39662

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

39662

SYNTHESIS OF BLOCK COPOLYMERS BY USING MULTI-MODE POLYMERIZATION

Ph.D. THESIS

İ. Ersin SERHATLI, M.Sc.

Date of Submission : 28 January 1994

Date of Approval : 5 April 1994

Supervisor : Prof. Dr. Yusuf YAĞCI

Other Committee Members : Prof. Dr. Selim KÜSEFOĞLU

: Assoc. Prof. Dr. Ümit TUNCA

YÜKSEKÖĞRETİM KURULU
DOKÜMANTASYON MERKEZİ

APRIL 1994

ACKNOWLEDGEMENTS

The study described in this thesis has been carried out at Istanbul Tecnical University, Science Faculty between March 1990 January 1994.

I wish to thank to Prof. Y.Yağcı for offering invaluable help in all possible ways and continous encouragement.

I would like to express my gratitude to Prof. E.Chiellini and Prof. G. Galli for their kind guidance in my carrying out some part of this study in the Pisa University, Macromolecules Laboratories from January 1993 July 1993.

Warm regards are expressed to Dr. U. Tunca, Dr. M.Acar, Dr. G.Hızal and Dr. A.Önen who have provided critique and friendly atmosphere.

I sincerely thank to Prof. M. Laus for spectral measurements in Bologna University.

Finally, I would also like to thank my parents for their patiance, understanding and moral support during all stages involved in the preparation of this thesis.

January 1994 İ. Ersin SERHATLI

CONTENTS

SUMMARY

Block copolymers are materials of importance because of their practical use in giving rise to an unique two-phase structure that often allows for non-linear responses in their physical and mechanical properties.

In this thesis, we have investigated the synthesis and physicochemical properties of several new classes of block copolymers. Up to now, various methods have been proposed and used for the synthesis of block copolymers. These methods are generally based on the use of either telechelic oligomers in polycondensation reactions or living polymerization techniques.

Due to the limitation on synthesizing block copolymers using classical single type polymerization mode, we have developed several transformation techniques. First example of the sequential combination of polymerization mechanisms involves the use of azo-linked polytetrahydrofuran as initiator for the polymerization of several vinyl monomers which makes it possible to synthesize polyether-vinyl block copolymers.

The 4.4'-azobis(4-cyano pentanoly chloride) when reacted with a silver salt of a low nucleophilic counter-ion in the presence of tetrahdyrofuran at both ends by an addition mechanism. Accordingly, in this reaction stage a macroinitiator is obtained based on polytetrahdyrofuran and possesing one reactive azo group in the main chain. In addition, this macroinitiator is used to initiate the free radical polymerization of different mesogenic methacrylate monomers.

A successful application of transformation approach described above to prepare block copolymers of structurally different monomers prompted us to examine the possibility of using other polymerization modes in a similar way. A promising pathway was opened by the so-called activated monomer to radical transformation polymerization.

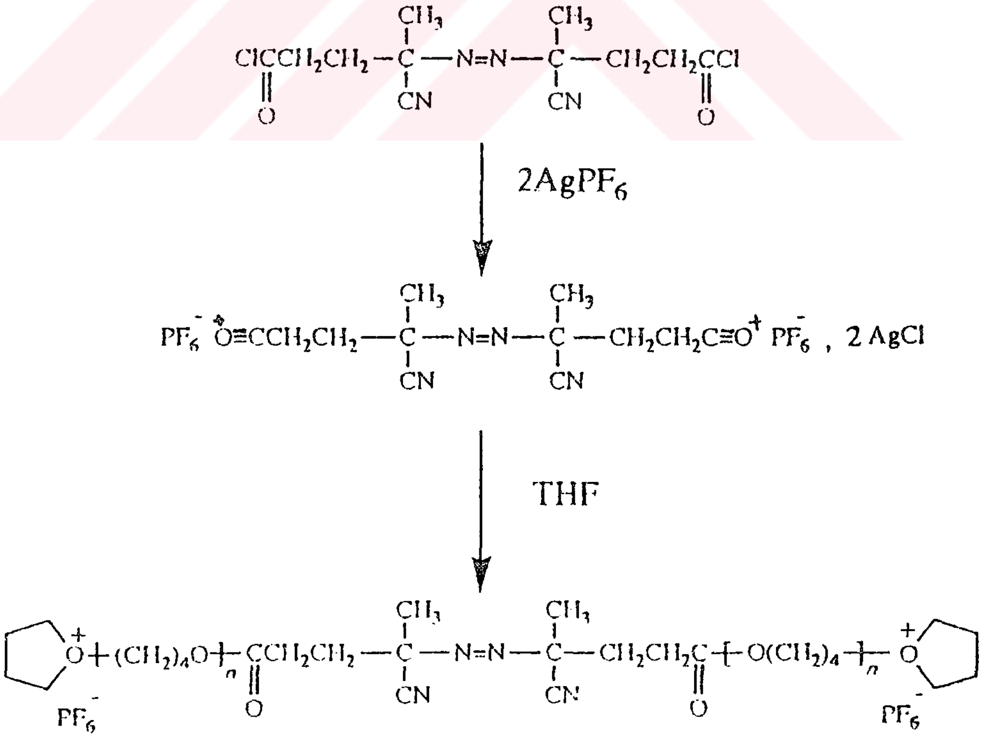
ÖZET

ÇOK YÖNTEMLİ POLİMERİZASYON İLE BLOK KOPOLİMER ELDESİ

Yapıları iyi aydınlatılmış yüksek teknoloji malzemelerine olan gereksinim, blok ve graft kopolimer sentezlerini önemli hale getirmiştir. Klasik sentetik yöntemlerle, ancak yapısal olarak uyumlu monomerlerin blok kopolimerleri sentez edilebilir.

Hidrofilik-Hidrofobik, sıvı kristal termoplastik elastomer sentezleri bu yöntemlerle sentez edilememektedir. Bu çalışmada, farklı polimerizasyon yöntemlerinin birleştirilerek sentezleri mümkün olmayan blok kopolimer eldesi gerçekleştirilmiştir. Bu yaklaşım genel olarak çogalma aşamasının değiştirildiği, Transformasyon Polimerizasyon olarak tanımlanabilir.

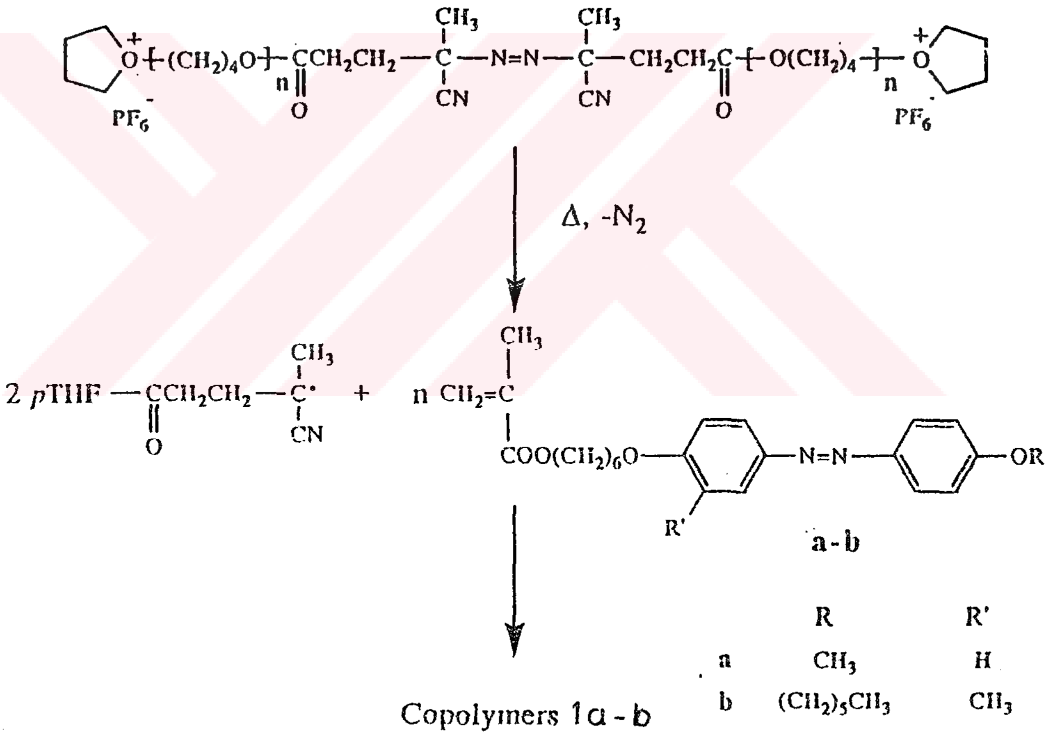
Polieter-Polivinil bloklarının kimyasal bağlı olarak sentezine olanak sağlayan ilk metod katyon-radikal transformasyonudur. Bu sistemde, uç gruplarında asit klorür işlevsel grubu içeren azo başlatıcısı tetrahidrofuran monomeri varlığında reaksiyona sokulduğunda yapısında azo grubu içeren politetrahidrofuran ele geçer.



(5)

Serbest radikal başlatıcı özelliğine sahip politetrahidrofuran çeşitli vinil monomerlerinin polimerizasyonunda kullanılmıştır. Ele geçen blok kopolimerlerinin yapısı spektral yöntemlerle aydınlatılmış, molekül ağırlıkları değişimi büyüklük ayırma kromatografisinde gösterilmiştir.

Aynı yöntemle elde edilen azo bağlı politetrahidrofuran sıvı kristal metakrilat monomerlerinin polimerleşmesinde başlatıcı olarak kullanılmıştır.



Kopolimer geçiş sıcaklıları homopolimerlerini sıcaklıkları ile uyumludur. Buda, politetrahidrofuran ve polimetakrilat sıvı kristal bloklarının faz ayrımına uğradığını ve farklı ısısal geçişlere sahip olduğunu göstermektedir. Politetrahidrofuran bloğunun erime entalpisinin kopolimer içindeki miktarı ile orantılı olmadığıda gösterilmiştir.

Tablo 1 de politetrahidrofuran, polimetakrilat ve blok kopolimerlerin fizikokimyasal özellikleri gösterilmektedir.

Tablo 1. Politetrahidrofuran, polimetakrilat ve blok kopolimerlerin fizikokimyasal özellikleri.

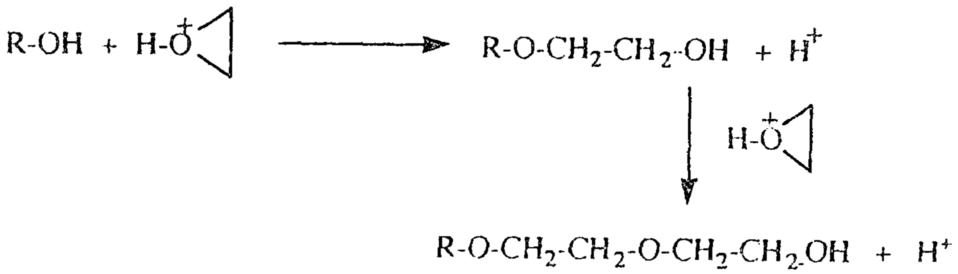
	$\frac{T_g}{K}$	$\frac{T_m}{K}$	$\frac{T_{SN}}{K}$	$\frac{T_i}{K}$	$\frac{\Delta H_m}{J \cdot g^{-1}}$	$\frac{\Delta H_{SN}}{J \cdot g^{-1}}$	$\frac{\Delta H_i}{J \cdot g^{-1}}$
5	—	303	—	—	68,6	—	—
1a	347	298	364	403	8,1	1,0	1,7
2a	348	—	367	409	—	1,9	3,3
1b(I)	364	302	—	369	16,9	—	1,6
1b(II)	366	301	—	371	4,3	—	2,7
2b	364	—	—	368	—	—	3,1

2a, 2b homometakrilat polimerlerini göstermektedir.

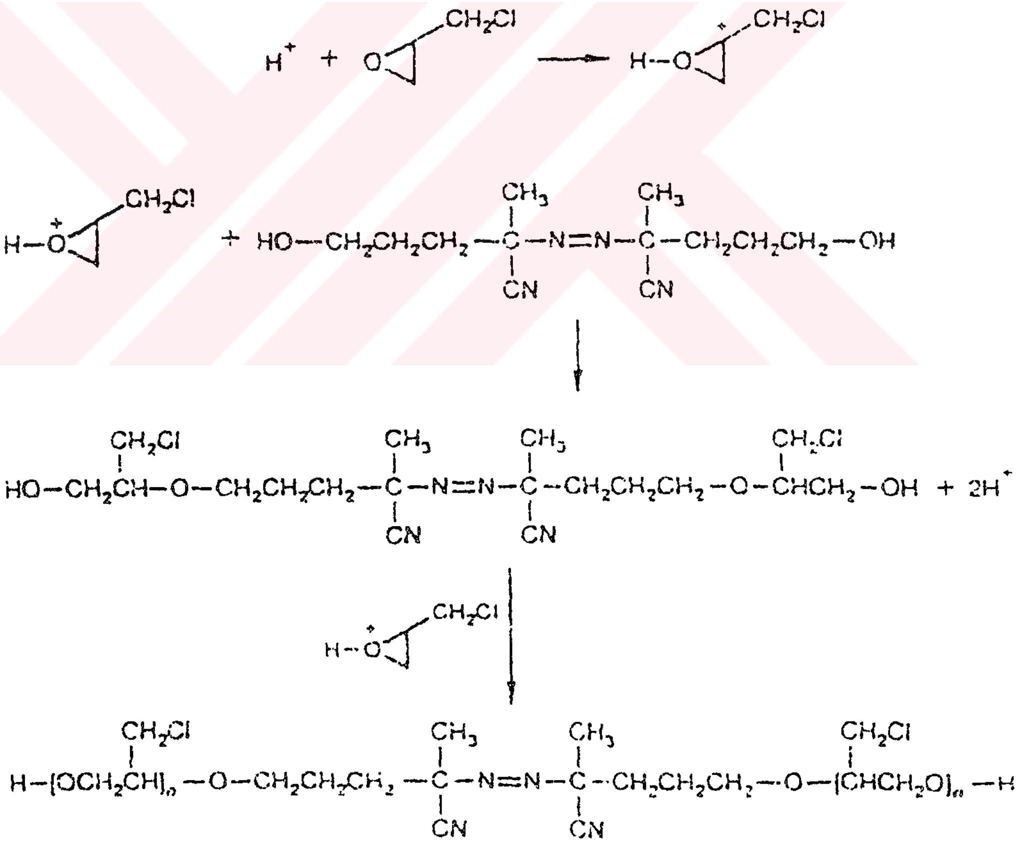
a) T_g. camsı gçiş sıcaklığı; T_m, T_{SN}, T_i. erime smektik-nematik izotropik sıcaklıkları; ΔH_m, ΔH_{SN}, ΔH_i. entalpi değerleri.

Diğer bir transformasyon yöntemi olarak aktive edilmiş monomer polimerizasyonu kullanılarak blok kopolimer sentezi gerçekleştirilmiştir.

Aktive edilmiş monomer polimerizasyonunda polimerizasyon protonlanmış monomerin HO- işlevsel gruplu molekülle reaksiyonu sonucu gerçekleşir.



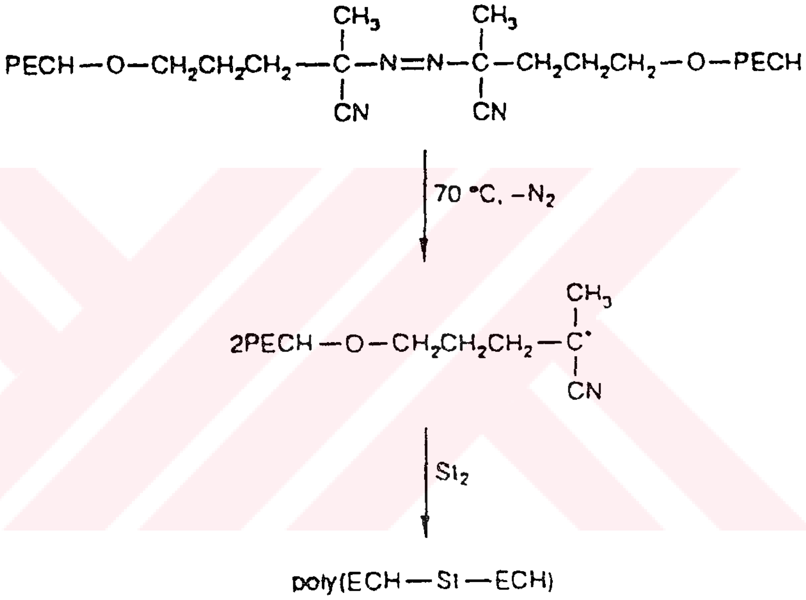
Bu yolla, uygun hidroksi azo-işlevsel grubu içeren moleküller epiklorhidrin ile polimerizasyonu sonucu yapısında azo grubu bulunan polimeri verir.



Polimerizasyon basit alkollerle yapıldığından çok yavaş şekilde yürür ve aynı koşullarda ancak %28 lik bir dönüşüme ulaşılır.

Polimer yapısındaki azo grubunun varlığı spektral ve ısısal ölçümlerle kanıtlanmıştır.

Isıya duyarlı azo grubunun 70^{0}C de parçalanmasıyla stiren monomeri varlığında blok kopolimer eldesi yapılmıştır. Ele geçen kopolimerin büyüklük ayırma kromatografisi yardımıyla molekül ağırlığı homopolimeri ile kıyaslanmıştır.



CHAPTER I. OBJECTIVES OF THE WORK

Block copolymers have recently been a subject of interest mainly from the practical viewpoint of material science. Block copolymers may exhibit diverse mechanical properties which are not shown by homopolymers. Synthesis of block copolymers having different combinations of components and molecular weight dustributions has been a subject of interest for many years.

The transformation approach in block copolymers synthesis, in which different propagating species are used, allows multiple combinations of monomers [1,2]. On the other hand, a variety of different molecular architectures of side-chain liquid crystalline polymers have been recently developed [3], including random [4] or alternating copolymers [5] and graft copolymer systems. This class of polymers includes, for instance, AB block copolymers comprised of amorphous/side-chain liquid crstalline [6,7] and amorphous/main chain liquid crystalline blocks [8].

Block copolymers with liquid crystalline blocks could give rise to microseparated phases, and their study may be of fundemental importance in elucidating the mesophase transitions of liquid crystals in restricted geometries. In addition, the ordering field of the thermotropic mesophase could exert significant effect on the structure and morphology of the other separated phase. Furthermore, new practical opportunities of the liquid crystalline block copolymers can be envisaged, ranging from their use as compatibilizers of polymer components to new materials with tailored properties for electrooptical applications.

CHAPTER II. INTRODUCTION

II.1. General Definition of Polymers

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

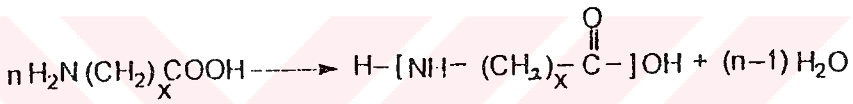
When only one species of monomer is used to build up a macromolecule, the product is called as a homopolymer. If the chains are composed of two types of monomer unit, polymer is called copolymer. When three or more different monomers are incorporated in one chain, a terpolymer results.

II.2. Polymerization Systems

The classical subdivision of polymers into main groups was made around 1929 by Carothers [9], who proposed that a distinction be made between polymers and those formed by chain reactions.

