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LIST of ABBREVIATIONS

THF	: Tetrahydrofuran
DMF	: N, N – Dimethyl Formamide
DMSO	: Dimethyl sulfoxide
DPE	: Diphenyl ether
ATRP	: Atom Transfer Radical Polymerization
CFRP	: Conventional Free Radical Polymerization
PIRP	: Photo-Induced Free Radical Polymerization
SFRP	: Stable Free Radical Polymerization
GPC	: Gel Permeation Chromatography
¹HNMR	: Proton Nuclear Magnetic Resonance Spectroscopy
DSC	: Differential Scanning Calorimetry
OP	: Optical Microscopy
St	: Styrene
MA	: Methyl acrylate
VAc	: Vinyl acetate
MMA	: Methyl methacrylate
LC	: Liquid Crystal
PLC	: Liquid Crystalline Polymer
MC-PLC	: Main-Chain Liquid Crystalline Polymer
SC-PLC	: Side-Chain Liquid Crystalline Polymer
LC6	: 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate
PLC6	: Poly(6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate)
PSt	: Polystyrene
AI	: 4-((E)-2-{4-[(2-bromopropanoyl)oxy]-1-cyano-1-methylbutyl}-1-diazenyl)-4-cyanopentyl 2-bromopropanoate
ACP	: 4, 4'-Azobis(4-cyano pentanol)
MBME	: α – Methylol Benzoin Methyl Ether
PI	: 2-methoxy-3-oxo-2, 3-diphenylpropyl 2-bromopropanoate
PMDETA	: N,N,N',N'',N'' pentamethyldiethylenetriamine
AIBN	: 2, 2' – azobis(2- methylpropanenitrile)
TEA	: Triethylamine
UV	: Ultra violet

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LIST of SYMBOLS

Φ_i	: Quantum Yield
f	: Initiator Efficiency
λ	: Wavelength
$h\nu$: Radiation
DP	: Degree of Polymerization
ΔH	: Enthalpy
M_n	: The Number Average Molecular Weight
M_w	: The Weight Average Molecular Weight
M_w/M_n	: The Molecular Weight Distribution
T_{N-I}	: The Transition Temperature from Nematic to Isotropic
T_g	: The Glass Transition Temperature
k_a, k_d	: Rate constants of activation and deactivation steps of the initiation in radical polymerization

NEW SYNTHETIC APPROACH FOR THE LIQUID CRYSTALLINE – AMORPHOUS BLOCK COPOLYMERS

SUMMARY

All the studies in this thesis can be grouped in two different procedures: In the first part, block copolymers of 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate (LC6) and styrene (St) were synthesized by combination of conventional free radical polymerization (CFRP) and atom transfer radical polymerization (ATRP). A difunctional azo-alkyl halide AI was synthesized and used as an initiator.

AI was prepared by esterification of 4, 4'-Azobis(4-cyano pentanol) (ACP) with 2-Bromopropionyl bromide and then polymerized in the presence of LC6 or St monomer by the thermal decomposition of the azo moiety at 80 or 110 °C. Consequently, PLC6 or PSt homopolymers possessing two reactive bromine end groups in the main chain was obtained. These macroinitiators PLC6 or PSt having bromine end groups was then isolated and subsequently used to initiate ATRP of the second monomer in the presence of CuBr/PMDETA catalytic system in order to synthesize the liquid crystalline-amorphous block copolymers.

In the second part of the thesis, benzoin alkyl halide photo initiator (PI) was synthesized by esterification of α - Methylol Benzoin Methyl Ether (MBME) with 2-Bromopropionyl bromide and subsequently polymerized in the presence of St or LC6 and a catalytic system of CuBr/PMDETA by ATRP at 110 °C. PSt or PLC6 homopolymers having photo-reactive benzoin moiety was obtained. These macroinitiators PSt or PLC6 possessing photo-reactive groups were then isolated and subsequently used to initiate PIRP of the second monomer under suitable wavelengths. Finally, the liquid crystalline-amorphous block copolymers were obtained.

