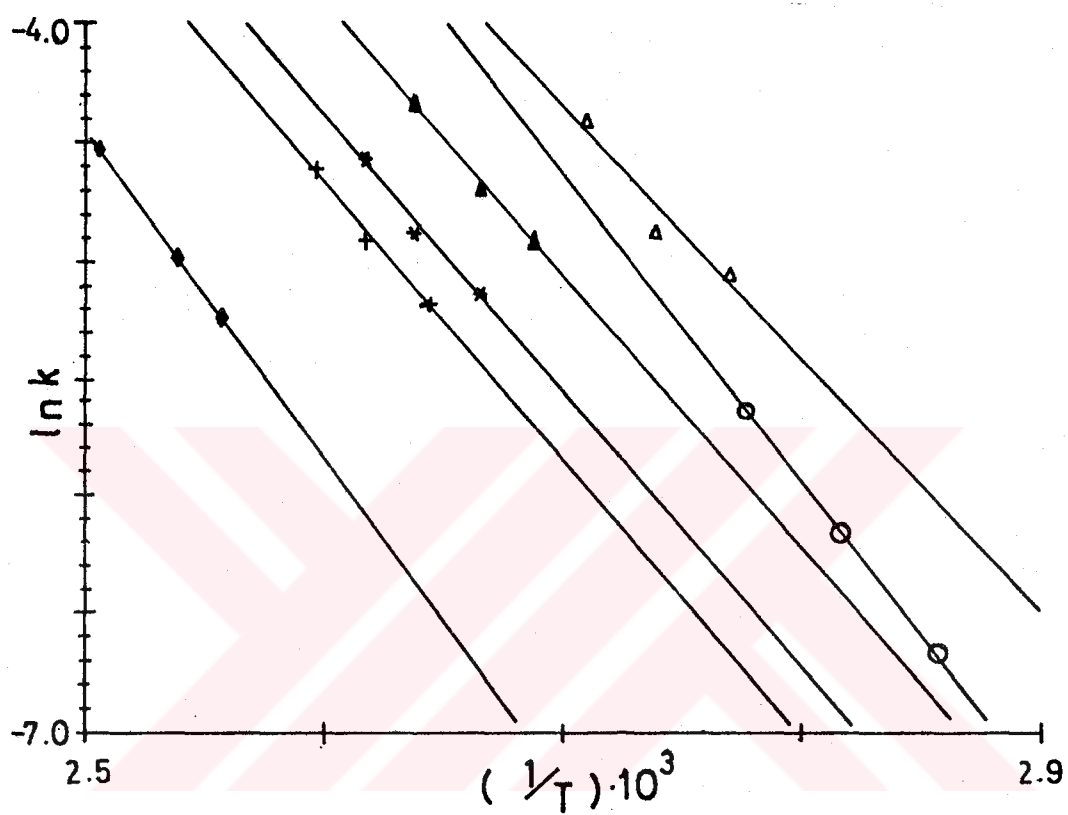Fig 4.5. DSC thermogram of PA-1 in MeSO$_3$H at a heating rate of 8°C/min

Fig 4.6. Arrhenius pot for the decomposition of azo initiator a heating rate of $8^{\circ}C/min$ in $MeSO_3H$. ($\blacklozenge$) PA-1 (in DMSO) ; ($\triangle$) PA-2 ; ($\blacktriangle$) PA-3 ; ($*$) PA-4 ; ($+$) PA-5; ($\circ$) ACPA.

TABLE 4.8

Kinetic Data[a] of the Decomposition of Polyamides obtained from DSC

Azo Compounds	$10^3 k_d$ (Temp)[b] Sec^{-1} (°C)	E_a (kJ/mole)
ACPA	1.27(77), 2.12(82), 3.59(87)	108
PA1	5.29(118),6.85(121),10.7(126)[c]	115
PA2	6.43(88), 7.68(92), 12.3(96)	90
PA3	7.43(99), 9.18(102),13.1(106)	96
PA4	5.88(102),7.60(106),10.4(109)	97
PA5	5.62(105),7.34(109), 9.9(112)	97

[a] Sample size : 1mg, heating rate : 8°C/min under nitrogen flow

[b] In MeSO$_3$H ($\sim$5 μL)

[c] In DMSO ($\sim$5 μL)

4.5. Kinetics of Low Conversion Polymerization of Styrene Initiated by PA-1.

PA-1 was utilized as a free radical initiator for the polymerization of styrene in DMSO. Typical results are shown in Tables 4.9 and 4.10. The conversion versus time plots of the polymerization at 60,70 and 80°C are presented in Figure 4.7. The logarithm of the rates of polymerization is plotted against the reciprocal of the absolute temperature, and an Arrhenius-type diagram (Figure 4.8) is obtained in which activation energy of 87 kJ/mole is calculated in the 60-80°C range.