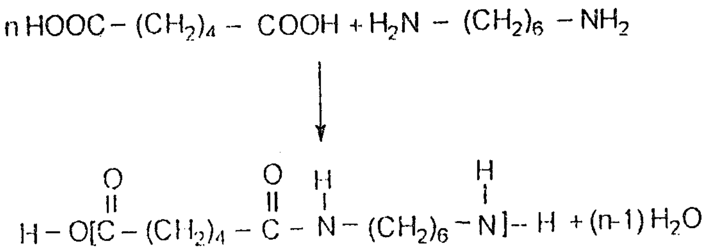
II.2.1. Condensation Polymerization

Many simple organic reactions are known in which two molecules become joined, typical examples being the condensation 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 a single monomer bearing two different functions as for example in the polymerization of an amino acid to a polyamide,



$$n\,H_2N(CH_2)_xCOOH \longrightarrow H-[NH-(CH_2)_x-\overset{\overset{O}{\|}}{C}-]OH + (n-1)\,H_2O \qquad (2.1)$$

of different molecules having the two functional groups as for example in the reaction of a diacid with a diamine to yield a linear polyamide.



$$\begin{array}{c} n\,HOOC-(CH_2)_4-COOH+H_2N-(CH_2)_6-NH_2 \\ \downarrow \\ H-O[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}]-H+(n-1)\,H_2O \end{array} \qquad (2.2)$$

II.2.2. Addition 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 centers proceeds in a series of rapid propagation step, until termination occurs, either by a chemical reaction of the centre or by exhaustion of the monomer supply,

$$\begin{aligned}
I^{*} + M &\longrightarrow IM^{*} \\
IM^{*} + M &\longrightarrow IMM^{*} \quad \textbf{Initiation} \\
I\text{-}(M)^{*} + M &\longrightarrow I\text{-}(M)_{n}\text{-}M^{*} \quad \textbf{Propagation} \\
I\text{-}(M)_{n} + M^{*} &\longrightarrow \textbf{Inactive Polymer} \quad \textbf{Termination}
\end{aligned} \tag{2.3}$$

Addition polymerization is classified into two free radical and ionic polymerization according to the structure of active growing species which may be either a radical or an ion. The types of unsaturated molecule readily undergoing addition polymerization include olefins, conjugated dienes, acetylenes and carbonyl compound with the first two types being of most importance.

II.2.2.1. Free Radical Polymerization

The complete polymerization proceeds in three main stages: Initiation, propagation, termination. The initiation step is considered to involve following reactions.

Decomposition of initiator:

$$I \xrightarrow{k_d} 2R. \qquad (2.4)$$

Photoinduced monomer reaction:

$$M \xrightarrow{h\nu} M. \qquad (2.5)$$

Reaction of initiator with monomer:

$$I + M \xrightarrow{k_d} RM. + \text{Residue} \qquad (2.6)$$

Thermally induced monomer reaction:

$$2M \longrightarrow .M\text{-}M. \qquad (2.7)$$

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

$$R\cdot + M \xrightarrow{k_i} M_1\cdot \qquad (2.8)$$

k_d and k_i are the rate constants of decomposition and initiation steps. Propagating contains the growth of $M_1\cdot$ by the successive of large numbers of monomers. In general terms

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \qquad (2.9)$$

where k_p is the rate constant of propagation. Propagation takes place very rapidly. The value of k_p for most monomers are in the range of 10^2-10^4 liter/mole.sec. The propagating polymer chain stops growing and terminates. Two radicals react other by combination,

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tc}} M_{n+m} \qquad (2.10)$$

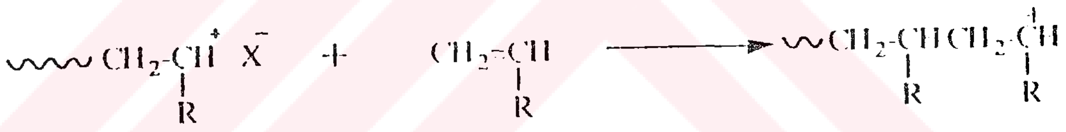
or, more rarely, by disproportionation in which hydrogen abstraction from one end to give two dead polymer chains, one is being an unsaturated and the other is saturated.

$$M_n\cdot + M_m\cdot \xrightarrow{k_{td}} M_n + M_m \qquad (2.11)$$

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.

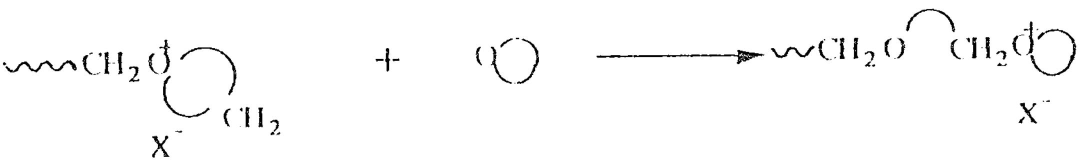
II.3. General Features of Cationic Polymerization

Polymerizations are generally considered as being cationic when they involve a positively charged active species acting as an electrophile towards the monomer. These species may be identified ionic or may appear only in a transition state. Generally, they are located at the end of a growing polymer molecule and react with the monomer acting as nucleophile, but in some cases the situation may be reserved (if the monomer is activated by an acid). Two main categories of monomers have been found to be polymerized by cationic polymerization. The first is that of ethylenic monomers, for which the reactive intermediate has been assumed to be carbocation (also called carbenium ion), the propagation being written schematically as in equation (2.12).



$$\sim\!\sim CH_2-\underset{R}{\overset{+}{CH}}\ \overset{-}{X} \;+\; CH_2=\underset{R}{CH} \longrightarrow \sim\!\sim CH_2-\underset{R}{CH}CH_2-\underset{R}{\overset{+}{CH}}\ X \qquad (2.12)$$

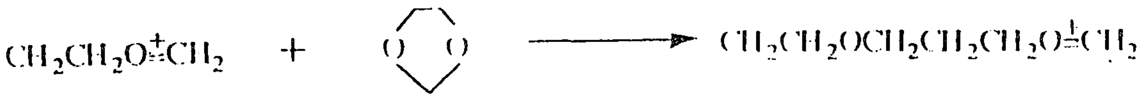
The secondary category is that of heterocylic monomers containing at least one heteroatom (O,S or P) in the ring, for which propagation has been shown various cases to involve onium ions, for example oxonium ions in the case of cyclic ethers equation (2.13).



(2.13)

For a third category of monomers including aldehydes and acetals, propagating resembles that of carbocationic polymerization, but strongly delocalized carbocations may be involved equations (2.14,15).

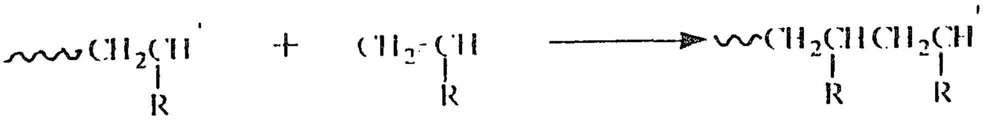
$$O\overset{+}{=}CH_2 \quad + \quad H_2CO \longrightarrow OCH_2O{=}CH_2 \qquad (2.14)$$



In carbocationic polymerization, the most important reactions competitive with propagation are transfer reactions, particulary those involving the monomer and termination reactions. Both have been found to decrease in non-reactive solvents of sufficiently high dielectric constants, particulary at low temparatures, the most used being chlorinated hydrocarbons (MeCl, CH_2Cl_2, EtCl, CCH_2Cl_2). Another particular feature of cationic polymerization is the influence of impurities particularly on the initiation step. Small quantities of polar compounds, have been found to modify strongly the reactivity of Friedel Crafts acids, which are generally the most efficient initiators for carbocationic polymerization, also giving polymers of high molecular weight.

II.3.1. Cationic Polymerization of Vinyl Monomers

The monomers fitted for cationic polymerization include all those with electron donating substituents, in which the polarization of the double bond makes them sensitive to electrophilic attack by a carbenium site.



$$\sim\sim CH_2\underset{R}{\underset{|}{C}}H^{+} + CH_2\text{-}\underset{R}{\underset{|}{C}}H \longrightarrow \sim\sim CH_2\underset{R}{\underset{|}{C}}HCH_2\underset{R}{\underset{|}{C}}H^{+} \tag{2.15}$$

Solvents used in cationic polymerizations should be stable towards acids and unable to react with electrophiles. Preferred are halogenated solvents such as methylene chloride, methly chloride, ethylene chloride, carbon tetrachloride, nitro compounds such as nitro methane or nitro benzene and also dioxane. The initiators able to include cationic polymerization of vinylic monomer can be classified in three categories;

a) **Protonic Acids**

Sulfuric acid (H_2SO_4), perchloric acid ($HClO_4$), fluorosulfonic acid (FSO_3H), trifluoromethyl-sulfonic acid (CF_3SO_3H) and even some cases trifluoro acetic acid (CF_3COOH) have been employed. The initiation reaction proceeds by protonation;

$$H^{+}A^{-} + CH_2\text{-}\underset{R}{\underset{|}{C}}H \longrightarrow CH_3\underset{R}{\underset{|}{C}}H^{+}A^{-} \tag{2.16}$$

b) **Lewis acids**

Such as $SnCl_4$, $AlCl_3$, BF_3, when reacted some nucleophilic compound, can also initiate the polymerization of vinylic monomers. These so-called "initiator-coinitiator" systems give complexes that are the real cationic initiators.

$$AlCl_3 + RCl \rightleftharpoons R^+AlCl_4^-$$

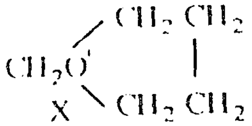
$$BF_3 + H_2O \rightleftharpoons H^+BF_3OH^- \qquad (2.17)$$

c) Carbenium Salts

Cationic polymerization can also be initiated by means of existing carbenium salts. The electrophilicity of these species is lower because substituent allowing delocalization of these charge.

II.3.2. Polymerizability of Tetrahydrofuran

The Tetrahyrofuran (THF) molecule is a planar five membered ring with some internal strain resulting from repulsion of eclipsed hydrogen atoms. Since the ring contains an oxygen atom with two unshared pairs of electrons, THF is a nucleophilic monomer where steric interference to potential electron acceptors is low. THF polymerizes only by a cationic ring-opening mechanism [10-14]. The propagating species in THF polymerizations is a tertiary oxonium ion;



(2.18)

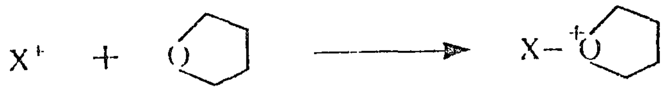
and , for reasons of electrical neutrality, must be associated with a negatively, charged species, the counter ion X . The early work of Meerwein and co-workers [15] has shown that polymerization continues only if the propagation rate is faster than the rate of irreversible reaction of the oxonium ion with its accompanying anion. Simple anions like Cl are not suitable counterions because the cation-anion complex is unstable with respect to THF and alkyl halides. Stable counterions are complex ions including anions like PF_6, AsF_6, SbF_6, $SbCl_6$, BF_4, SO_3CF_3, SO_3F, ClO_4.

A suitable temperature and limited solvent, depending on the temparature, are also critical factors, because the polymerization of THF is an equilibrium process. Hence, for every temperature there is an equilibrium monomer concentration.

II.3.3 General Mechanism of Polymerization of Tetrahydrofuran and Initiator Systems

a) Initiation

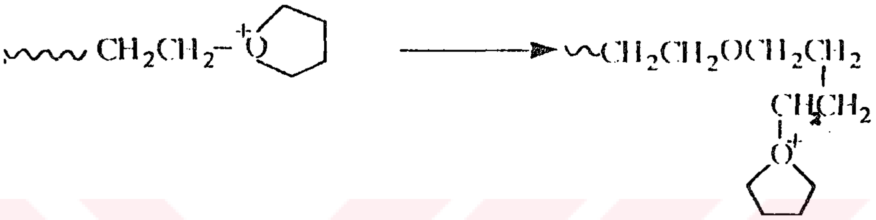
A strongly electrophilic cation X with an anion of nucleophilic power co-ordinates with the ether oxygen to form an oxonium ion.



(2.19)

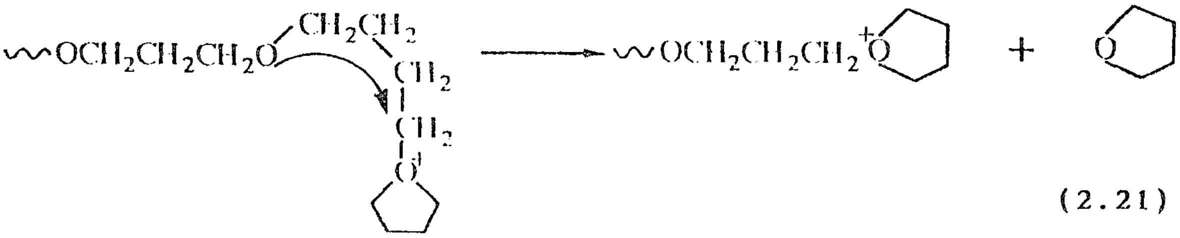
b) Propagation

The propagating species is now generally accepted as being the tertiary oxonium ion [16-18]. Nucleophilic attack by monomer will occur at the carbon atoms α to the tertiary oxonium species, the attack taking on place on ring α producing chain growth.



(2.20)

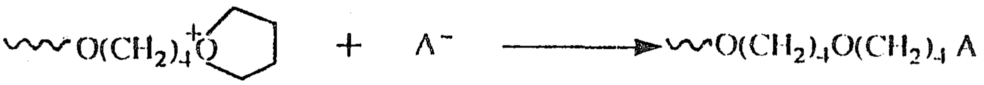
The growing chain carries the positive charge and is balanced by the counter ion of the initiating species. The depropagation reaction proceeds by a similar nucleophilic attack by the penultimate oxygen atom, leading to monomer explusion.



(2.21)

c) Termination

The stability of the anion will govern the molecular weight of the polymer because a possible termination step is the reaction of the anion with the polymer chain. In general we may write,



(2.22)

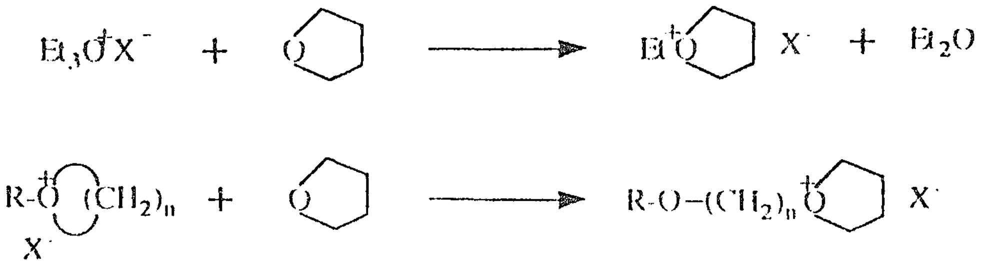
where A is the terminating anion.

Termination may also be due to either impurities in the system or a deliberately added reagent, i.e. OH from H_2O.

II.3.3.1. Initiator Systems

a) Oxonium Salts

Important tertiary oxonium salts include cyclic and acyclic trialkyloxonium ions [2,10,19].

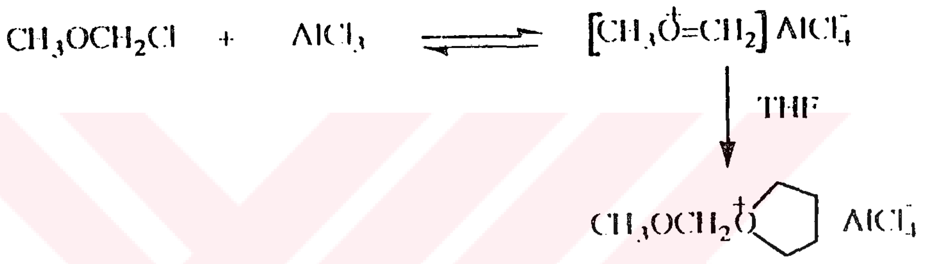


(2.23)

These are prepared by reacting Friedel-Crafts halides with epoxide in diethylether.

b) Carboxonium Ion Salts

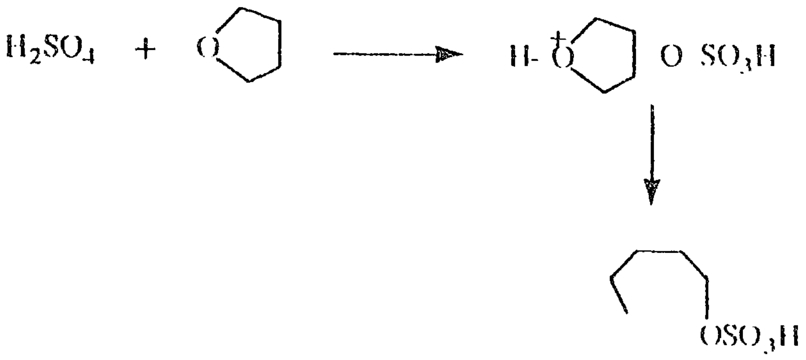
Again Friedel-Crafts halides are used and upon their reaction with organic molecules containing labile halogen atoms e.g. the α-chloro ethers, for example;



(2.24)

c) Protonic Acids

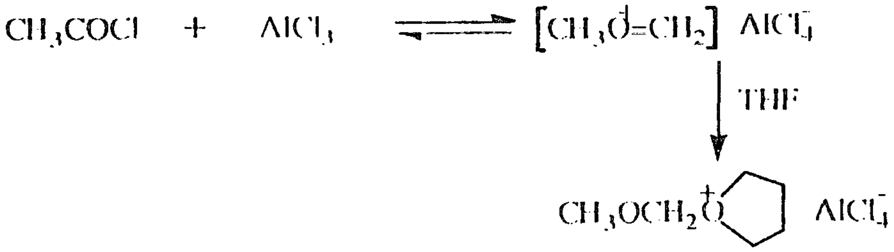
The factor which decides whether or not a protonic acid may be used as an initiator is the nucleophilicity of the resulting anion. Thus sulphuric acid is not suitable since the bisulphate ion is a stronger nucleophile than THF.



(2.25)

d) Acylium Ion Salts

Acylium salts which initiate polymerization of cyclic ethers are formed upon reaction of acid chloride with Friedel-Crafts halides,

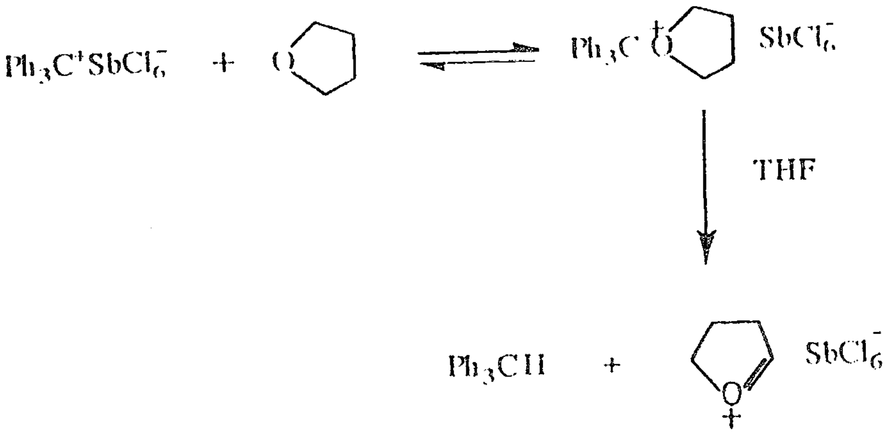


(2.26)

e) Stable Carbocation Salt

Preformed stable carbocation salts, in particular triphenylmethyl (Ph_3C) and cycloheptatrienyl (C_7H_7) salts, provide the reproducible initiation mechanism and allow for full characterization on the polymerization.