SIVI KRİSTAL – AMORF BLOK KOPOLİMERLER İÇİN YENİ SENTETİK YAKLAŞIMLAR

ÖZET

Bu tezde yapılan çalışmaların tümü iki prosedüre ayrılabilir: Birinci kısımda, 6-(4-Siyanobifenil-4'-oksi)hekzil akrilat (LC6) ve stiren (St) monomerlerinin blok kopolimerleri, serbest radikal polimerizasyonu (CFRP) ve atom transfer radikal polimerizasyonunun (ATRP) kombinasyonu sonucu sentezlenmiştir. İki fonksiyonlu azo-alkil halojenür olan AI, sentezlenmiş ve başlatıcı olarak kullanılmıştır.

AI 4, 4'-Azobis(4-siyano pentanol) (ACP) ile 2-Bromo propionil bromürün esterleşme reaksiyonundan hazırlandı ve sonra termal azo parçalanması yoluyla 80 veya 110 °C'de LC6 veya St monomerleri varlığında polimerizasyon gerçekleştirildi. Sonuç olarak, ana zincirlerinin her iki ucunda reaktif brom bulunan PLC6 veya PSt homopolimerleri elde edildi. Her iki ucunda brom bulunan PLC6 veya PSt, ortamdan ayrıldıktan sonra, blok kopolimer sentezi için CuBr/PMDETA katalizatör sistemi varlığında ikinci monomerin ATRP'sinde makrobaşlatıcı olarak kullanıldı.

Tezin ikinci bölümünde ise, bir benzoin alkil halojenür foto başlatıcı (PI), α – Metilol Benzoin Metil Eter (MBME) ile 2-Bromo propionil bromürün esterleşme reaksiyonu sonucu sentezlenerek St veya LC6 ve CuBr/PMDETA katalizatör sistemi varlığında 110 °C'de ATRP gerçekleştirildi. Foto-aktif benzoin grubu içeren PSt veya PLC6 homopolimerleri elde edildi. Foto-aktif grup içeren PSt veya PLC6, ortamdan ayrıldıktan sonra, uygun dalgaboyu altında ikinci monomerin fotopolimerizasyonunda makrobaşlatıcı olarak kullanıldı. Sonuç olarak, sıvı kristal-amorf blok kopolimerler elde edildi.

1. INTRODUCTION

Block copolymers often have so many useful and unique properties, either in the solid state or in solution, because of the thermodynamic incompatibility of the constituent blocks. The superiority of the block copolymers in advanced materials technology attracts attention academically and industrially. Therefore, the synthesis of block copolymer is also popular area that has being developed continuously. There are so many routes to synthesize block copolymers, including living polymerizations (e.g. ionic, controlled / “living” radical) and end – group transformations.

The transformation polymerization which allows to combine various polymerization mechanisms is one of the major methods to obtain well defined block copolymers. The studies of block copolymer synthesis certainly show variety by utilizing transformation routes. The variety of monomers are also achieved.

Free radical polymerization has distinct advantages over other polymerization methods, such as tolerance to trace impurities and less stringent conditions, and is also be able to polymerize a wide range of monomers. On the other hand, the presences of irreversible termination and transfer reactions which lead to the poor control of macromolecular structures including degrees of polymerization, polydispersities, end functionalities, chain architectures and compositions are significant.

Controlled radical polymerization such as atom transfer radical polymerization (ATRP), radical addition fragmentation (RAFT), stable radical mediated radical polymerization (SFRP) provides the preparation of many novel polymeric materials that could not be previously achieved via conventional radical polymerization. These materials termed well – defined polymers have low polydispersities, also controlled end functionalities and compositions.

Block copolymers with liquid crystalline blocks could give rise to micro – separated phases. Liquid crystalline (LC) block copolymers have been given much attention lately because of their potential use as polymeric materials for advanced technology, especially in engineering and processing. It is desirable to combine the properties of liquid crystalline and isotropic (I) polymers by forming an LC/I block copolymer. This kind of a system is expected to show a microphase – separated structure with coexisting isotropic and anisotropic phases. However, the microphase separation in LC/I block copolymers is important, it is also necessary to synthesize polymeric materials with well-defined structure and narrow molecular weight distribution.

This study can be grouped in two different classes: using a difunctional (azo-alkyl halide) initiator and another difunctional (benzoin-alkyl halide) initiator. In the first class, using a difunctional initiator containing a decomposable thermolabile azo and an ATRP initiator functionality and in the second class, a photolabile benzoin and an ATRP functionality, liquid crystalline-amorphous block copolymers were synthesized by applying combination of conventional free radical polymerization (CFRP)-ATRP or photo-induced free radical polymerization (PIRP)-ATRP.