For the polymerization of a vinyl monomer such as styrene, in which termination occurs exclusively by combination, the rate of polymerization is given by

$$R_p = k_p \ [M] \left(\frac{f \cdot k_d \ [I]}{k_t} \right)^{1/2} \tag{4.7}$$

where [I] and [M] denote the initiator and monomer concentration and k_d, k_p and k_t are the thermal decomposition, polymerization and termination rate constants, respectively. f is called the initiator efficiency.

A plot of $\log R_p$ against $\log[M]$ at constant [I] is shown in Figure 4.9, where the slope which refers to the order of the rate in monomer concentration is equal to the theoretical value of unity. George and Ward [40] have reported a value of 1.16 as the order of the monomer concentration for polymerization of styrene initiated by poly (bisphenol A-4,4'-azobis-4-cyanopentanoate)(BPA) in DMF.

A plot of $\log R_p$ versus $\log$ [I] at constant [M] is also shown in Figure 4.9. There is a gradient of 0.43 which exhibits general behavior of this type of initiation.

For free radical polymerization the inverse degree of polymerization $(1/\bar{P}_n)$ is related to the rate of polymerization by [18].

TABLE 4.9

Polymerization of Styrene in DMSO at 70°C in the presence of PA-1[a]

$[I]_o \cdot 10^3$ (mole/liter)	$R_p \cdot 10^5$ (mole/liter.sec)	$[M]_o$ (mole/liter)	$[\eta]$ (dL/g)	$(1/\bar{P}_n)10^4$	Yield (%)
0.415	2.51	6.84	1.45	2.1	1.39
1.66	4.68	6.84	1.08	3.2	2.59
3.32	5.70	6.84	0.90	4.1	3.15
4.98	7.11	6.84	0.52	8.8	3.93
5.05	6.48	5.19	-	-	4.74
8.83	8.17	5.19	-	-	5.97
12.6	9.48	5.19	-	-	6.93

[a]Polymerization time 60 min.

TABLE 4.10

Polymerization of Styrene in DMSO at 70°C in the presence of PA-1[a]

$[M]_o$ (mole/liter)	$[M]$ (mole/liter)	$R_p \times 10^5$ (mole/liter·sec)	$[\eta]$ (dL/g)	$(1/\bar{P}_n)10^4$	$[S]$ (mole/liter)
4.61	4.37	3.29	0.71	5.8	6.54
5.19	4.92	3.64	0.75	5.3	5.61
5.76	5.48	4.34	0.81	4.8	4.67
6.34	6.03	4.41	0.80	4.9	3.74
6.92	6.59	4.97	0.85	4.5	2.80