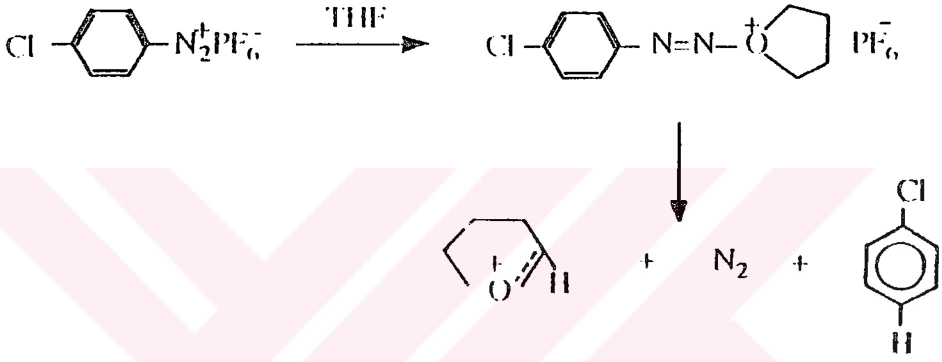
Mechanistically it is known that initiation of THF polymerization by stable organic cations occurs by a hydride ion transfer process.



(2.27)

f) Aryl Diazonium Salts

Arly diazonium salts can be induced to decompose thermally and photochemically. These reactions have been shown by Dreyfuss [18-21], to be effective of polymerization of THF and other cyclic ethers, using p-chlorophenyl diazonium hexafluorophosphate.



(2.28)

II.4. Multi-Mode Polymerization

Various methods have been proposed and used for the synthesis of block copolymers. These methods are generally based on the use of either telechelic oligomers in polycondensation reactions or living polymerization techniques. The end groups of a telechelic oligomer can react with the end groups of another oligomer or with a difunctional small molecule to give block copolymers.

The application of multi-mode polymerization i.e., the transformation reactions depends critically on the feasibility of the polymerization modes to prepare polymers with functional groups to act as macroinitiator for the second monomer. Functionalization may be achieved by initiation, termination and transfer processes. Hovewer, most work concentrated on transformations between anionic, cationic and free radical polymerization.

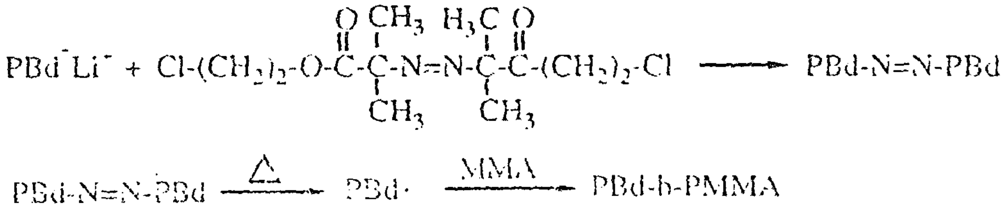
The range of transformation reactions has been expanded in recent years as a result of the development of new polymerization system. Many attemps have been made to increase the number of combinations of monomers which can be incorporated into block and graft copolymers by transforming one mode of chain propagation into another and simultaneously changing the polymerizable monomer.
Although few reviews [22-25], related to polymerizations involving transformation approach have already been published [26], there is a growing interest in the area. Many new studies have been reported recently regarding the synthesis of block and graft copolymers using the transformation approach.

Such reactions are classfied on the basis of interconversion between propagation mechanism; metathesis, anionic, cationic, free radical, group transfer, activated monomer and Ziegler-Natta.

II.4.1. Anionic to Radical Transformation

This approach is the most widely applied process of the transformation techonology. In principle, a range of block copolymers of anionically polymerizable monomers (acrylates, methacrylates, acrylonitriles and other vinyl monomers) are accesible with this route.

An important characteristic of this process structure of resultant block copolymer is determined by both the functionality of the anionic initiator and termination mode of the particular monomer involved in radical process. By suitably selected combinations, di-, tri- and multi-block copolymers may be prepared.
As an example of this type of reaction, polybutadiene chain prepared by anionic polymerization was terminated with bis (2-chloroethyl azo disobutyrate). This initiator was used for the radical polymerization of Methylmethacrylate [27] scheme (2.1).



$$PBd^-Li^+ + Cl\text{-}(CH_2)_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{CH_3}{\overset{H_3C}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_2\text{-}Cl \longrightarrow PBd\text{-}N{=}N\text{-}PBd$$

$$PBd\text{-}N{=}N\text{-}PBd \xrightarrow{\Delta} PBd\cdot \xrightarrow{MMA} PBd\text{-}b\text{-}PMMA$$

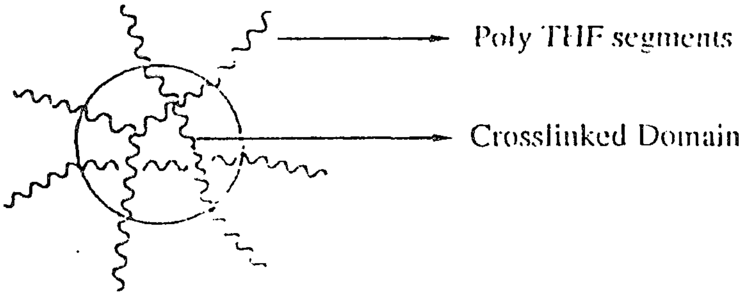
Scheme 2.1.

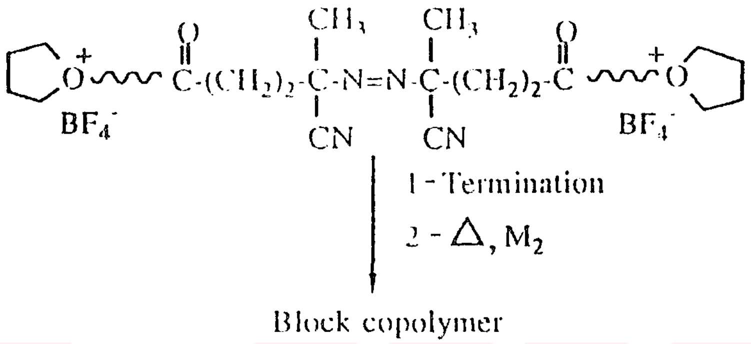
II.4.2. Cationic to Radical Transformation

In addition to anionic to radical transformations, corresponding cationic to radical transformation reactions has become attractive because of the recent discovery of living cationic polymerization systems involving vinylether, styrene and isobutylene.

They are based on the rapid equilibration between small amounts of active carbenium ions and large amount of either dormant covalent species or dormant onium ions. Until very recently, only tetrahydrofuran polymerization fulfilled the living conditions which is critical requirement in the preparation of macroinitiators for a quantitave introduction of functional groups.

Therefore, most of the reported cation to radical transformation involved polytetrahydrofuran (PTHF) as cationic segment. More recent development in this theme has been associated with the use of functional azo initiator. Yagci et. al. [28,29] have synthesized PTHF containing a central azo-linkage by cationic ring opennig polymerization of THF initiated by 4,4'-azobis(cyanopentanoly chloride) in the presence of a silver salt with non-nucleophilic counter ion. Spectroscopic and degradation studies [30] showed that polymers obtained via this initation method contain one azo linkage per chain. The functionalized PTHF was used [31] as an initiator for copolymerization of styrene and divinyl benzeneto prepare macroporous beads with good swelling properties as PTHF segment stays out of the crosslinked domain scheme (2.2).

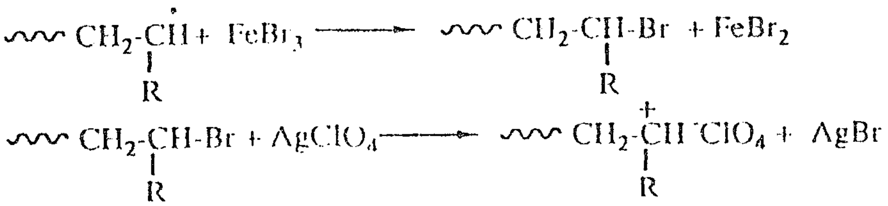




Scheme 2.2

II.4.3. Radical to Cationic Transformations

So far, all applied radical to ionic transformation polymerizations are based on mainly radical to cationic process using redox or transfer agent to functionalize the radicals. For example, such as ferric bromide to a macroradical yields polymeric bromine adduct [32]. This polymer was employed to generate a carbocation which is capable of initiating copolymerization by reacting with silver salts such as $AgClO_4$, $AgPF_6$ or $AgSbF_6$ scheme (2.3).



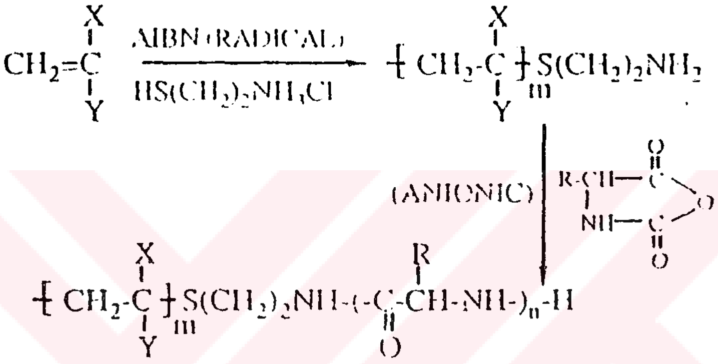
$$\sim CH_2\text{-}\underset{R}{\dot{C}H} + FeBr_3 \longrightarrow \sim CH_2\text{-}\underset{R}{CH}\text{-}Br + FeBr_2$$

$$\sim CH_2\text{-}\underset{R}{CH}\text{-}Br + AgClO_4 \longrightarrow \sim CH_2\text{-}\underset{R}{\overset{+}{C}H}\ {}^-ClO_4 + AgBr$$

Scheme 2.3

II.4.4. Radical to Anionic Transformations

The radical polymerization of MMA and styrene in the presence of 2-mercaptoethylammonium chloride as a chain transfer agent [33] yielded polymers having terminal amino group. Anionic polymerization of amino acid NCAs was effectively in initiated by the macroinitiator to yield corresponding AB type block copolymers. Scheme (2.4).

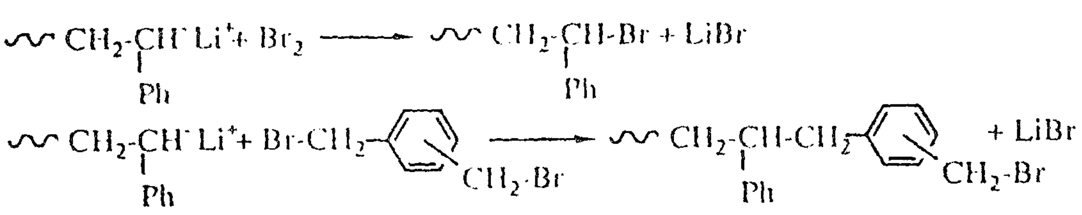


Scheme 2.4

II.4.5. Anionic to Cationic Transformation

Anion to cation or reverse transformation reactions were successfully employed to prepare block copolymers. The particular advantage of these transformations is that both anionic and cationic block can be prepared under living polymerization conditions.

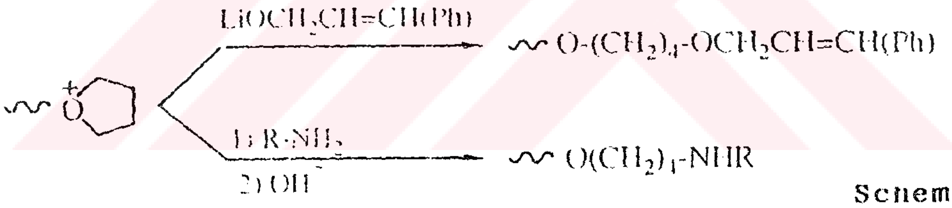
In this connection prominence must be given again to work of Richards and co-workers [34-36] demonstrating the great versatility of the transformation terminated polystyrene by direct reaction of excess bromine-xylene dibromide with living polystyrene. Scheme (2.5).



Scheme 2.5

II.4.6. Cationic to Anionic Transformation

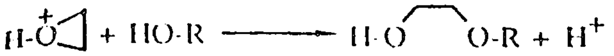
The reverse mode cation to anion transformations have reported by several research groups. In 1982, Richards and co-workers [37] had reported the termination of living PTHF with lithium salt of an alcohol possessing a styryl unit or with primary amino [38] to yield polymers with a terminal group capable of being reacted with a strong nucleophile. Scheme (2.6).



Scheme 2.6

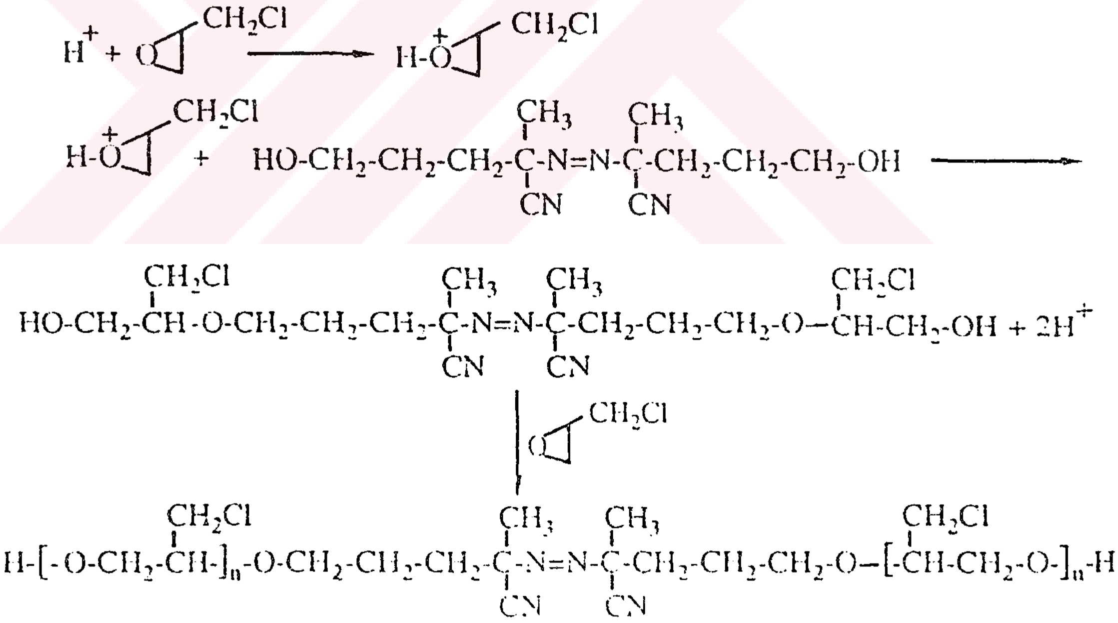
II.5. Transformations Involving Activated Monomer Polymerization

Polymerization by activated monomer mechanism opened up promising pathway for transformation reactions. Recently, Penczek, Kubisa and co-workers [39-42] have found that the cationic polymerization of oxiranes may proceed in the presence of hyroxyl containing compounds by the activated monomer (AM) mechanism which may be represented generally as follows scheme (2.7).



Scheme 2.7

Thus, the propagation involves the reaction of a protonated (activated) monomer molecule with a nucleophile site in the neutral growing macromolecule. More recently, Yagci et al. [43] adapted this procedure to the transformation reactions. Thus 4,4' azobis(4-cyanopentanol) was used in AM polymerization of epichlorhidrine(ECH) to produce polymers with azo-linkage in the main chain. Scheme (2.8).



Scheme 2.8

II.6. Liquid Crystals

The liquid crystal state occurs on the phase diagram between the crystal and the liquid phases. As such it is an unusually fascinating state because it combines properties of both phases. But some specific properties of liquid crystals are different from liquid and solids.

These are;

1) Formation of monocrystals application of normal magnetic and electric field.

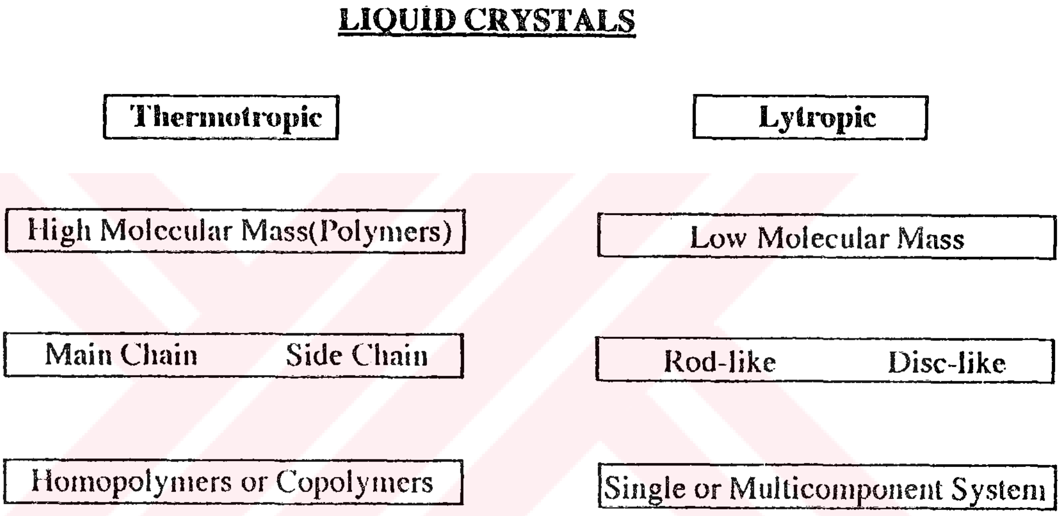
2) Optical activity.

3) Sensitivity to temperature, which results in color changes. Phase change's can be shown as follows;

$$\text{SOLIDS} \underset{\text{Cool}}{\overset{\text{Heat}}{\longleftrightarrow}} \text{LIQUID CRYSTAL} \underset{\text{Cool}}{\overset{\text{Heat}}{\longleftrightarrow}} \text{LIQUID}$$

On cooling the system, the process reverse itself. Liquid crystal state is more ordered than liquid state but less ordered than solid state.

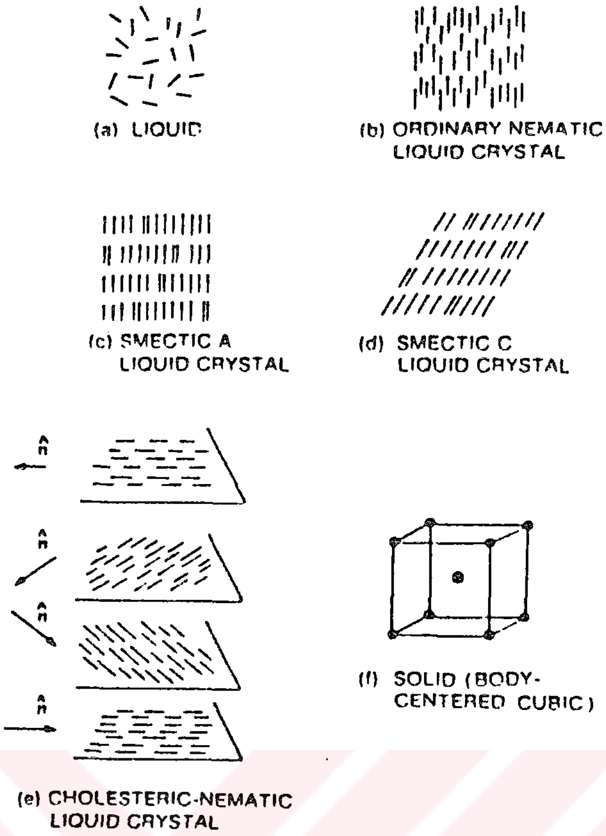
The earlier clear recognation of liquid crystals is usually attributed to the Austrian , Friedrich Reinitzer who in 1888 noted that a carefully purified sample of cholesteryl benzoate melted at 146.6^{0}C to give a colorful cloudy fluid which, when further heated suddenly clarified at 180.6^{0}C. Lehmann using a polarizing microscope equipped with a hot stage, confirmed Reinitzer's observations and joined the term " Liqiud Crystal " to denote the partially ordered fluid phase that forms upon melting the crystalline state.