2. THEORETICAL PART

2.1 Free Radical Polymerization

2.1.1 Conventional Free Radical Polymerization

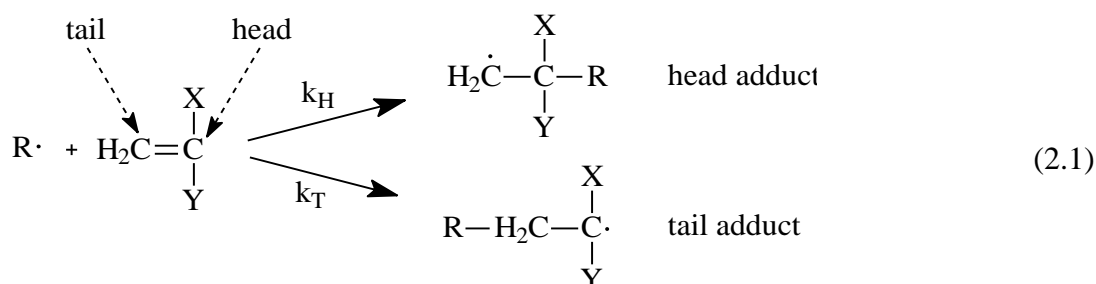
One of the most common and useful reaction for making polymers is free radical polymerization. It is used to make polymers from vinyl monomers, that is, from small molecules containing carbon-carbon double bonds.

The basic mechanism of free radical polymerization as we know it today, was laid out in the 1940s and 50s. The essential features of this mechanism are initiation and propagation steps, which involve radicals adding to the less substituted end of the double bond (“tail addition”), and a termination step, which involves disproportionation or combination between two growing chains [1].

2.1.1.1 Free Radical Reactions

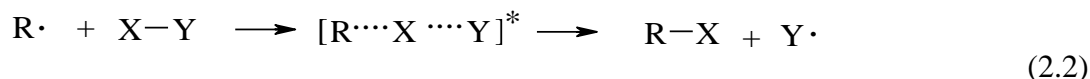
a) Addition to Carbon – Carbon Double Bonds:

With few exceptions, radicals are observed to add preferentially to the less highly substituted end of unsymmetrically substituted olefins (i.e. give predominantly tail addition – see (2.1)) [1].



b) Hydrogen Atom Transfer:

Atom or radical transfer reactions generally proceed by what is known as a S_H2 mechanism (substitution, homolytic, bimolecular) which can be depicted schematically as follows [1]:



The relative propensity of radicals to abstract hydrogen or add to double bonds is extremely important. In radical polymerization, this factor determines the significance of transfer to monomer, solvent, e.t.c. and hence the molecular weight and end group functionality. It also provides one basis for initiator selection.

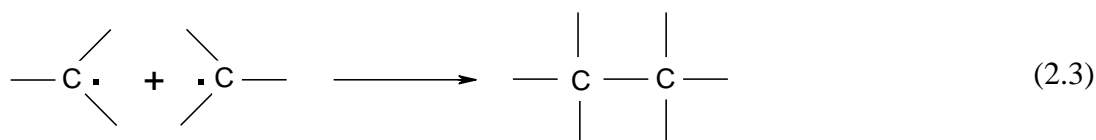
The hydrogen abstraction:addition ratio is generally greater in reactions of heteroatom – centered radicals than it is with carbon – centered radicals. One factor is the relative strengths of the bonds being formed and broken in two reactions. The difference in exothermicity (Δ) between abstraction and addition reaction is much greater for heteroatom – centered radicals than it is for carbon – centered radicals.

A number of studies have found that increasing nucleophilicity of the attacking radical favors abstraction over addition to an unsaturated system (benzene ring or double bond) [2,3].

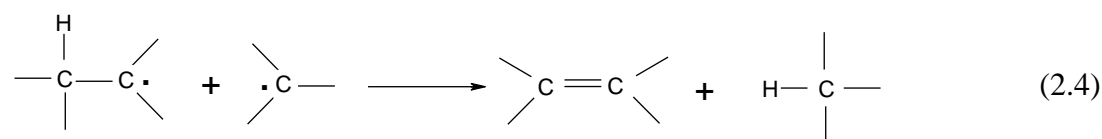
c) Radical – Radical Reactions:

Radical – radical reactions are, in general, very exothermic and activation barriers are extremely small even for highly resonance stabilized radicals. As a consequence, reaction rate constants often approach the diffusion controlled limit (typically $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The reaction may take several pathways [1]:

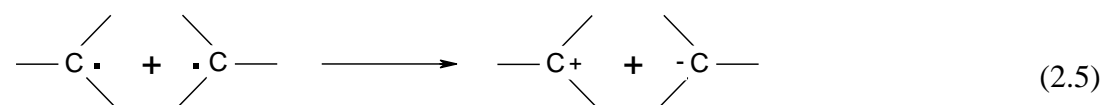
I. Combination, which usually but not invariably, takes place by a simple head to head coupling of radicals.