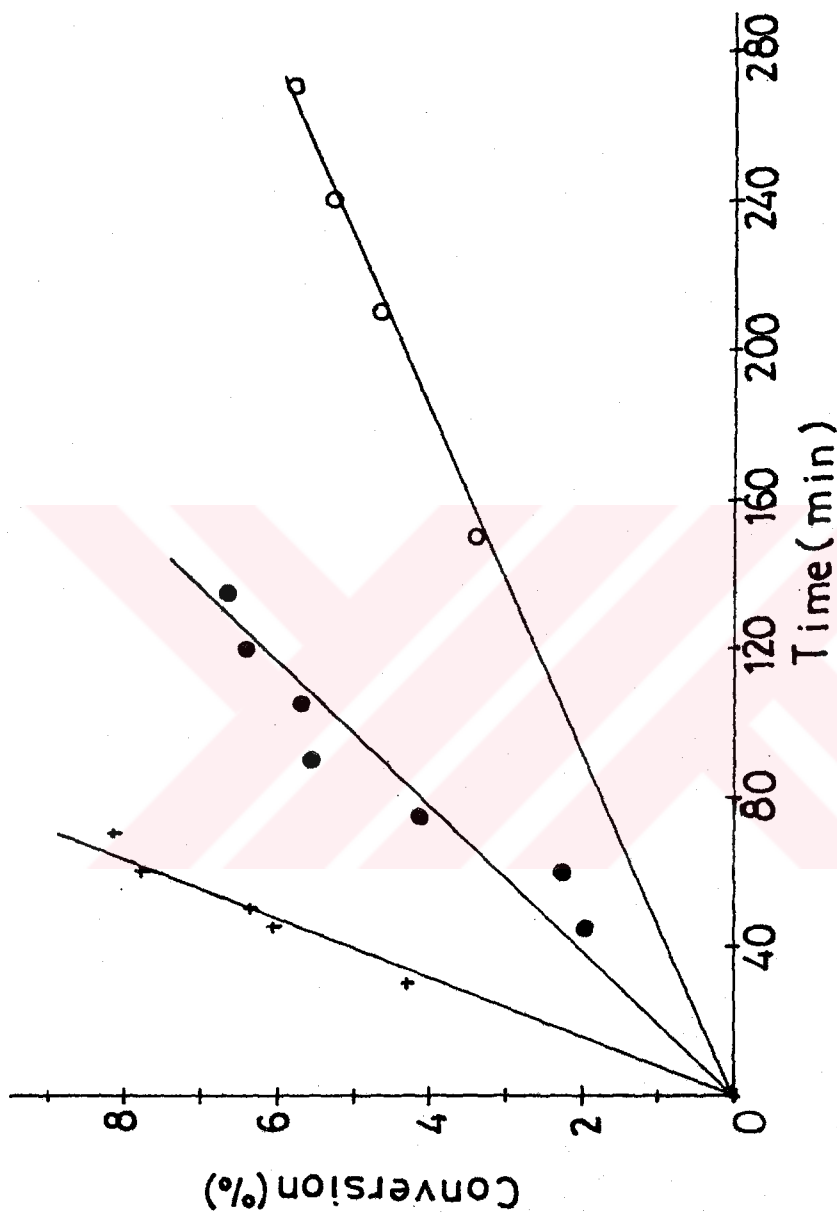[a] $[I]_o = 2.1.10^{-3}$ M, $[I]=2.0.10^{-3}$ M in all experiments and polymerization time is 60 min.