Scheme 2.9 liquid crystal state

We recognize two major classes of liquid crystals, the thermotropic and lytropic liquid crystals in scheme (2.9). The thermotropic liquid crystals are either nematic or smectic. The nematic means thread and describes the thread like structures that are observed under a microscope. In the nematic structure the molecules maintain a parallel or nearly parallel arrangement to each other. They are mobile in three directions and can rotate about one axis. The smectic means grease or slime. The smectic structure is stratified with the molecules arranged in layers, their long axis lie parallel to each other in the layers, approximately normal to the plane of the layers. The molecules can move in two directions in the plane and they can rotate about one axis. Within the layers, the molecules can be arranged either in neat rows or can be randomly distributed. Included with the nematic liquid crystals is a subclass which is referred to as cholesteric-nematic liquid crystals and often called cholesteric in the literature. Many of these compounds are derivatives of cholesterol. In the cholesteric-nematic liquid crystals the molecules pack in layers about 2000A^0 thick. This is in contrast to the smectic structure where layer thickness is about the length of the molecule or about 20A^0.

The various liquid crystalline structures are schematically illustrated in Fig. 2.1. It should be noted that in real liquids the molecules are randomly arranged Fig 2.1.a. In the nematic state, the long axis of the molecule lie essentially parallel Fig. 2.1.b, while in the smectic A structure Fig. 2.1.c the molecules show two dimensional order. Within layer the molecules are randomly distributed while between layers the molecule arrangement is equally spaced. The molecules in smectic C liquid crystals are packed in equidistant layer as we fluid with smectic A liquid crystals Fig. 2.1.d. In the cholesteric-nematic state Fig. 2.1.e the molecules are arranged in each layer like those in the nematic structure but a necessary twist is superimposed on the layers resulting in a helical structure. The solid crystalline state has order in three dimensions, as represented by a body centered cubic packing Fig. 2.1.f.



(a) LIQUID

(b) ORDINARY NEMATIC LIQUID CRYSTAL

(c) SMECTIC A LIQUID CRYSTAL

(d) SMECTIC C LIQUID CRYSTAL

(e) CHOLESTERIC-NEMATIC LIQUID CRYSTAL

(f) SOLID (BODY-CENTERED CUBIC)

Fig 2.1. Liquid Crystalline Structures

The liquid crystalline state then has molecular order in one dimension (the nematic structure) or in two dimensions (for most smectic structures) but not in three dimensions like a real crystal. Therefore, the liquid crystalline state is more structured than the liquid state, but less structured than the solid state. It should also be noted that liquid crystals are optically anisotropic that is, they can transit light waves of different velocities in different directions. When viewed between crossed Nicol prisms of a polarizing microscope, intense color bonds are seen. In the cholesteric-nematic structure, color changes correspond to change in temparature.

The lyotropic liquid crystals differ from thermotropic liquid crystals for they are obtained by dispersing a compound with another compound one of which is a solvent, e.g. water. They are strongly birefringent. Most detergents, soaps and surfactants dispersed in water will form lyotropic liquid crystals. These compounds are amphiphiles, for they possess in their molecular structure an ionic group that is water soluble and an organic part that is insoluble in water. As we have indicated, an important property of liquid crystals is that they possess both mobility and structural order. In addition, liquid crystals respond to a variety of external stimuli-light sound, mechanical pressure, temperature, electric and magnetic fields as well as changes in its chemical environment behavioral properties that we associate with living cells. Many thousand organic substances and some polymers exhibit liquid crystallinity.

The general, common molecular framework, which usually is depicted as a rod or cigar-shaped entity. A number of organic compound and biological tissues behave as liquid crystals. Attention has been given to liquid crystal phenomena, largerly because of their practical applications and the presence of liquid crystals in certain disease states. Liquid crystals are used widely in electric display devices, e.g, digital watches and calculators. Oscillographic and television displays using liquid crystal screens also are being developed. Other applications include radiation and pressure sensors, optical swicthes and shutters, and thermography. Polymers that form the intermediate phase are important in the fabrication of light-weight, ultra light strength and temparature resistant fibers. Liquid crystals also appear to play an important role in the structure and biochemical function of living tissue, where their characteristic combination of order and flow mobility is particularly well-suited to life processes.

II.6.1. Liquid Crystalline Polymers (LCP)

The study of liquid crystal (LC) properties in polymer systems holds out much promise for the future, not only because such systems will provide us with new knowledge about both polymers and liquid crystals, but also from the standpoint of their technological importance. As pointed out by Finkelmann et al. (1978) and by Finkelmann (1980) in this recent review of thermotropic liquid crystalline polymers, numerous instances are to be found in the literature of polymer systems exhibiting an anisotropic structure in their glassy state but no liquid crystal phase above the glass transition temparature. Only more recently has it been possible to obtain liquid crystal phases similar to those formed by low molecular weight (M_w) systems by heating macromolecular polymeric materials.

Three different structure are known:

1) Non-amphiphlic cylindrical.
2) Non-amphiphlic dics-like.
3) Amphiphlic monomer units.

To form a polymeric main chain these mesogenic elements can be connected in two different way;

i) Head to tail, forming " L.C main chain polymers".
ii) Head to head, resulting on " L.C side chain polymers".

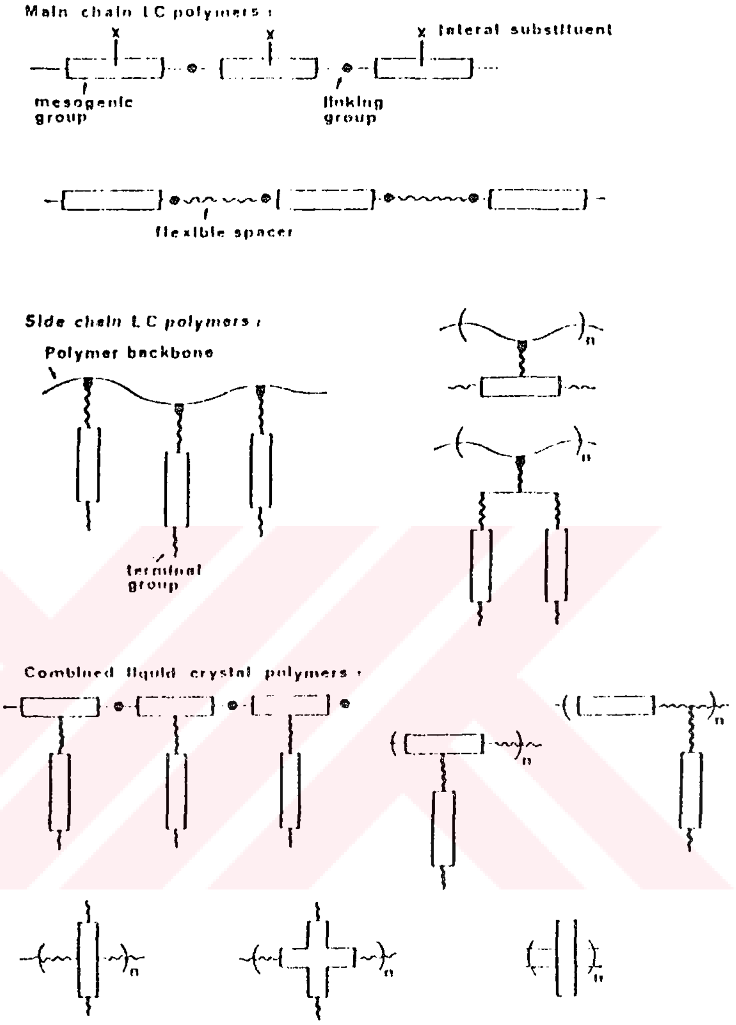
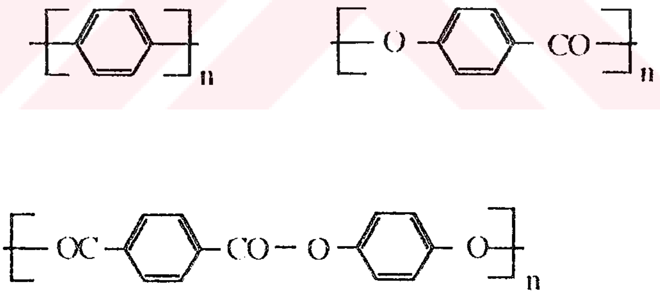


Fig 2.2. Typical structural modifications for LCP's.

Side chain polymers consist of two elements. One element is the polymer backbone which can be widely varied in chemical physical properties. The other element is the mesogenic side chain for which also a large number of chemical constitutions are conceivable. Compared with the monomeric L.C in principle the only change of the mesogenic moiety is the restriction of translational and rotational motions due to the linkage to the backbone. These restrictions should be more or less influenced by the physical properties of the main chain and in which way the rigid mesogenic moiety is linked to the backbone. During the past few years it has been proved that nematic, cholesteric and smectic L.C side chain polymers can be made, exhibiting a thermodynamically homogeneous L.C state.

II.6.1.1. Main Chain Liquid Crystal Polymers (MC LCP)

The basic structure in MC LCP's are benzene rings interlinked of para positions:

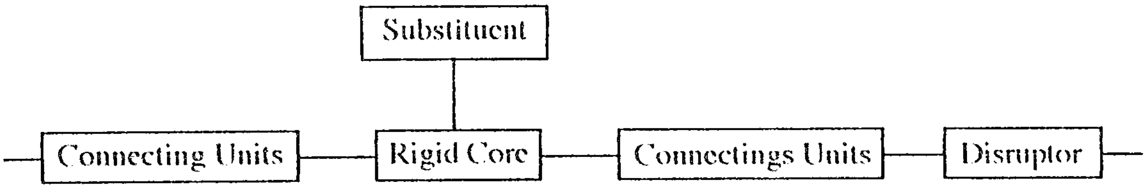


Scheme 2.10. Basic structures in Main Chain Liquid Crystal Polymers

Liquid crystalline properties are observed for oligomers of poly(p-phenylene) with n=5-7 but when n>7 decomposition occurs below the melting temperature [44]. Melting points of 610 and 600^{0}C were measured by DSC for poly(p-hydroxybenzoic acid) and poly(p-phenylene terephthalate), respectively [45]. Hence, the problem of thermotropic MC LCP design to lower the melting point to a melt processable range without destroying lc formation. There are three possible ways of accomplishing this by disturbing the perfect regularity of simple but intractable para linked aromatic polymers[45,46-50].

1) Introduction of disraptors (flexible spacers or rigid links) into the straight polymer chains.
2) Substitution of aromatic rings.
3) Copolymerization.

It should be noted that usually it is necessary to use a combination of at least two of these approaches to lower the melting point sufficiently for melt processability and to achieve high mechanical properties. MC LCP's are depicted below in schematic form along with examples of chemical structural subunits;

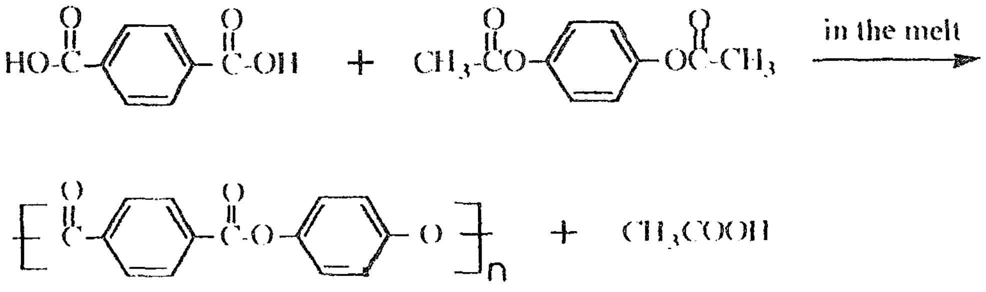


Scheme 2.11. Schematic form of chemical structural subunits

The rigid core usually consist of at least two aromatic rings connected in the para positions by short rigid links. The structures of typical MC LCP's can include as linkages between aromatic rings, aside from direct attachment the imino, azo, azoxy, trans-vinylene, ester and methylene groups. As discussed above, substituents such as F, Cl, Br, CH_3, phenyl or n-alkly groups may be introduced into the mesogenic units.

The most commonly used connecting units joining rigid core to disruptor are ester and ether groups. More recent studies now include the use of amide, imine, urethane and carbonate groups. The flexible spacers are usually sequences of the polymethylene type.

MC LCP's of the ester type have been the most widely synthesized because they can be prepared by the traditional methods of condensation polymerization. Interfacial condensation reactions or solution polycondensation from diphenols and dicarboxylic acid chlorides have been used but the majority of polyesters are now prepared by transesterification.



(2.29)

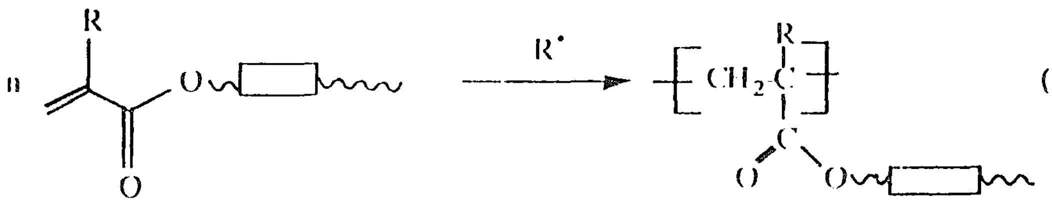
Direct reaction of diacids and diols in the presence of a suitable catalyst have also been reported [51]. Other MC LCP's have been synthesized. Examples are polyazomethines [52,53] polyesteramides [54-56], polyaminoesters [57], polyetheresters [58], polythioesters [59,60], polyamides [61] and polyisocyanates [62].

II.6.1.2. Side Chain Liquid Crystal Polymers (SC LCP)

Many reviews have recently been published on the development of SC LCP. Academic interest has focused largely on characterizing these systems and understanding their structure-property relationships[47,48,63-72]. Electrooptic phenomena exhibited by these polymers have also been considered in terms of potential device applications [73]. In SC LCP's the mesogenic groups are linked to an existing polymer backbone either directly or via flexible spacer units Fig 2.2.

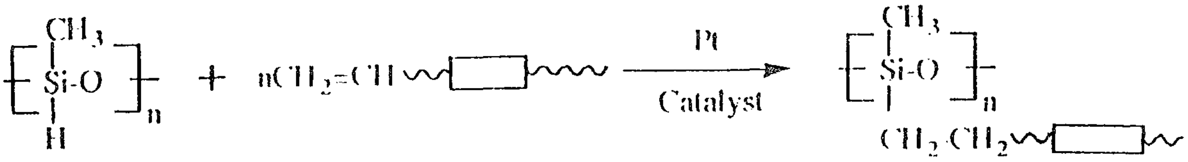
Coupled with steric interactions between the side groups the tendency toward a statistical distribution of chain conformations hinders the ordered arrangement of the mesogenic groups and L.C is suppressed. Decoupling of the side groups by using a flexible spacer allows the main chain motion to occur without disturbance of the anisotropic arrangement of the side chains. The polymer then may exhibit L.C properties. The most common backbone so far considered are poly-acrylate, -methacrylate, and -siloxane systems. Typical spacer groups consist of between 3 and 12 methylene units.

SC LCP's of the acrylate, methacrylate or chloroacrylate type have been the most widely synthesized because they can be prepared by free radical polymerization [74-77].



(2.30)

Anionic [78,79], group transfer [80,81] and cationic [82-84] polymerizations have been used to obtain different tacticities, molecular weights and polydispersities and to vary the nature of the polymer backbone. Polycondensation reactions have been successfully applied to preparation of SC LC polyesters [85,86] with flexible, semi-flexible and rigid backbones. SC LC polysiloxanes are usually prepared by an addition process, commencing with contains reactive functional groups (Si-H) to which the mesogenic groups are appended [87].



(2.31)

II.6.1.3. Types of Side Chain Liquid Crystal Polymers

Essentially, three things can be varied in an SC LCP: the backbone, the spacer and the mesogen.

II.6.1.3.1 The Backbone

Most of the work in the literature refers to SC LCP's with acrylic, methacrylic or siloxane backbones. Studies of the temperature range over which liquid crystal phases are stable a little contradictory, probably due to a lack of comparability of molecular mass of the polymers.

The general indication is that the glass transition temperature decreases and clearing temparature increases, with increasing chain flexibility.

II.6.1.3.2. The Spacer

A spacer is not always a requirement for liquid crystalline behaviour; the mesogenic unit can be attached to the backbone directly. Short spacer of fewer than six methylene units tend to lead to nematic phases whilst longer spacers lead to smectic phases. Clearing temparatures show an odd-even effect for the number of spacer units [88], and then to be higher for an even number of units.

II.6.1.3.3. The Mesogen

The mesogenic unit usually consists of a biphenyl group, or two or more aromatic rings joined together by a functional group. Increasing the lenght of the mesogen by having more aromatic rings tends to increase the temperature range over which the liquid crystalline phases is stable. The end group in the para position has an effect upon the phase behaviour of the polymers. Polar groups such as -CN tend to lower clearing temparatures, where as long chain alkoxy groups give more stable thermotropic phases with high clearing temparatures.

II.6.1.4. Copolymers

Random copolymers of a mesogenic and non-mesogenic monomer give an SC LP copolymer in which the effect of the mesogen is diluted. This rarely crystalline phase observed but does have a profound influence on the various transition temperatures. There will also be a minimum mesogenic content below which all thermotropic behaviour is lost.

Much of the earlier work in this area has been done with acrylic monomers. It is interesting that a recent paper has described the sythesis of copolymers of mesogenic methacrylate monomers and poly(methyl methacrylate) macromonomers [89]. Reports of block copolymers have recently appeared where one block is poly(methacrylate) and the other is a mesogenic methacrylate monomer. Group transfer polymerization catalysed by methylaluminium porphyrins, have been successfully employed for this purpose.

The future of SC LP synthesis is likely to be influenced by the developments in other aspects of polymer synthesis. The synthesis of monodisperse polymers with well-defined stereochemistry and sequence distribution is an area of considerable activity and the application of this work to SC LP's is vital for the development of future applications.

CHAPTER III. EXPERIMENTAL

III.1. Materials

III.1.1. Purification of Materials

III.1.1.1. Tetrahydrofuran (Merck)

Refluxed over KOH to remove peroxides and then distilled over sodium wire (66.5^{0}C/760 mm Hg).

III.1.1.2. 4,4' Azobis(4-cyano pentanoic acid) (Fluka)

It was used without further purification.

III.1.1.3. Silver hexaflourofosfate (Aldrich)

It was used without further purification.

III.1.1.4. Methylmethacrylate (Akril Kimya)

Washed twice with aq. 5% NaOH to remove inhibitors, hen with water, dried with $CaCl_2$ and distilled under reduced pressure (46^0C/100 mm Hg). Middle fraction was collected and freshly used.

III.1.1.5. Styrene (Petkim)

Washed with aq. 5% NaOH to remove inhibitors, then water, dried with $CaCl_2$ several hours and distilled under reduced pressure (50^0C/25mm Hg). Middle fraction was collected and immediately used.

III.1.1.6. Ethylacrylate (Akril Kimya)

Washed repeatedly with aq. NaOH until free from inhibitors such as hydroquinone, then washed with saturated aq. $CaCl_2$, dried with $CaCl_2$ and distilled under reduced pressure.

III.1.1.7. Acrylonitrile (Petkim)

Washed with dilute H_2SO_4, then with dilute Na_2CO_3 and water. Dried with Na_2SO_4, by shaking with moleculer sieve. Fractionally distillation.