II. Disproportionation, which involves the transfer of a β – hydrogen from one radical of the pair to the other.



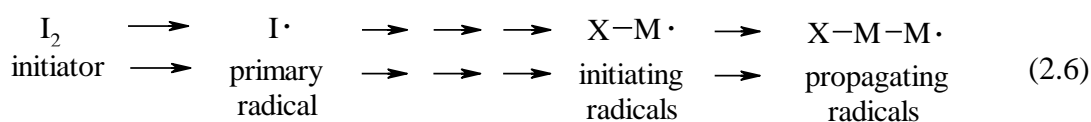
III. Electron transfer, in which the product is an ion pair.



The latter pathway is rare for reactions involving only carbon – centered radicals.

2.1.1.2 Initiation

Initiation is defined as the series of reactions commencing with generation of primary radicals and culminating in addition to the carbon – carbon double bond of the monomer so as to form initiating radicals (2.6) [1,4].



The yield of primary radicals produced on thermolysis or photolysis of the initiator is usually not 100%. The conversion of primary radicals to initiating radicals is dependent on many factors and typically is not quantitative. The primary radicals may undergo rearrangement or fragmentation to afford new radical species (secondary radicals) or they may interact with solvent or other species rather than monomer.

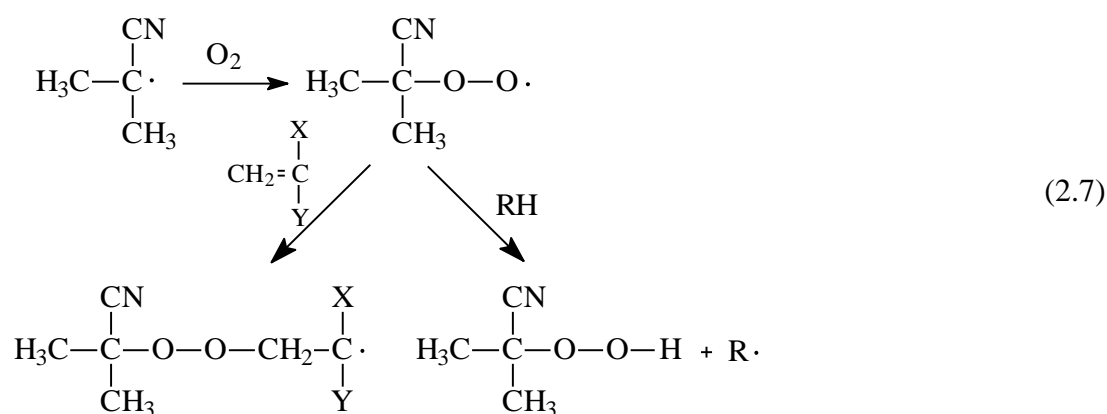
The reactions of the radicals (whether primary, secondary, solvent derived, etc.) with monomer may not be entirely regio- or chemo – selective. Reactions, such as head addition, abstraction or aromatic substitution, often compete with tail addition [1].

It should be possible to choose an initiator according to its suitability for use with a given monomer or monomer system so as to avoid the formation of undesirable end group or, alternatively, to achieve a desired functionality.