Fig 4.7. Time-Conversion curves for solution polymerization of St at varioustemperatures. [St]= 6.84 M, [PA-1]=3.32.10^{-3} M, solvent: DMSO, (o) 60°C ; (●) 70°C ; (+) 80°C.
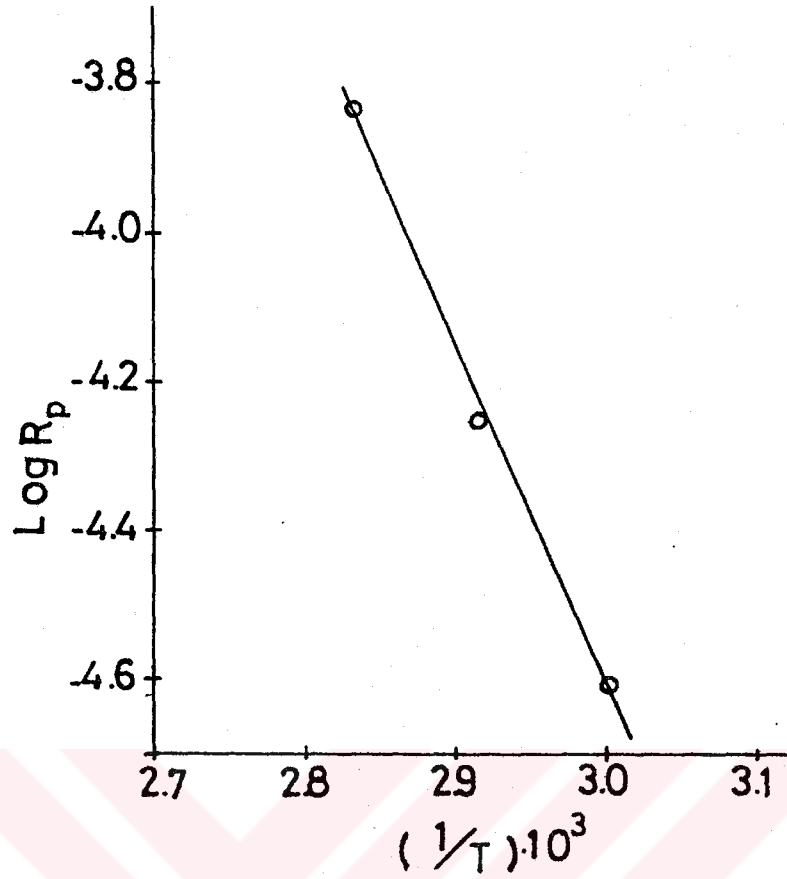
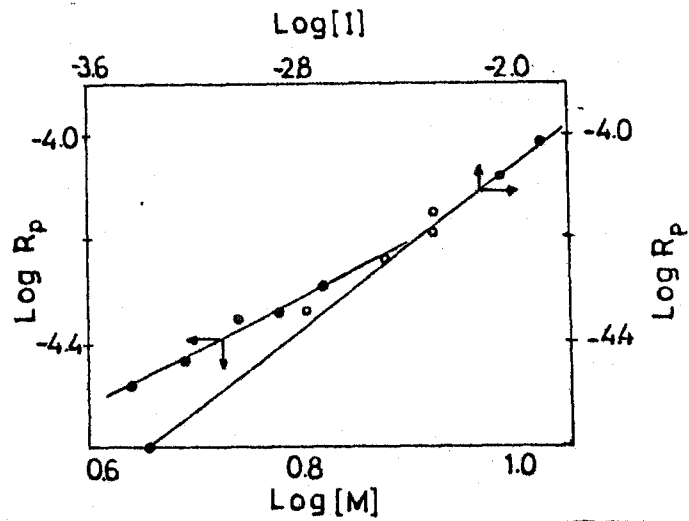Fig 4.8. Plot of log R_p vs 1/T for solution polymerization of styrene initiated by PA-1, solvent : DMSO.

Fig 4.9. Plot of log R_p vs log [M] or log [I] for polymerization of styrene initiated by PA-1 in DMSO at 70°C .

$$\frac{1}{\bar{P}_n} = (fk_d \ \frac{[I]}{R_p}) + C_s \cdot \frac{[S]}{[M]} + C_M + C_I \cdot \frac{[I]}{[M]} \qquad (4,8)$$

If it is assumed that transfer to initiator and primary radical combination are unsignificant and C_s and [S] refers to chain transfer to solvent and the solvent concentration, respectively. If C_s is less than 10^{-5}, then the second term on the right hand side in eq.(4.8) will be small compared with the other two terms over the range of [M] considered. Thus a plot of $(1/\bar{P}_n)$ against $([I]/R_p)$ will be linear with a slope equal to fk_d if fk_d is constant. The results for polymerization at constant [I] but varying [M] and also at constant [M] but varying [I] can thus be analyzed by a similar graphical method Figure 4.10 shows plots of $(1/\bar{P}_n)$ against $([I]/R_p)$. The linearity of the plot at constant initiator concentration also indicates that C_s is effectively zero. Similar plot of $(1/\bar{P}_n)$ versus $([I]/R_p)$ at constant monomer concentration gives deviation from linearity only at higher initiator concentrations (Fig 4.10).

The values of fk_d for PA-1 which are calculated from these graphs together with the literature value of ACPA are given in Table 4.11.

For varying initiator concentration but constant [M], a plot of $(1/\bar{P}_n)$ versus $(1/R_p)$ will give a straight line where intercept equals to $C_s([S]/[M])+C_M$, if C_I is neglected, from which C_s was determined as $0.1.10^{-4}$ using literature value [71] of C_M as $0.6.10^{-4}$ and was in a good agreement with a literature value given for DMSO $(0.54-0.48.10^{-4}$ at 50-60^{0}C) [72].