III.1.1.8. Choloroform (Merck)

Shaken with several portions of conc.H_2SO_4 washed throughly with water and dried with $CaCl_2$ before filtering and distilling (61^0C/760 mm Hg).

III.1.1.9. Benzene (Merck)

Purified by shaking with conc. H_2SO_4 then with water, dilute NaOH and water, followed by drying with $CaCl_2$ and distilled over sodium wire (80.1^{0}C/760 mm Hg).

III.2. Preparation of Materials

III.2.1. Preparation of 4,4'-Azobis(4-cyano pentanol) (ACP)

28.65 g hydrazine sulphate was dissolved in 300 ml of water contained into a round bottom baloon. 45 g acetopropanol was added, followed by slow addition of a solution of 21.6 g soduim cyanide in 200 ml of water. The mixture was allowed to stand overnight. A freezing mixture was then placed around the flask and the solution made acid with 1:1 HCl. Bromine was added very slowly with mechanical stirring at 2^{0}C. The addition took all day and continued until a yellow coloration appears in the solution. Excess bromine was removed by adding sodium bisulphite. The precipitate was filtered off. The mixture was containing of two isomers, racemic and meso, one of which was soluble the other insoluble in cold chloroform.
Seperation was effected by recrystallization from warm chloroform, the filtrate was precipitated into petroleum ether [90].

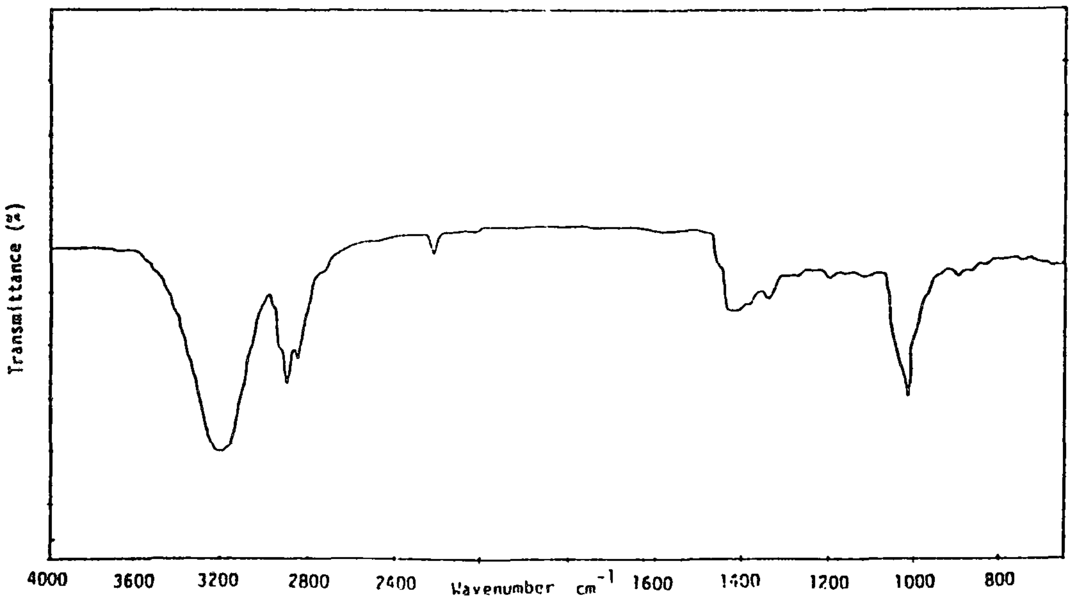


Fig. 3.1 I.R spectra of azo-initiator ACP on KBr disc.

III.2.2. Preparation of 4,4' Azobis(4-cyanopentanoyl chloride) (ACPC)

4,4' Azobis(4-cyano pentanoic acid) (ACPA) was converted to its acid chloride by the modified procedure of Simuonescu [91], 10 g of ACPA was suspended in 100 ml of anhydrous benzene and stirred until dissolution. 20 g of phosphorus penta chloride was added to the solution in portions within 30 minutes under cooling with ice. The stirring was continued for another 1.5-2.0 h at 0^0C and then reaction mixture was allowed to stand two hours and protected from light. After filtering, the clear solution was distilled under vacuum and nitrogen not exceeding 30^0C for removal of benzene and phosphorus oxychloride. The resulting 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 n-hexane until the apprearance of turbidity. After keeping at low temperature, solvent was removed by syringe and the acid chloride was dried and stored under nitrogen in refrigerator m.p: 94-96.5^{0}C . In all these operations, contact with atmospheric moisture and temperatures above 30^{0}C were avoided. I.R. spectra of ACPC is shown in Fig 3.2.

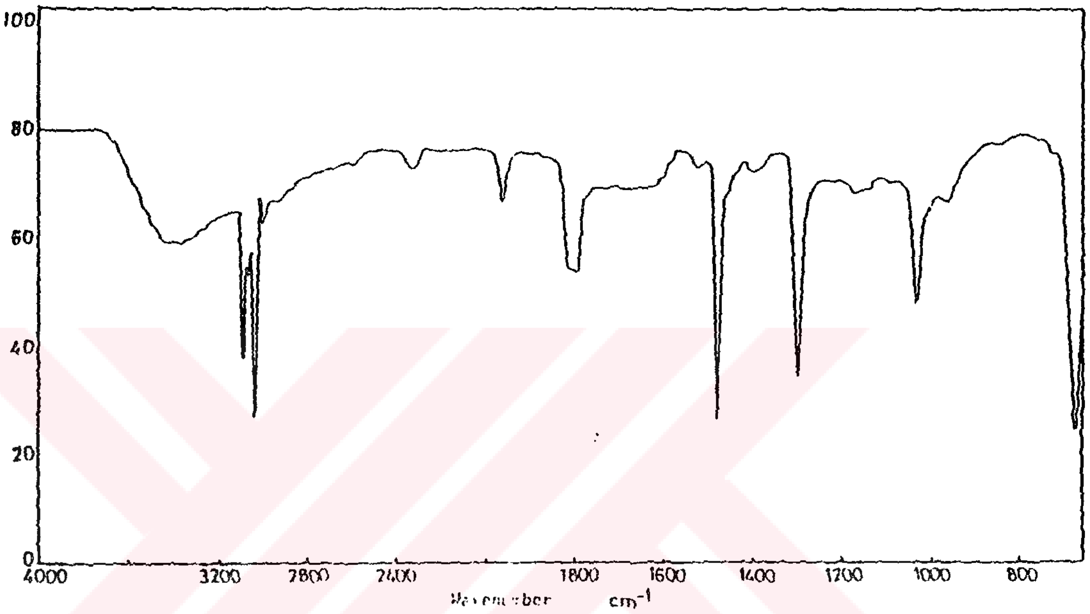


Fig. 3.2 I.R. spectra of ACPC on KBr disc.

III.2.3. Preparation of Azo Containing Polytetrahydrofuran (PTHF)

In a typical polymerization reaction 1.42 g (4.5 mmol) of ACPC and 2.5 g (9.9 mmol) of $AgPF_6$ were dissolved in 100 ml THF at room temperature under dry nitrogen. After reacting for about two minutes at the same temperature, the reaction mixture was filtered and polymer was recovered by precipitation into cold water. The polymer was dissolved in diethylether, and the ether solution was washed with water and then dried over Na_2SO_4. After removing the solvent, the polymer sample was dried under high vacuum. Reaction yields typically ranged from 40 to 50 %.

III.2.4. Activated Monomer Polymerization of Epichlorhidrine

Epichlorhidrine (ECH) 2 g ($2.17.10^{-2}$ mol) was added dropwise (0.1 $g.h^{-1}$) to a solution of 0.147 g ($5.83.10^{-4}$ mol) of ACP containing 0.01 g of BF_3.THF complex in 4ml of $CHCl_3$. After addition of ECH the solution was kept at room temperature for an additional 24 h. The product was washed with water to remove the catalyst and dried under vacuum after evaporating the solvent, a viscous liquid was obtained (0.727 g, 28% yield of ECH).

III.2.5. Block Copolymerization of Polyepicholorhidrine

An appropriate solution of the above obtained Polyepicholorhidrine (PECH) and styrene were placed in pyrex tubes. The mixture was degassed in the usual manner prior to heating at 70^{0}C in thermostated bath. At the end of 150 min, polymer was obtained from the reaction mixture by precipitation into methanol.

III.2.6. Preparation of Liquid Crystalline Block Copolymers

In a typical copolymerization reaction, the required amounts of relevant monomer and macroinitiator were dissolved in 200 ml and of THF. The reaction mixture was introduced in a pyrex glass ampoule, thoroughly freeze-thaw degassed and then sealed under vacuum. After reacting for variable time periods at 70^{0}C, the copolymer was precipitated by addition of a ten-fold excess of methanol, filtered and purified from PTHF by extaction with boiling ethanol in a Kumagawa extractor. The copolymer was then dried in vacuo for 16h.

II.4. Apparatus

III.4.1. High Vacuum System

A pyrex high vacuum line contains, B-14 sockects, mercury diffusion pump, Edwards two stage rotary oil pump and two liquid nitrogen traps, one between diffusion pump and backing pumps. The vacuum obtained is usually about 10^{-4} torr. Schmeatic representation of high vacuum system is shown in Fig. 3.3.

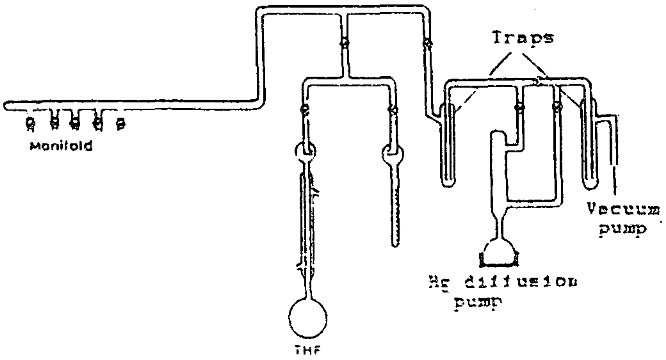


Fig. 3.3 Schematic representation of high vacuum system.

III.3.2. ^1H-^{13}C NMR Spectroscopy

^1H-^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Gemini 200 spectrameter, in $CDCl_3$ using tetramethylsilane as internal standart.

III.3.3. I.R. Spectroscopy

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

III.3.4. UV Spectroscopy

UV spectra were recorded by Shimadzu UV 160 A using $CHCl_3$ as a solvent.

III.3.5. Differential Scanning Calorimetry (DSC)

The thermal and liquid crystalline properties of the polymers were studied by a combination of DSC by Perkin Elmer DSC-7 at a scanning rate of 10 $K.min^{-1}$.

III.3.6. Optical Microscopy

Reicher-Polyvar hot stage polarized light microscopy was used by equipped with a programmable Mettler FP 52 heating stage at a scanning rate of 10 K.min^{-1}.

III.3.7. Size Exclusion Chromatography (SEC)

The M_n values of obtained polymers, which can dissolve in THF were calculated from SEC according to polystyrene standart samples, using Knauer M-64 instrument or 590 Waters chromatograph of THF as eluent at flow rate of 1 ml.min^{-1} at 20 min, equipped with refractive index and ultraviolet detectors , using a Shodex SEC/A-803, two Ultrapac column were used for measurements.

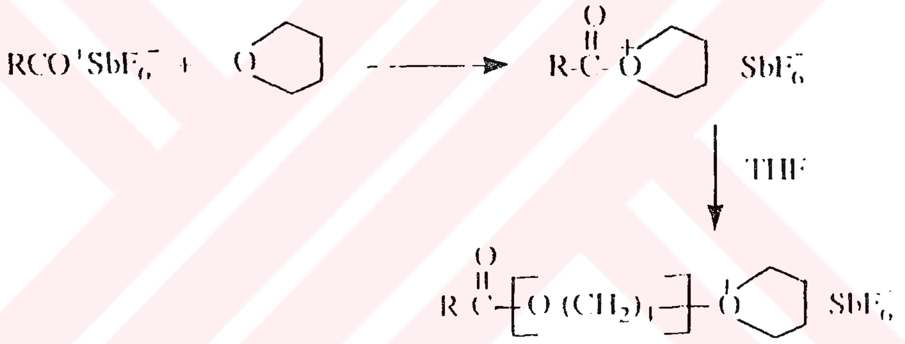
III.3.8. Elemental Analysis

Elemental analyses were performed on a F and M model 185 CHN analyser.

CHAPTER IV. RESULTS AND DISCUSSION

IV.1. Synthesis Block Copolymers by Combination Free Radical and Cationic Polymerization Mechanism

Oxocarbenium salts ($R-C=O\ X$) with complex metal halide anions like BF_4, PF_6, $SbCl_6$,SbF_6 etc. are quite efficient initiators for the polymerization of THF. Initiation by these salts is quantitive, rapid and proceeds by addition according to the following sequence of reactions [92].

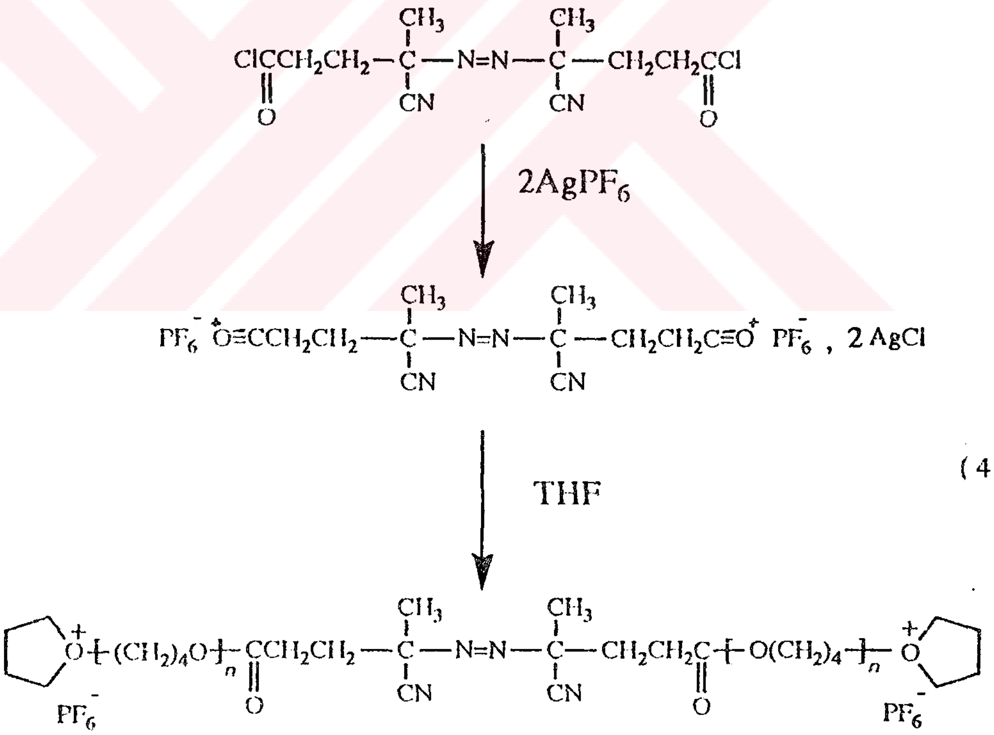


(4.1)

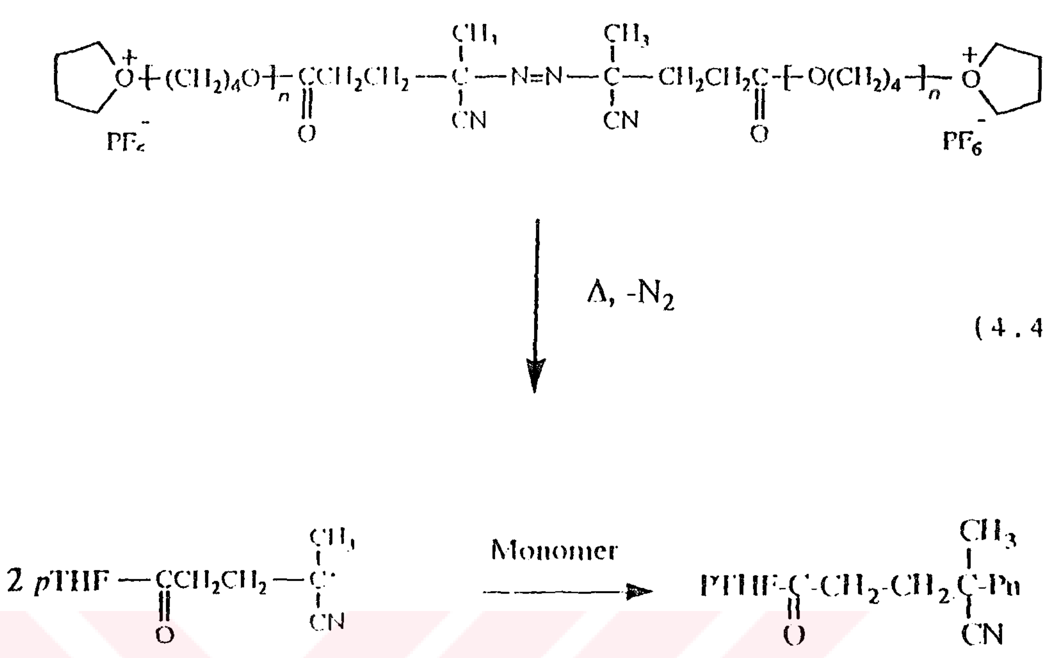
The participation of the ester end group in the possible chain transfer to the polymer can be neglected [93] since the nucleophilicity of these end groups is lower than ether bonds in the polymer backbone. Oxocarbenium salts can easily prepared by mixing the corresponding acid halide using silver salt technique.

$$RCOCl + AgSbF_6 \longrightarrow RCO^{+}SbF_6 + AgCl \qquad (4.2)$$

Franta and co-workers [92] prepared several multifunctional oxocarbenium salts which provide chain growth in two or three independent branches. On the other hand, ACPC 3 is useful intermediate in preparing functional polymers [94,95] and block copolymer [96]. Therefore, it seemed appropriate to use the acid chloride 3 in conjuction with a silver salt for the preparation of a difunctional azo-oxocarbenium salt which provides a convenient initiation process for the cationic polymerization. In this purpose, PTHF containing labile azo group in the main chain were prepared by reacting diacid chloride with silver salts eq. 4.3. Polymerization conditions and results are shown in table 4.1. PTHF which was obtained via this initiation method contained one azo-linkage per macromolecular chain.



(4.3)



(4.4)

Table 4.1. Preparation of PTHF with azo group

$[THF] = 12,3 mol.1^{-1} [ACPC] = 4,5.10^{-2} mol.1.^{-1}, [AgPF_6] = 9.10^{-2} mol.1^{-1}, Temp = 0^{\circ}C$

Run No	Time (min)	Conversion (%)	$\bar{M}_n^a.10^{-3}$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	35	11	34.0	1.17
2	80	37.5	66.0	1.10
3	110	42	82.0	1.57

[a] Determined by G.P.C. measurements.

With the aid of this polymer, block copolymers of THF can be obtained by heating at 70^{0}C in the presence of vinyl monomer. PTHF attached radicals can start the polymerization of a vinly monomer which is contained in the system according to eq. 4.3.

We will throughly demonstrate the case of azo-linked PTHF for initiating polymerization of vinyl monomers namely styrene (St), Methylmehacrylate (MMA), Ethyl Acrylate (EA), Acrylonitrile (AN). Typical results concerning block copolymerization of PTHF with various vinyl monomers are shown in table 4.2.