A typical polymerization system comprises many components besides the initiators and the monomers. There will be solvents, additives (e.g. transfer agents, inhibitors) as well as a variety of adventitious impurities which may also be reactive towards the initiator –derived radicals [1].

a) Reaction with Oxygen:

Radicals, in particular carbon – centered radicals, react with oxygen [5]. Thus, for polymerizations carried out either in air or in incompletely degassed media, oxygen is likely to become involved in, and further complicate, the initiation process [1,5].



b) Initiator Efficiency:

The proportion of radicals which escape the solvent cage to form initiating radicals is termed the *initiator efficiency* (f) which is formally defined as follows [1]:

$$f = \frac{\text{[Rate of initiation of propagating chains]}}{n \cdot \text{[Rate of initiator disappearance]}} \quad (\text{Eq:2.1})$$

where n is the number of moles of radicals generated per mole of initiator. The effective rate of initiation (R_i) in the case of thermal decomposition of an initiator ($\text{I}_2 \rightarrow 2\text{I}\cdot$) is then:

$$R_i = 2 k_d f [I_2] \quad (\text{Eq:2.2})$$

Reactions which lead to loss of initiator or initiator – derived radicals include the cage reaction of the initiator – derived radicals, primary radical termination, transfer to initiator and various side reactions. It is important to note that the initiator efficiency is typically not a constant. The importance of the above – mentioned process increases as monomer is depleted and the viscosity of the polymerization medium increases [1].

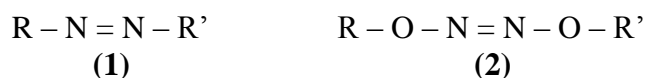
c) Initiators:

More commonly, the initiators are azo-compounds, peroxides or benzoin derivatives that are decomposed to radicals through the application of heat, light or a redox process.

In general, initiators which afford carbon – centered radicals (e.g. dialkyl diazenes, aliphatic diacyl peroxides) have lower efficiencies for initiation of polymerization than those which produce oxygen – centered radicals. Exact values of efficiency depend on the particular initiators, monomers and reaction conditions [1].

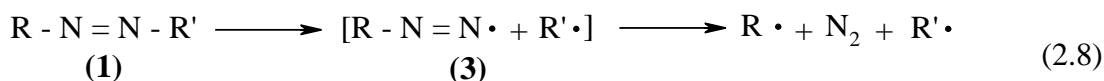
I. Azo – compounds

Two general classes of azo – compounds will be considered in this section, the dialkyldiazenes (1) and the dialkyl hyponitrites (2).



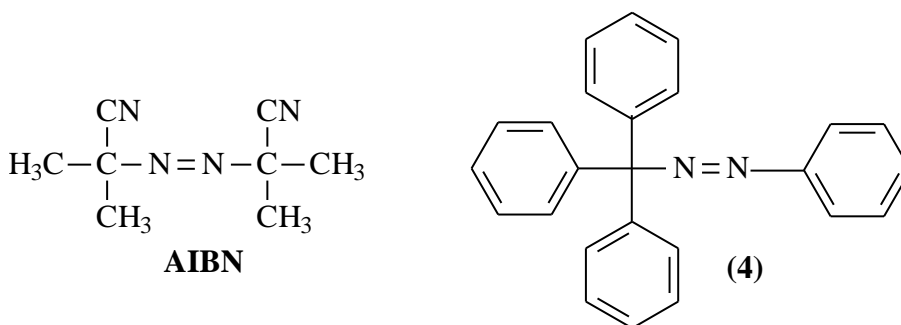
• Dialkyldiazenes

Dialkyldiazenes (1, R = alkyl) are sources of alkyl radicals. While there is clear evidence for the transient existence of diazenyl radicals (3; see (2.8)) during the decomposition of certain unsymmetrical diazenes [6] and of cis – diazenes [7], all isolable products formed in thermolysis or photolysis of dialkyldiazenes (1) are attributable to the reactions of alkyl radicals [1].



In the composition of symmetrical azo compounds the intermediacy of diazenyl radicals remains a subject of controversy. However, it is clear that diazenyl radicals, if they are intermediates, do not have sufficient lifetime to be trapped or to initiate polymerization [6].

2, 2' – azobis(2- methylpropanenitrile) [better known as azobis(isobutyronitrile) or AIBN] is the most known symmetrical dialkyldiazene. Also, triphenylmethyl azobenzene (4) is one of the unsymmetrical dialkyldizenes [1].