The plot of the reciprocal degree of polymerization $(1/\bar{P}_n)$versus $([I]/[M])$ is shown in Figure 4.11. The C_I value for PA-1 in styrene polymerization was calculated from the initial slope of the straight to be $C_I=0.47$. A curve of $(1/\bar{P}_n)$ versus R_p gives a deviation at higher initiator concentration which is a significant indication of presence of C_I (Figure 4.12). In general, azonitriles are hardly susceptible

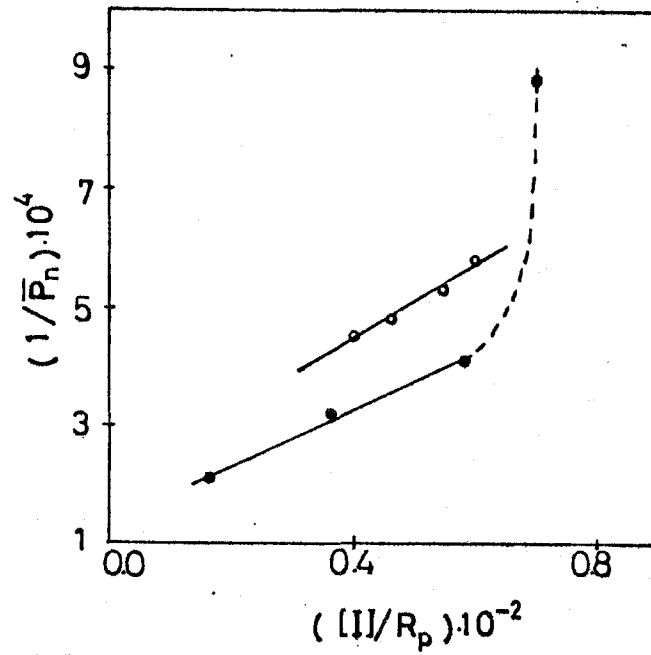Fig 4.10. $(1/\bar{P}_n)$ as a function of $([II]/R_p)$ for the polymerization of styrene in DMSO at $70^\circ C$ in the presence of PA-1 as an initiator (o) at constant $[I] = 2.1.10^{-3} M$; ($\bullet$) at constant $[M] = 6.84$ M.
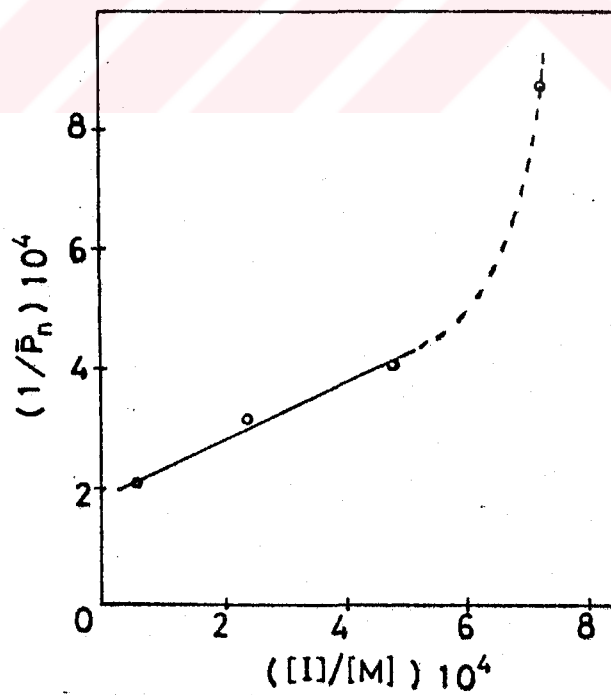

Fig 4.11. Plot of the reciprocal degree of polymerization $(1/\bar{P}_n)$ versus $[II]/[M]$ for styrene polymerization in DMSO at $70^\circ C$ initiated by PA-1.

TABLE 4.11

The Values of fk_d and f in the polymerization of styrene initated by different initiators.