Table 4.2. Block Copolymerization of PTHF with various monomers at 70^0C

Run No	Monomer ($mol.l^{-1}$)	PTHF (g/l)	Time (min)	Conversion (%)	$\overline{M}_n, 10^4$ of Block Copolymer	$R_P.10^4$ ($mol.L^{-1}.S.^{-1}$)	PTHF Content Block Copolym (%)
4	MMA (9,4)	50^a	30	5,0	28,1	2,6	8,17
5	MMA(9,4)	50^a	75	24,0	39,1	4,9	5,90
6	MMA(9,4)	$14,2^a$	60	3,2	27,9	0,83	8,26
7	St(8,7)	$27,5^b$	30	2,2	34,0	1,2	15,4
8	St(8,7)	$27,5^b$	75	4,5	40,6	0,88	11,3
9	EA(9,24)	$27,5^b$	30	40,0	94,7	20,6	5,0
10	AN(15)	$27,5^b$	30	2,0	-	1,57	-

$^a\overline{M}_n$ initial PTHF = 34.000

$^b\overline{M}_n$ initial PTHF = 66.000

Notably, the molecular weight and concentration of thermo-labile PTHF and polymerization time affect the conversion and composition of block copolymer. It is also interesting to note the higher yields in the case of EA which may be attributed to the relatively higher polymerizability of the related monomers [97].

The block copolymer composition has been determined in several examples ^{1}H-NMR and SEC measurements.
The NMR spectra of poly(St-b-THF) in Fig 4.1. displays

signals at 1.2-1.9 ppm CH_2CH_2(PSt), CH_2(PTHF), 3.4 ppm OCH_2(PTHF) and 6.4-7.2 ppm Ph(PSt).

The ratio of the integrated intensity of the peaks at 3.4 and 6.4-7.2 ppm indicates the mol ratio of PSt/PTHF segments to be approximately 6.9 in the block copolymer.

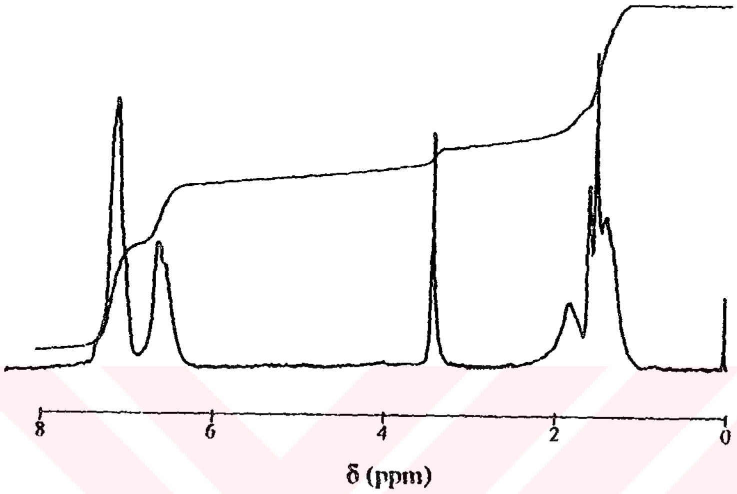


Fig. 4.1 ^{1}NMR spectra of Poly(St-b-THF).

The agreement of this value with that obtained from SEC measurement 6.4 is remarkable. SEC analysis also indicates the formation of block copolymer.
Fig 4.2. shows the SEC charts recorded with the active PTHF and block copolymer after extraction with ethanol.

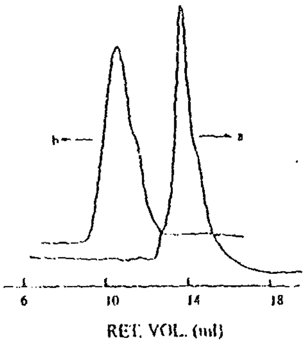
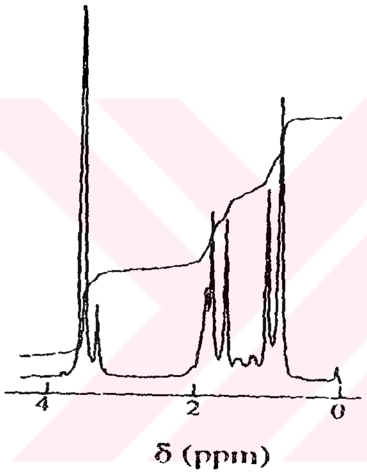


Fig. 4.2 SEC charts of PTHF(a), Poly(St-b-THF)(b).

The new peak at higher molecular weight is ascribed to the block copolymer. IR spectrum of purified block copolymer shows a characteristic ether bonds of the PTHF at 1100 cm^{-1} in addition to the usual PSt bands.

Similarly, ^{1}H-NMR spectrum of the block copolymer of MMA and THF posseses characteristic signals of both segments Fig 4.3. As can be seen from Fig 4.4. significant molecular weight increase due to block copolymerization was observed in this case also.



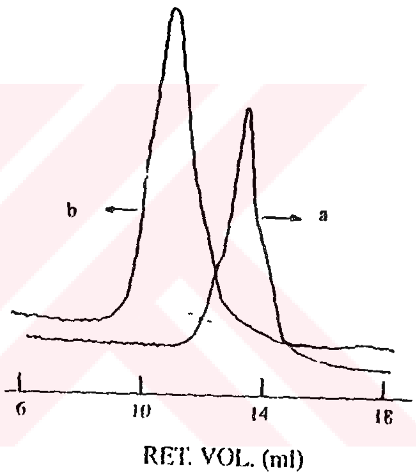


Fig. 4.3 ^{1}H-NMR Spectra of Poly(MMA-b-THF).

Fig. 4.4 SEC Charts of PTHF(a), Poly(MMA-b-THF)(b).

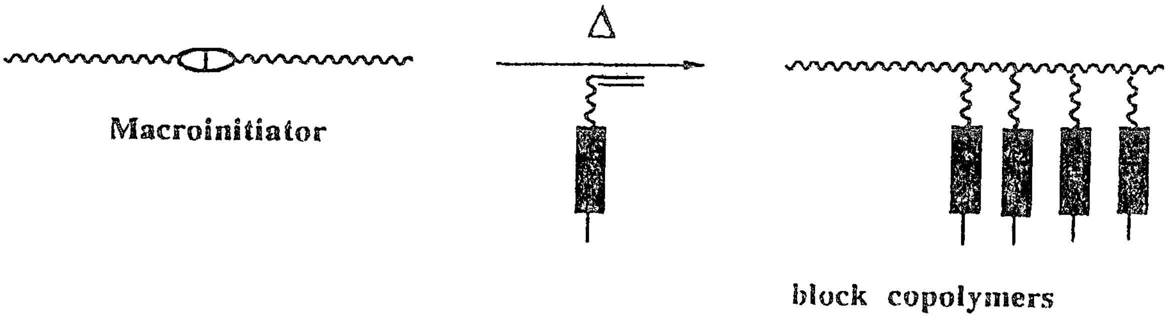
It should be pointed out that the termination mode of vinyl monomers used in the second stage plays an important role in the structure of the resultant block copolymers.

Notably, a block of structure ABA is obtained, if termination of macroradicals consisting of vinyl monomers occurs by combination as in the case of styrene. On the other hand, block copolymers of the structure AB will be formed, if termination of macroradicals occurs by disproportination as in the case of MMA.

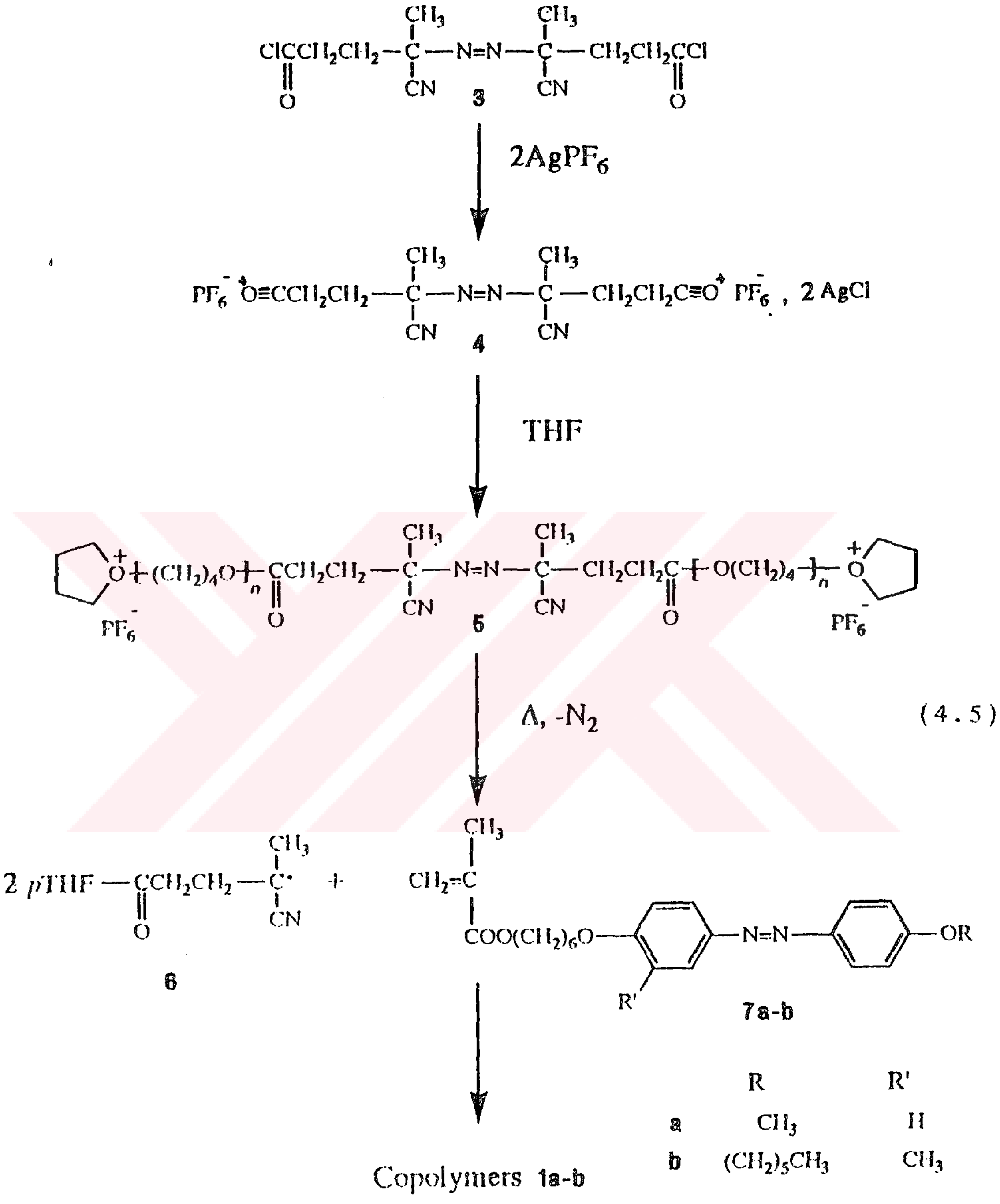
IV.2. Preparation of Liquid Crystalline-Polyether Block Copolymers

In order to incorporate liquid crystalline segment to polyether chains, similar synthetic approaches was used. For this purpose, PTHF having initiating functionality was separetly prepared by using similar azo-oxocarbenium initiation. Polymers with various chain length were prepared for the subsequent step.

Macroinitiator is also used to initiate the free radical polymerization of the methacrylate type mesogenic monomers through the thermal decomposition of azo group at 70^0C. Scheme 4.1.



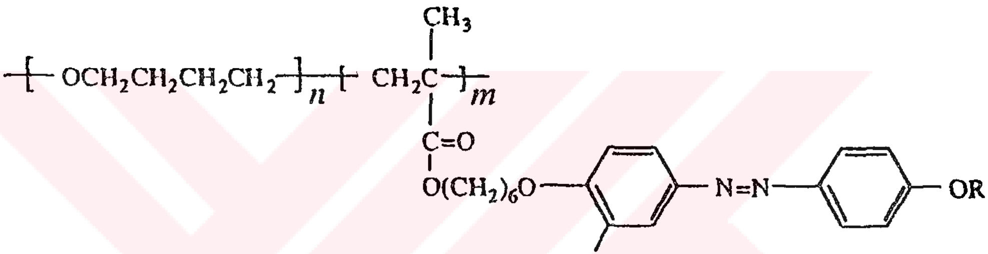
YÖK



(4.5)

	R	R'
a	CH_3	H
b	$(CH_2)_5CH_3$	CH_3

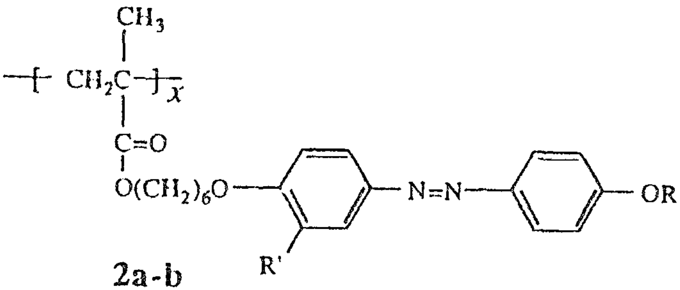
These AB block copolymers are constituted by one PTHF block (block A) and one liquid crystalline polymethacrylate block (block B). The latter is built up from either one of two methacrylate monomers containing azo benzene mesogenic unit variously substituted, which have proved to form nematic or smectic and nematic, mesophases in the relevant homopolymers. The thermal and liquid crystalline properties of the block copolymers 1a-b are described and compared with those of PTHF and polymethacrylates 2a-b obtained from the homopolymerization of corresponding mesogenic monomers;



1a-b

	R	R'
a	CH_3	H
b	$(CH_2)_5CH_3$	CH_3

(4.6)



2a-b

	R	R'
a	CH_3	H
b	$(CH_2)_5CH_3$	CH_3

Two samples of copolymer 1b were obtained with different molecular weights, by using different monomeric ratios in the feed mixture and reaction times Table 4.3. These samples were identified with the reference marks 1b(I) and 1b(II).

Table 4.3 Concentration of methacrylate monomers 7a,b and macroinitiator 5. reaction time and conversion for the synthesis of block copolymers 1a-b.

Sample	[7] / mol · L^{-1}	[5] / g · L^{-1}	Reaction time in min	Conv. of 7 in %
1a	0,27	19,0	1440	9
1b(I)	0,17	42,2	110	7
1b(II)	0,20	20,0	140	47

All copolymers were precipitated several times from choloroform solutions into methanol to eliminate unreacted monomers and were purified by exraction in ethanol where PTHF homopolymer is soluble. Residual traces of polymethacrylate homopolymer could still be present but were not detectable by SEC or NMR. The conversion of the methacrylate monomers ranged from 7 to 47% Tab. 4.3. The structure of the copolymers was established by ^{13}C NMR and ^{1}H-NMR spectoscopy Fig. 4.5, while the copolymer composition was evaluated from the ^{1}H-NMR spectra and confirmed by elemental analysis. Assignment of the various signals was made by combined chemical shift calculations and comparasion of the spectra with those of monomers and low-mass intermediate compounds. Integration of the signals in the ^{1}H-NMR spectrum Fig. 4.5(A) at 3.4 ppm, due to the methylene groups next to the oxygen atoms in the PTHF block, and at 7.8 and 6.9 ppm, relevant to the aromatic hydrogens of the relative amount of the different blocks.

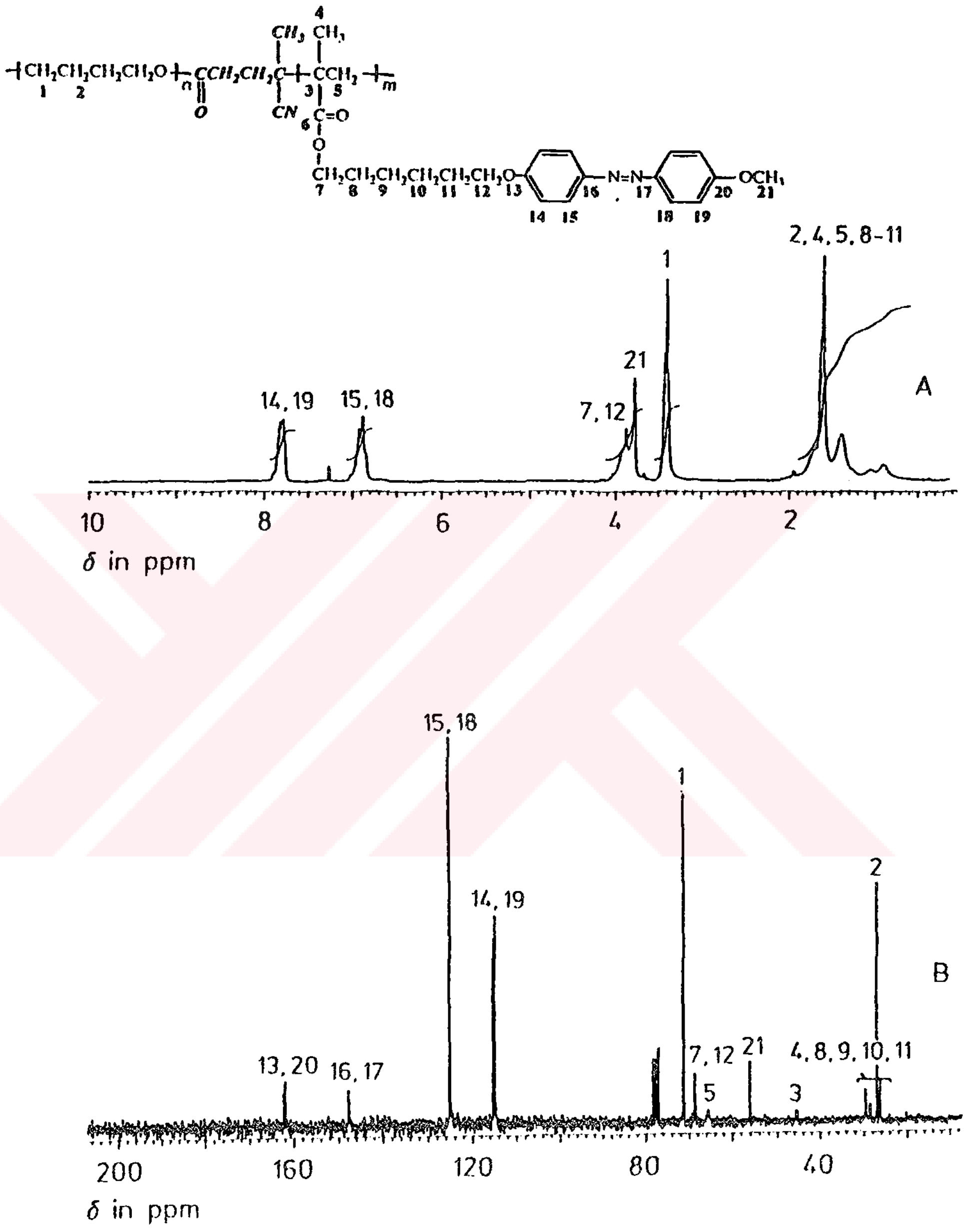


Fig. 4.5 ^1H-NMR(A) and ^{13}C NMR(B) spectra of block copolymer 1a (chemical shifts δ from TMS).

The weight per cent values so calculated of the PTHF block range from 14 to 48%. These data agree with those obtained from the elemantal analysis Tab. 4.4.

Table 4.4 Composition data and molecular weight chacracterstics of macroinitiator 5 and block copolymers 1a-b.

Sample	%C	%H	%N	Wt.-% of *p*-THF by CHN data	Wt.-% of *p*-THF by ^{1}H NMR	$\frac{\bar{M}_n}{g \cdot mol^{-1}}$ [a]	$m(n)$ [b]
5	66,0	11,4	0,1	≈ 100	100	27 000	— (380)
1a	68,6	8,2	4,6	35	33	41 000 [c]	70 (190) [c]
1b(I)	69,8	10,1	3,1	46	48	28 000 [c]	30 (190) [c]
1b(II)	72,0	8,6	5,1	12	14	96 500 [c]	170 (190) [c]

[a] By SEC, in chloroform at 30 °C.