Thermal decomposition

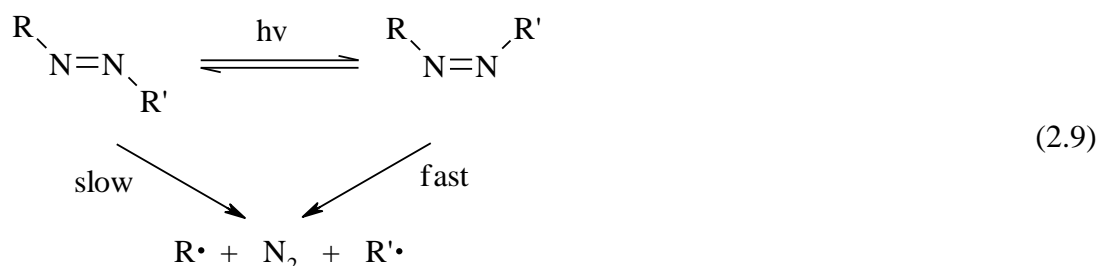
Thermolysis rates (k_d) of dialkyldiazenes (1) show a marked dependence on the nature of R (and R'), steric factors and solvents. The values of k_d increase in the series where R (= R') is aryl, primary, secondary, tertiary, allyl. In general, k_d is dramatically accelerated by α – substituents capable of delocalizing the free spin of the incipient radical [6].

Photochemical decomposition

The trans – dialkyldiazenes have $\lambda_{\text{max}} = 350 - 370 \text{ nm}$ and $\varepsilon = 2 - 50 \text{ M}^{-1} \text{ cm}^{-1}$ and are photolabile. They are, therefore, potential photoinitiators [6,8]. The efficiency and rate of radical generation depends markedly on structure [6].

Alicyclic cis – dialkyldiazenes are very thermolabile when compared to the corresponding trans – isomers, often having only transient existence under typical reaction conditions. It has been proposed that the main light – induced reaction of the

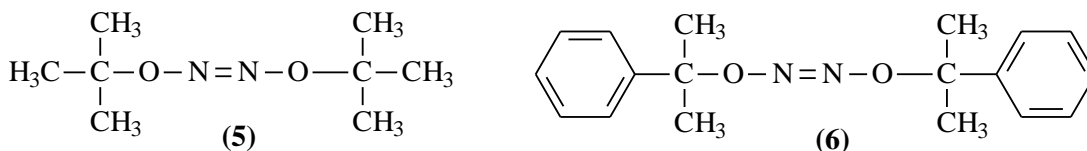
dialkyldiazenes is trans – cis isomerization. Dissociation to radicals and nitrogen is then a thermal reaction of the cis – isomer (2.9) [1,6].



An important ramification of the photolability of azo – compounds is that, when using dialkyldiazenes as thermal initiators, care must be taken to ensure that the polymerization mixture is not exposed to excessive light during its preparation [1].

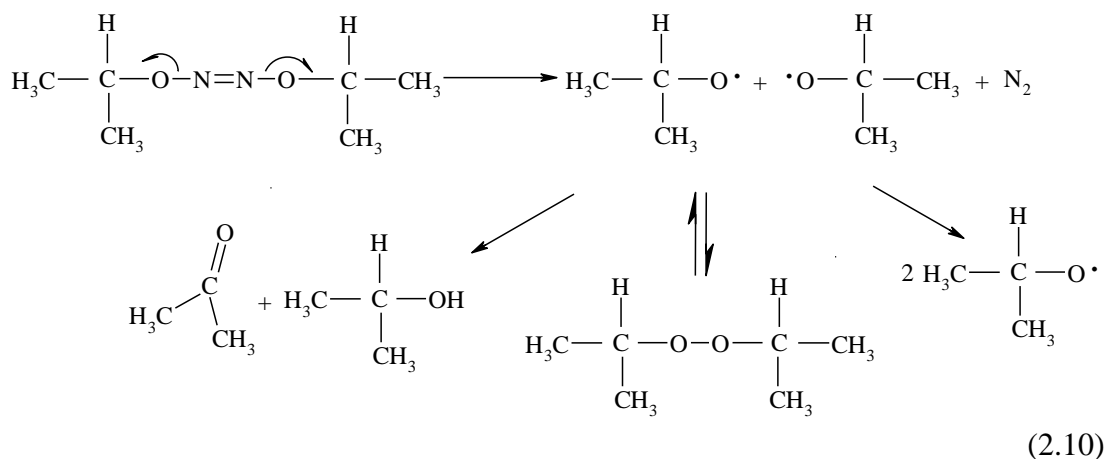
- **Hyponitrites**

The hyponitrites, derivatives of hyponitrous acid ($\text{HO} - \text{N} = \text{N} - \text{OH}$), are low temperature sources of alkoxy or acyloxy radicals.



While di – t – butyl (5) and dicumyl hyponitrites (6) have proved convenient sources of t – butoxy and cumyloxy radicals respectively in the laboratory [9,10]. Their photochemistry is largely a neglected area.