Initiator	Solvent	Temp (°C)	$10^6 \cdot f \cdot k_d$ (sec^{-1})		$k_d \cdot 10^5$ (Sec^{-1})	Value of f		Ref
			At Const.[I]	At const.[M]		At const. [I]	At const. [M]	
PA-1[a]	DMSO	70	6.14	4.77	3.7	0.17	0.13	This work
ACPA	DMF	60	8.07	8.16	1.33	0.61	0.61	40
BPA	DMF	60	5.88	5.68	2.08	0.28	0.27	40

[a]Measured by DSC at a heating rate of 8°C/min ; sample size : ∼ 1 mg.

to transfer reaction and commonly preferred as initiators in polymeri-
zation. However, in our case, the amide groups present in the
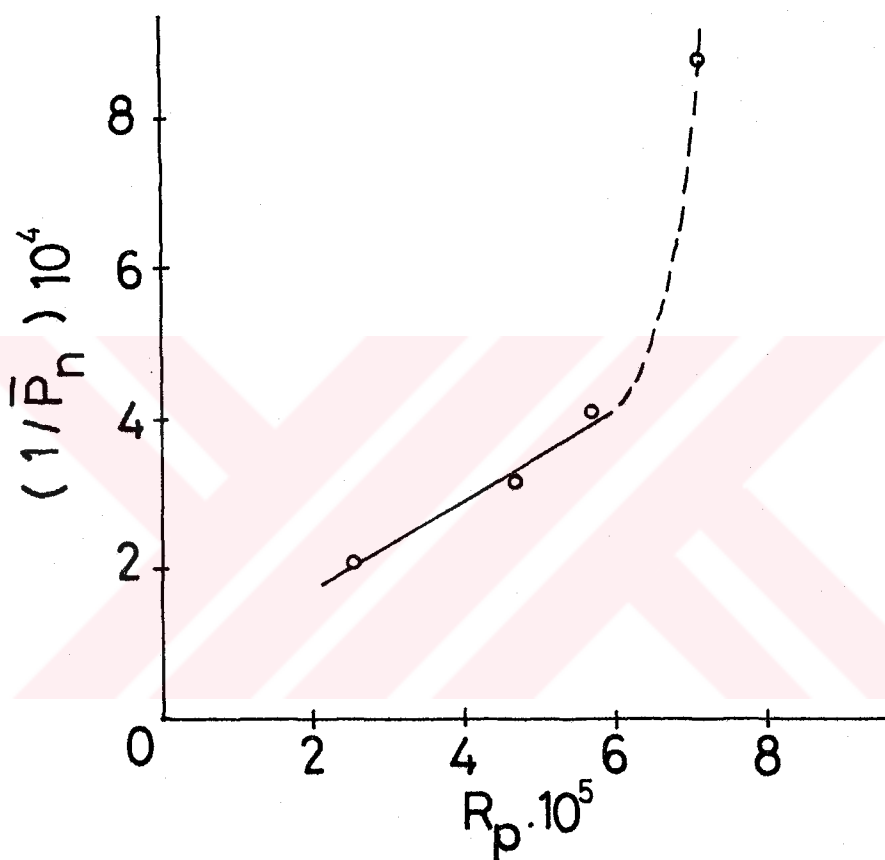initiator may contribute to relatively higher value of C_I.

Fig 4.12. Plot of the $(1/\bar{P}_n)$ versus R_p.

5. CONCLUSIONS

In conclusion, it is clear that macroazonitriles can be synthesized using well known polyamide chemistry. Initiator efficiencies of the macroazonitriles are adjusted by the number of-$N=N$- linkages in the main chain, whereas crown ether segments contribute to the ion binding capability of both initiator and resultant vinyl polymer.

Conventional condensation and interfacial condensation reactions may conveniently be employed for the synthesis. Interfacial polymerization is particularly useful since solution condensation is more sensitive to the monomer purity and stoichiometry than interfacial polymerization although it proceeds at appreciable rates.

The detailed kinetic investigations revealed that macroazonitriles showed general behavior of free radical initiation and can be used as an effective initiator for the synthesis of polymers with crown ether moieties.

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BIOGRAPHY

He was born in Bolu in 1958. He was graduated from 'Pertevniyal Lisesi' in 1975. He admitted to 'Istanbul Technical University', Chemistry Faculty' and was graduated as a chemical engineer in 1980. He was then registered as a MSc student to the same faculty and obtained MSc degree in chemical engineering in 1982, after which was experienced as a research engineer in industry for a year. He was then rejoined the University as a research assistant in 1984. He was awarded a MONBUSHO scholarship by Japanese Government to carry out research in Nagoya Institute of Technology for 14 months.

His main research interests are cationic polymerization polycondensation and synthesis of polymers with special properties.

He is co-author of four scientific papers published in international journals.