[b] Number-average degree of polymerization of the polytetrahydrofuran block (*n*) and polymethacrylate block (*m*).

[c] Evaluated from the molecular weight of **5**, taking into account the copolymer composition, as determined by ^{1}H NMR, and the stoichiometry of the reaction.

A clear proof of the block copolymer formation was obtained by SEC with dual detection by refractive index and ulraviolet recordings. The wavelenght of 360 nm, at which PTHF is transparent, was used for the ultraviolet detector. The SEC traces of the sample 1b obtained using both detectors are reported in Fig. 4.6 as a typical example. They are practically superposable in terms of shape and peak position, thus indicating the formation of a copolymer in which both polymetacrylate and PTHF blocks of different lenghts are uniformly distributed over the whole macromolecular species determining the molecular weight dispersion curve.

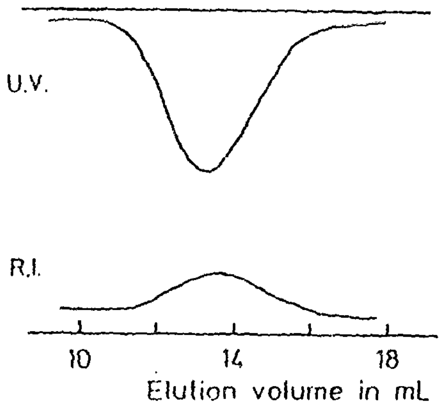


Fig. 4.6 SEC charts of block copolymer **1b(I)** by UV and RI dedection

A number-average molecular weight Mn=27.000 g.mol^{-1} was determined by SEC for the macroinitiator 5. The M_n values of the block copolymers 1a-b, as estimated from the molecular weight of the macroinitiator 5 taking into account the stoichiometry of the reaction and the weight ratio of the blocks, as determined by ^{1}H-NMR, ranged from 28.000 to 96.500 g. mol^{-1}. Accordingly, the average degree of polymerization of the PTHF block of copolymers 1a, 1b(I) and 1b(II) is n=190, while average degree of polymerization of the polymethacrylate block is m=70, 30 and 170, respectively.

The thermal behaviour of block copolymers 1a-b and macroinitiator 5 was studied by DSC measurements and polarizing microscopy. The phase transition temparatures and relevant thermodynamic parameters are collected in Table. 4.5.

Table 4.5 Physicochemical properties of PTHF 5, block copolymers 1a-b and polymethacrylates 2a-b[a]

Sample	$\frac{T_g}{K}$	$\frac{T_m}{K}$	$\frac{T_{SN}}{K}$	$\frac{T_i}{K}$	$\frac{\Delta H_m}{J \cdot g^{-1}}$	$\frac{\Delta H_{SN}}{J \cdot g^{-1}}$	$\frac{\Delta H_i}{J \cdot g^{-1}}$
5	—	303	—	—	68,6	—	—
1a	347	298	364	403	8,1	1,0	1,7
2a	348	—	367	409	—	1,9	3,3
1b(I)	364	302	—	369	16,9	—	1,6
1b(II)	366	301	—	371	4,3	—	2,7
2b	364	—	—	368	—	—	3,1

[a] T_g: glass transition temperature; T_m, T_{SN}, T_i: melting, smectic-nematic, isotropization temperatures; ΔH_m, ΔH_{SN}, ΔH_i: corresponding enthalpies.

The liquid crystalline behaviour of polymechacrylate homopolymers 2a and 2b obtained from the free radical polymerization of monomers 7a and 7b, respectively, has already been described in refs [98] and [99]. Both polymethacrylates 2a and 2b are amorphous in nature. The former presents smectic A and nematic mesophases, where as the latter presents a nematic mesophase. Their phase transition parameters are also collected in Table. 4.5 for comparison.

The DSC heating traces of macroinitiator 5, block copolymers 1a, 1b(I) and 1b(II) and polymethacrylate 2b are reported in Fig. 4.7.

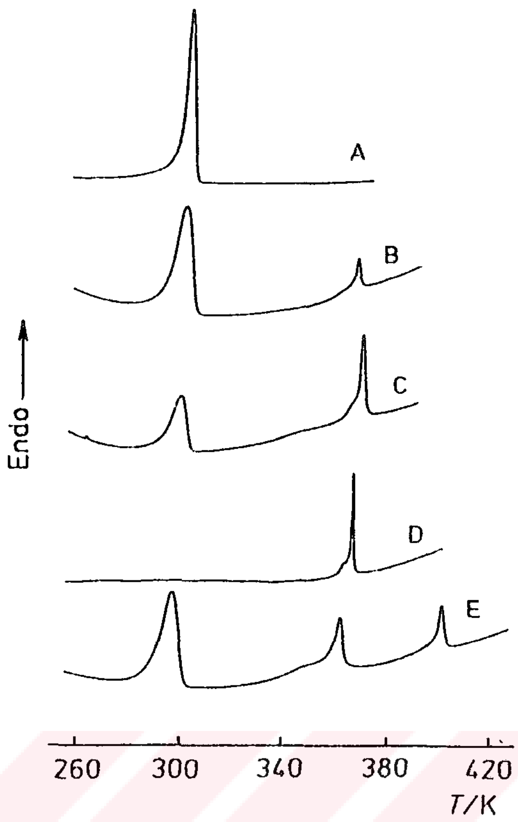


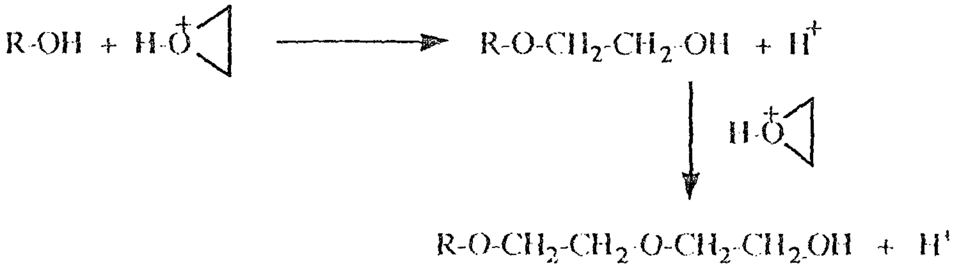
Fig. 4.7 DSC second heating curves (10K.min^{-1}) for polymer 5(A), block copolymers 1b(I)(B) and 1b(II)(C), polymethacrylate 2b(D) and block copolymer 1a(E).

In DSC heating curve of the macroinitiator 5 Fig.4.7(A), one endothermic peak is centered at 303 K corresponding to the melting transition. Polymethacrylate 2b shows one endothermic peak at 368 K Fig. 4.7(D) corresponding to the nematic-isotropic transition. This transition is preceded by the glass transition at 364 K. The DSC heating curves Figs. 4.7(B) and 4.7(C) of the two block copolymer samples 1b(I) and 1b(II) are very similar. In both cases, a step at about 364 K and two endothermic transitions are observed centered at about 302 K and 370 K. Comparison of these curves with the ones of macroinitiator 5 and polymethacrylate 2b reveals that the lower temparature endothermic transition is associated to the melting transition of the polytetrahyrofuran block, where as the step and the higher temperature endothermic transition are associated to the glass transition and to the nematic-isotropic transition of the polymetcrylate block. An anologous behaviour is also shown by the block copolymer 1a. In the DSC heating curve Fig. 4.7(E) three endothermic transitions centered at 298, 364 and 403 K are observed. The first transition corresponds to the melting transition of PTHF block and the others correspond to the smectic-nematic and nematic-isotropic transitions of the polymethacrylate block. The glass transition appears as a step at 347 K.

The phase transition temparatures of the copolymers are very similar to those of corresponding homopolymers, thus suggesting PTHF and polymethacrylate blocks are strongly segregated and undergo distinct transitons. However, the melting entalpy of the PTHF blocks is not directly proportional to the PTHF content in the copolymers, which should be H_m= 23, 33 and 10 $J.g^{-1}$ for 1a, 1b(I) and 1b(II) respectively. Comparison of these values with the experimental ones Table 4.5 reveals that a strong decrease in the crystallization propensity of the polytetrahydrofuran blocks occurs in the block copolymers with respect to the orijinal PTHF macroinitiator 5. On the other hand, if we assume the isotropization entalpy of the polymethacrylate blocks to be directly proportional to the polymethacrylate content, the isotropization entalpy H_i of samples 1a, 1b(I) and 1b(II) should result in 2.2, 1.6 and 2.7 $J.g^{-1}$, respectively. These values are in agreement with the experimentally observed ones, thus indicating that the presence of the PTHF blocks does not effect, in a significant way, the isotropization transition of the polymethacrylate blocks. Furthermore, no differences are observed for the smectic-nematic transition of copolymer 1a relative to homopolymer 2a [100].

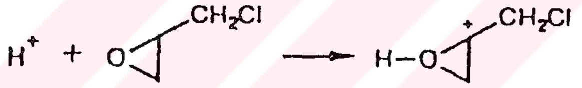
IV.3. Synthesis of Block Copolymers by Combination of an Activated Monomer and Free Radical Polymerization Mechanism

A successful application of transformation approach described above to prepare block copolymers of structurally different monomers prompted us to examine the possibility of using other polymerization modes in a similar way. A promising pathway was opened by the so-called activated monomer to radical transformation polymerization. As discussed in section 2.5. Activated monomer polymerization is considered to proceed through the reaction of the protonated monomer with an alcohol R-OH,

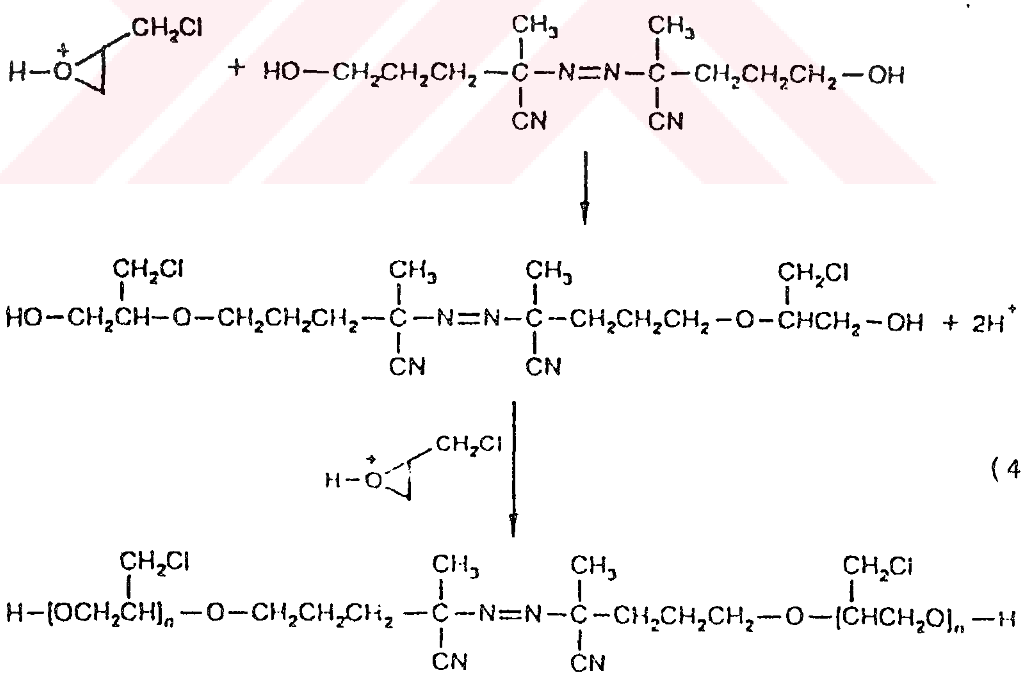


(4.7)

This way structurally desired functional groups may be incorporated to polymers by selecting a suitable hydroxy functional compounds, because the corresponding alkoxy group RO- chemically linked to the resulting polymer. It seemed, therefore, appropriate to use hydroxy functional azo initiator in this particular polymerization to obtain polymers which are capable of initiating subsequent free radical polymerization. For this purpose, epicholorohidrine was polymerized efficiently using 4,4' azobis (4-cyanopentanol) as a hydroxyl-containing compound by the AM polymerization mechanism according to the following reactions;



(4.8)



(4.9)

PECH

Polymerization was conducted under typical conditions, i.e., by slow addition of ECH to a solution of initiator containing catalyst. Reaction was considerably slower than in the presence of simple diols (e.g., ethyleneglycol(EG)) and only 28% conversion was obtained under conditions sufficient to reach complete conversion in the polymerization initiated with EG. From the initial concentrations and conversion, the expected DP_n can be calculated as equal to 10.4, which corresponds to M_n=1180.

Fig. 4.8 shows the ^{1}H-NMR spectrum of the product in $CDCl_3$ solvent.

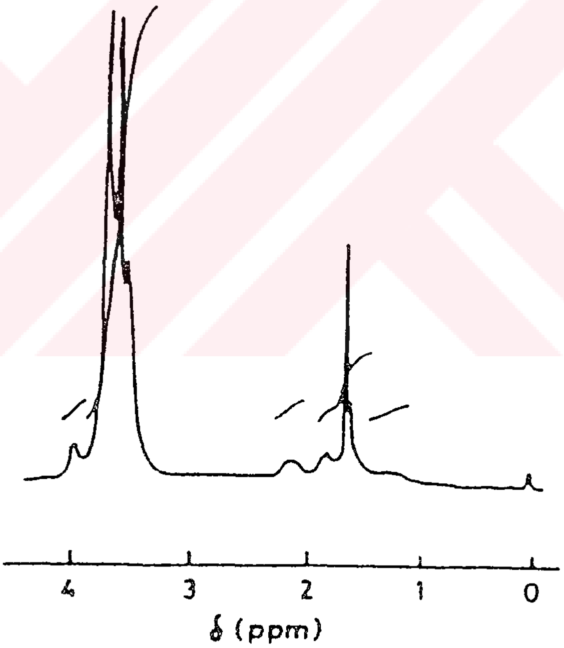


Fig. 4.8 ^{1}H-NMR spectrum of PECH with an azo linkage.

YÖK

The spectrum yields an M_n that is in agreement with the M_n obtained from SEC measurements (M_n=1500); the five protons of the ECH repeating units appear in the 3.6-3.8 ppm region. At 4.0 ppm the signal of the HOCH terminal units is present (the content of primary hydroxyl end groups in the AM polymerization of ECH is below 5 mol %). The signals of the CH_3 and CH_2 groups of the azoinitiator moiety appear between 1.7 and 2.3 ppm. The integration ratios agree within +15% with the structure shown in reaction with an average n of 5. Further evidence for the thermal degradation of polymers produced by means of AM polymerization. As can be seen from the SEC chromatograms in Fig. 4.9 , after thermolysis of PECH in methylene chloride in the presence of diethyl allylmalonate at 70^{0}C, a significant reduction in the molecular weight was observed.

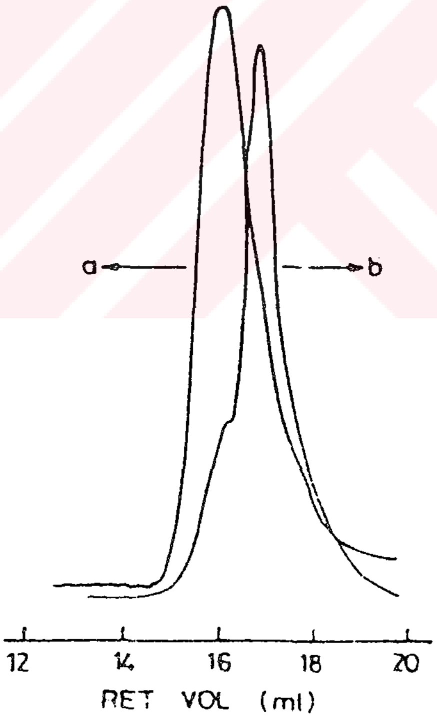


Fig. 4.9 SEC traces for PECH (a) before and (b) after thermolysis

The number of chain scissions per macromolecule, $N_s=(Mn_0/M_{n1})-1$, is found to be about 0.6, where M_{n0}(2200) and M_{n1}(1400) denotes the number average molecular weight of PECH were studied by DSC according to Nuyken's method [101]. The activation energy for the decomposition was estimated to be 120 $kJ.mol^{-1}$ from the DSC trace Fig. 4.10 as measured in a solvent-free system, which is in good agreement with the reported value for polymeric azo initiators [102].

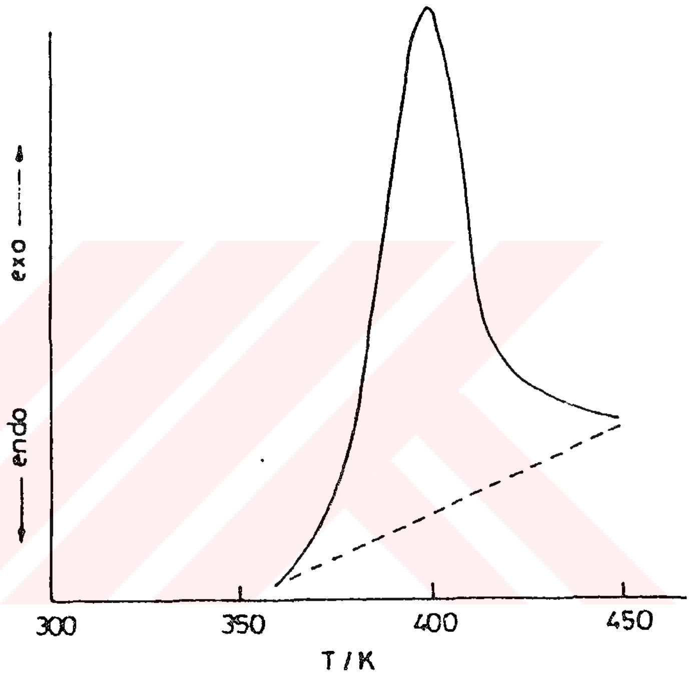
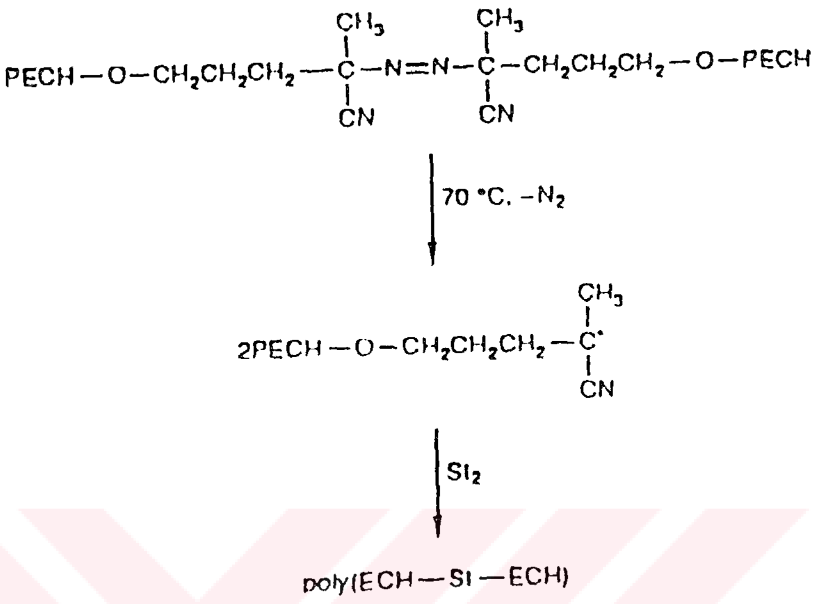


Fig. 4.10 DSC thermogram of PECH with an azo linkage; heating rate $10^0C\ min^{-1}$ under a nitrogen flow.

PECH having an azo linkage was used in the polymerization of St. A solution of St(7.7 $mol.l^{-1}$) in methylene chloride containing 57 $g.l^{-1}$ PECH was heated at 70^0C for 2 h to produce a block copolymer of St and ECH with a yield corresponding to 12.5% conversion of St.



(4.10)

A control experiment under similar experimental conditions without PECH produced very little polymer after the same reaction time. By SEC analysis, the formation of block copolymer was evident as shown in Fig. 4.11 where SEC traces recorded with the prepolymer PECH and block copolymer shows a unimodal molecular weight distribution and does not possess a peak at high elution volume corresponding to unreacted PECH. Dual SEC detection by refractive index and ultraviolet recording allowed a clear assignment of the block copolymer formation, as homo-PECH is transparent at the wavelenght (254 nm) of the ultraviolet dedector.

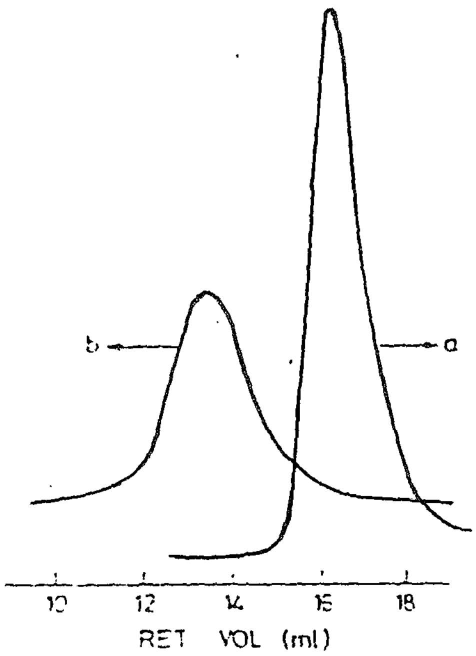


Fig. 4.11 SEC traces for **(a)** PECH with an azo linkage (M_n=2200) and **(b)** the poly(ECH-b-St)

The block copolymer structure was also assigned by means of spectral measurements. The IR spectrum of the block copolymer shows the characteristics bands of both St and ECH segments. The NMR spectrum of the copolymer Fig. 4.12 displays signals at 1.2-2.0 ppm (CH_2 and CH of St segments), 3.55-3.8 ppm (CH_2, CH_2Cl and CH protons of ECH segments), and 6.5-7.3 ppm (C_6H_5 of St segments). The NMR spectrum apprears to have a St/ECH ratio of about 10:1. This value agrees with that obtained from SEC measurements (10.6:1). The type of block copolymer greatly depends on the kinetic behaviour of the particular monomer involved. Initiation of St polymerization by means of azo-linked PECH is expected to yield PSt molecules with a PECH unit at each end since termination occurs by radical-radical combination.

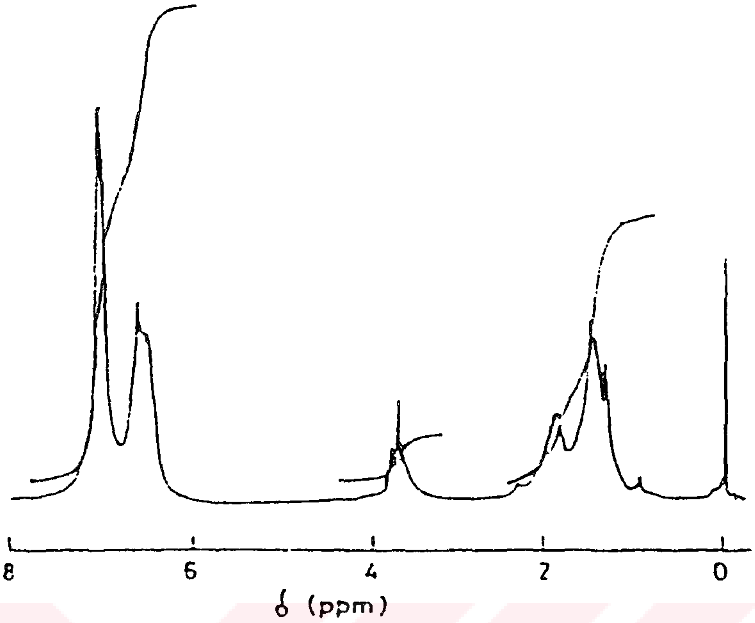


Fig. 4.12 ^1H-NMR spectrum of block copolymer of poly(ECH-b-St)

CHAPTER V. CONCLUSIONS

In this thesis, we have provided three examples of transformation reactions with the emphasis on the cationic-radical polymerization processes. These processes were based on the preparation of macroinitators by cationic polymerization. Functional future of the macroinitiator was derivated from the delibrately introduced azo groups which are capable of initiating free radical polymerization. The advantage of this technique is that one component of the block copolymer is prepared by living polymerization and fully characterized prior to the preparation of block copolymer. As expected final properties of block copolymers obtained in this study, depend on the several factors;

Position and the number of azo group, molecular weight of the macroinitiator, extend of the molecular weight change during formation of the initiating side and the type of monomer employed in the second stage hence, the termination mode of the polymerization involved.

As the ultimate objective is to prepare well defined materials, the importance of these transformation systems will be greater. The application of the materials obtained by transformation reactions are also of interest.

As shown in this thesis, the range of possible block copolymer consisting monomers with different chemical nature, i.e block copolymers of liquid crystalline and crystalline segments, are accessible through these routes.

REFERENCES

[1] SOUEL T., SCHUE F., ABADIE M., RICHARDS D.H., Polymer 18, 1292, 1977.

[2] RICHARDS D.H., Polym. J., 12, 89, 1981.

[3] PERCEC V., PUGH C., Side Chain Liquid Crystal Polymers, Mc Ardle C.B., Ed., Blackie, Glasgow p.30,1989.

[4] CHIELLINI E., GALLI G., ANGELONI A.S., LAUS M., CARETTI D., Macromolecular Assemblies in Polymeric Systems, Stroeve P., and Balazs A.C., Eds., ACS Symposium Series No. 493. p.280, 1992.

[5] LAUS M., BIGNOZZI M.C., ANGELONI A.S., GALLI G., CHIELLINI E., Macromolecules, in press.

[6] ADAMS J., GRONSKI W., Liquid Crystalline Polymers, Weiss R. A., and Ober C.K., Eds., ACS Symposium Series No. 435, p.174 1990.

[7] ZASCHKE B., FRANK W., FISCHER H., SCHMUTZLER K., ARNOLD M., Polym. Bull. 27, 1 (1991).

[8] AUMAN B.C., PERCEC V., Polymer 29, 938 (1988).

[9] CAROTHER W.H., Chem. Rev., 8, 353 (1931).

[10] HEDRICK R.M., and GABBERT J. D., US Patent 3, 944, 629 (1976).

[11] HEDRICK R.M., and GABBERT J. D., US Patent 3, 993,709 (1976).

[12] HEDRICK R.M., and GABBERT J. D., US Patent 4, 31, 164 (1977).

[13] SAEGUSA T., MATSUMOTO Q., and HASKIMOTO Y., Macromolecules, 3, 377 (1970).

[14] YAMASHITA Y., and CHIBA K., Polym. J., 4, 200 (1973).

[15] YAMASHITA Y., HANE T., J. Polym. Sci. Polym. Chem. Ed., 11, 425 (1973).

[16] PLESH P.M., The Chemistry of Cationic Polymerization Pergamon Press, New York, (1963).

[17] FURUKAWA J., and SAEGUSA T., Polymerization of Aldehydes and Oxides, New York, Interscience Publishers (1963)

[18] DREYFUSS M.P., and DREYFUSS P., J. Polym. Sci.,A1 2179 (1966).

[19] YAMASHITA Y., HIROTA M., NABUTOKI K., NAHAMURA Y., HIRAO A., KOZAWA K., CHIBA., MATSUI H., and HATTORI G., J. Polym. Sci., B-8, 481 (1970).

[20] BERGER G., LEVY M., VOFSI D., Polym. Lett., 4, 183 (1966).

[21] DREYFUSS M.P., and DREYFUSS P., Polymer, 6, 93 (1965).

[22] RICHARDS D.H., Br. Polym. J., 12, 89 (1980).

[23] RICHARDS D.H., Dev. Polym. J., 1, 1 (1979).

[24] SCHUE F., Encyclopedia of Polymer Science and Engineering, J. Wiley Sons, New York, Vol 11, p.359 (1965).

[25] STEWART M.T., New Methods of Polymer Synthesis, Ed., Ebdon J.R., Blackie Sons, New York, p.107 (1991).

[26] YAGCI Y., and MISHRA M.K., Macroinitiators in Multi-Mode Polymerization

[27] REN Q., ZHANG H., ZHANG X., HUANG B., J. Polym. Sci., Polym. Chem. 31 (4), 847 (1993).

[28] YAGCI Y., Polym. Commun., 27, 25 (1985).

[29] YAGCI Y., ONEN A., SERHATLI I.E., HIZAL G.,Makromol. Chem. Macromol Symp., in press

[30] HIZAL G., and YAGCI Y., Polymer 30, 722 (1989).

[31] AKAR A., AYDOGAN C., TALINLI N., YAGCI Y., Polym. Bull., 15, 293 (1986).

[32] NICORA C., BORSINI G., and RATTI L., J. Polym. Sci., Polym. Lett. Ed., 4, 151 (1966).

[33] TANAKA M., MORI A., IMANISHI Y., and BAMFORD C.H., Int. J. Biol. Macromol., 7, 173 (1985).

[34] BURGESS F.J., CUNLIFFE A.V., MACCALLUM J.K., and RICHARDS D.H., Polymer, 18, 7 (1977).

[35] BURGESS F.J., CUNLIFFE A.V., MACCALLUM J.K., and RICHARDS D.H., Polymer, 18, 726 (1977).

[36] BURGESS F.J., CUNLIFFE A.V., DAWKINS J.V., and RICHARDS D.H., Polymer, 18, 733 (1977).

[37] ABADIE M.J.M., SCHUE F., SOUEL T., and RICHARDS D.H., Polymer, 23, 445 (1982).

[38] COHEN P., ABADIE M.J.M., SCHUE F., and RICHARDS D.H., Polymer, 23, 1105 (1982).

[39] PENCZEK S., KUBISA P., MATYSASEWSKI K., and SZYMANSKI K., Cationic Polymerization and Related Process, Ed., Goethals, Academic Press, New York, p.140, (1984).

[40] BREZEZINSKA K., SZYMANSKI K., KUBISA P., and PENCZEK S., Makromol. Chem. Rapid Commun., 7, 1 (1986).

[41] PENCZEK S., KUBISA S., and SZYMANSKI R., Makromol. Chem., Macromol. Symp., 3, 203 (1986).

[42] KUBISA S., Makromol. Chem., Macromol. Symp., 13/14, 203 (1988).

[43] YAGCI Y., SERHATLI I.E., KUBISA S., and BIEDRON T., Macromolecules, 26, 2397 (1993).

[44] PRESTON J., Angew. Makromol. Chem., 109/110, 1 (1982).

[45] JACKSON W.J., Br. Polym. J.,12, 154 (1980).

[46] OBER C.K., JIN J.I., LENZ W.R., Adv. Polym. Sci. 59, 103 (1986).

[46] OBER C.K., JIN J.I., LENZ W.R., Adv. Polym. Sci. 59, 103 (1986).

[47] CHUNG T.S., Polym. Eng. Sci., 26, 901 (1986).

[48] COX M., Liquid Crystal Polymers., Rapra Report, No.4, Pergomon Press, Oxford (1987).

[49] VARSHNEY S.K., Rev. Makromol. Chem. Phys., C-26, 551 (1986).

[50] KOIDE N., Mol. Cryst. Liq. Cryst. 139, 47 (1986).

[51] DU PONT US Patent 4, 93, 595 (1976).

[52] GRIFFIN A,C., BRITT T.R., HUNG R.S.L., and STEELE M.L., Mol. Cryst. Liq. Cryst., 105, 305 (1984).

[53] MILLAND B., THIERRY A., and SKONLIOS A., Mol. Cryst. Liq. Cryst. Lett., 41, 263 (1978).

[54] EASTMAN Kodak Co. KUHFUSS H.F., and JACKSON W. J., J. Appl. Polym. Sci., 25, 1685 (1980).

[55] SEK D., WOLINSKA A., and JANESZEK H., J. Polym. Mater., 3, 225 (1986).

[56] KHAN A.H., MELNTYRE J.E., MILBURN A.H., Polymer, 24, 1610 (1983).

[57] GALLI G., LAUS M., ANGELONI A.S., FERRUTTI P., CHIELLINI E., Makromol. Chem. Rapid Commun., 4, 681 (1983).

[58] JEDLINSKI Z., FRANEK J., KUZIW P., Makromol. Chem. 187, 2317 (1986).

[59] ANGELONI A.S., LAUS M., BURGIN E., GALLI G., and CHIELLINI E., Polym. Bull., 13, 131 (1984).

[60] LAUS M., ANGELONI A.S., FERRUTTI P., GALLI G., CHIELLINI E., J. Polym. Sci. Polym. Lett., 22,587 (1982).

[61] GRIFFIN A.C., BRITT T.K., CAMPELL G.A., Mol. Cryst. Liq. Cryst. Lett., 82, 145 (1982).

[62] AKARONI S.M., Macromolecules, 14, 222 (1981).

[63] NOEL C., Recent Advances in Liquid Crystalline Polymers, L.L. Chapoy Ed., Elsevier Applied Science Publishers p.135 (1985).

[64] NOEL C., Polymeric Liquid Crystals, A. Blumstein Ed., Plenum Press, New York p.21 (1985).

[65] NOEL C., Makromol Chem. Macromol. Symp., 22, 95 (1988).

[66] FNKELMANN H., REHAGE G., Adv. Polym. Sci., 60/61, 99 (1984).

[67] SHIBAEV V., and PLATE N.A., Adv. Polym. Sci., 60/61, 173 (1984).

[68] VARSHNEY S.K., Rev. Macromol. Chem. Phys.,C26, 551 (1986).

[69] KOIDE N., Mol. Cryst. Liq. Cryst., 139, 47 (1986).

[70] CSER F., HORVATH J., NYITRAI K., and HARDY G., Israel J. Chem., 24, 252 (1985).

[71] FINKELMANN H., Polymer Liquid (A. Ciferi, W.R. Krigbaum and R.B. Meyer Eds.,Academic Press, New York p.35 (1982).

[72] SHIBAEV V.P., PLATE N., Pure Appl. Chem., 57, 1589 (1985).

[73] COLES H.J., Developments in Crystalline Polymers D.C. Bassett Ed., vol 2, p.297, Elsevier Applied Science (1988).

[74] DECOBERT G., DUBOIS J.C., ESSELIN S., and NOEL C., Liq. Cryst., 1, 307 (1986).

[75] LACOUDRE N., Le BORGNE A., SPASSKY N., VARION J.P., Le BARNY P., DUBAS J.C.,ESSELIN S., FRIEDRICH C., NOEL C., Mol. Cryst. Liq. Cryst. 155, 113 (1988).

[76] NOEL C., FRIEDRICH C., LEONARD V., Le RARNY P., RAVAUX G., and DUBOIS J.C., Makromol. Chem. Macromol. Symp., 24, 283 (1989).

[77] SPASSKY N., LACAUDRE N., Le BORGNE A., VARION J.P., JUN C.L., FRIEDRICH C., and NOEL C., Makromol Chem. Macromol. Symp., 24, 271 (1989).

[78] FROSINI A., LEVITA G., LUPINACCI D., MAGAGNINI P.L., Mol. Cryst. Liq. Cryst., 66, 21 (1981).

[79] HAHN B., WENDORFF J.H., PORTUGALL M., RINGSDORF H., Cool. Polym. Sci., 259, 875 (1981).

[80] KREUDER W., WEBSTER O. W., RINGSDORF H., Macromol Chem. Rapid Commun., 7, 5 (1986).

[81] PUGH C., PERCEC V., ACS Polym. Prepr., 26(2), 303 (1985).

[82] RODRIGUEZ J.P., and PERCEC V., J. Polym. Sci. Polym. Chem. Ed., 24, 1363 (1986).

[83] RODRIGUEZ J.P., and PERCEC V., J. Polym. Sci. Polym. Chem. Ed., 25, 2269 (1987).

[84] CSER F., NYITRAI K., HORVATH J.,and HARDY G., Eur. Polym. J., 21, 259 (1985).

[85] RECK B., and RINGSDORF H., Makromol. Chem. Rapid Commun., 6, 291 (1985).

[86] BERG B., KRONE V., and RINGSDORF H., Makromol. Chem. Rapid Commun., 7, 381 (1986).

[87] FINKELMANN H., and REHAGE G., Makromol. Chem. Rapid Commun., 1, 31 (1980).

[88] GEMMEL P.A., GRAY G.W., LACEY D., ALIMOGLU A., and LEDWITH A., Polymer 26, 615 (1985).

[89] HEFFT M., and SPRINGER J., Makromol. Chem. 193, 329 (1992).

[90] BAMFORD C.H., JENKINS A.D., WAYNE R.P., Trans Faraday 56, 932 (1960).

[91] SIMIONESCU C.R.I. SIK K.M., COMANITA E., DIMITRU S., , Eur. Polym. J.,20, 267 (1984).

[92] FRANTA E., J.Polym. Sci. Polym. Symp. Edn., 56, 139 (1976).

[93] PENCZEK S., MATYJASZEWSKI K., J. Polym. Sci. Polym. Symp. Edn., 56, 255 (1976).

[94] BAMFORD C.H., LEDWITH A., and YAGCI Y., Polymer 19, 354 (1978).

[95] YAGCI Y., TUNCA U., and BICAK N., J. Polym. Sci. Polym. Lett.,24, 491 (1986).

[96] LAVERTY J.J., and GARDLAND Z.G., J. Polym. Sci. Polym. Chem. Edn., 15, 2001 (1977).

[97] HIZAL G., TASDEMIR H., YAGCI Y.,Polymer, 30, 722 (1989).

[98] CHIELLINI E., GALLI G., ANGELONI A.S., LAUS M., CARETTI D., Macromolecular Assemblies in Polymeric Systems, P. Stroeve and Balazs A.C., Eds. ACS Smposium Series No. 493 p.280 (1990).

[99] ANGELONI A.S., COMPAGNARI I., CARETTI D., ALTOMARE A., CHIELLINI E., GALLI G., SOLARO R., LAUS M., Gazz. Chim. Ital., 120, 171 (1990).

[100] GALLi G., CHIELLINI E., YAGCI Y., SERHATLI I.E., LAUS M., BIGNOZZI M.C. ANGELONI A.S., Makromol. Chem.Rapid Commun., 14, 185 (1993).

[101] NUYKEN O., GERUM J., STEINHAUSEN R., Makromol. Chem. 180, 1497 (1979).

[102] TUNCA U., YAGCI Y., Polym. Chem.Edn.,29, 1721 (1990).

BIOGRAPHY

I.Ersin SERHATLI was born in Istanbul in 1964. He was graduated from Kazim Ismen Lisesi in 1981. He admitted Istanbul Technical University, Chemistry-Metallurgical Faculty and was graduated as a Chemical Engineer in 1987.

He was registered as a M.Sc. student to the Institute of Science and Technology of the same university and obtained MSc. degree in Chemistry in 1990.

He was awarded with a grant by Italian Government to carry out research in Pisa University, Chemistry Department for the period of January 1993-July 1993.

He has been working as a research assistant at Organic Division of Istanbul Technical University since 1983. He is the co-author of six scientific papers published in international journals.