A proportion of radicals is lost through cage reaction with formation of the corresponding dialkyl peroxides or ketone plus alcohol (2.10) [11]. The disproportionation pathway is open only to hyponitrites with α – hydrogens.



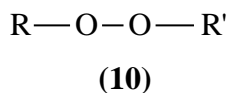
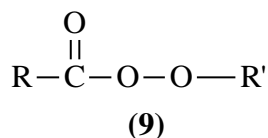
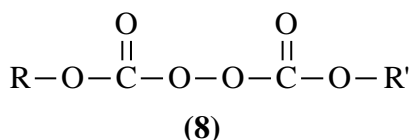
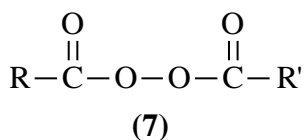
Also, bifunctional azo compounds are commonly used in polymerization reactions (Table 2.1).

Table 2.1. Bifunctional Azo Compounds Used Frequently in Polycondensation and Addition Reactions

Formula	Abbreviation	Ref. Synthesis
$\left(\begin{array}{c} \text{O} \qquad \qquad \text{CH}_3 \\ \qquad \qquad \\ \text{HO}-\text{C}-(\text{CH}_2)_2-\text{C}-\text{N}=\text{N} \\ \qquad \qquad \\ \text{CN} \end{array} \right)_2$	ACPA	[12]
$\left(\begin{array}{c} \text{O} \qquad \qquad \text{CH}_3 \\ \qquad \qquad \\ \text{Cl}-\text{C}-(\text{CH}_2)_2-\text{C}-\text{N}=\text{N} \\ \qquad \qquad \\ \text{CN} \end{array} \right)_2$	ACPC	[13,14]
$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{HO}-(\text{CH}_2)_3-\text{C}-\text{N}=\text{N} \\ \\ \text{CN} \end{array} \right)_2$	ACPO	[15]

II. Peroxides

Many types of peroxides (R – O – O – R) are known. Those in common use as initiators include: diacyl peroxides (**7**), peroxydicarbonates (**8**), peresters (**9**), dialkyl peroxides (**10**), hydroperoxides, and inorganic peroxides (e.g. persulfate) [1,16].



- **Diacyl peroxides**

They are sources of acyloxy radicals which in turn are sources of aryl or alkyl radicals.

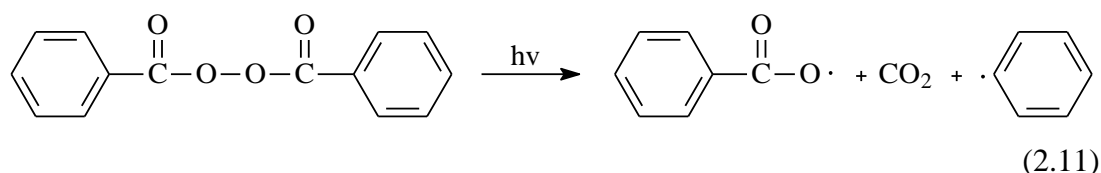
Thermal decomposition

The rates of thermal decomposition of diacyl peroxides (7) are dependent on the substituents R. The rates of decomposition increase in the series where R is: aryl ~ primary ~ alkyl < secondary alkyl < tertiary alkyl. This order has been variously proposed to reflect the stability of the radical (R•) formed on β – scission of the acyloxy radical, the nucleophilicity of R, or the steric bulk of R [1].

Observed rates of disappearance for diacyl peroxides show marked dependence on solvent and concentration [17].

Photochemical decomposition

Diacyl peroxides have continuous weak absorptions in the UV to ca. 280 nm [18]. Although the overall chemistry in thermolysis and photolysis may appear similar, substantially higher yields of phenyl radical products are obtained when dibenzoin peroxide (BPO) is decomposed photochemically. It has been suggested that, during the photodecomposition of BPO, β – scission may occur in concert with O – O bonds rupture and give rise to formation of one benzoyloxy radical, one phenyl radical, and a molecule of carbon dioxide (2.11) [19]. Time resolved EPR experiments have shown that photochemical decomposition of BPO does produce benzoyloxy radicals with discrete existence. It is, nonetheless, clear that the photochemically generated benzoyloxy radicals have substantially shorter life times in solution than those generated thermally [20].



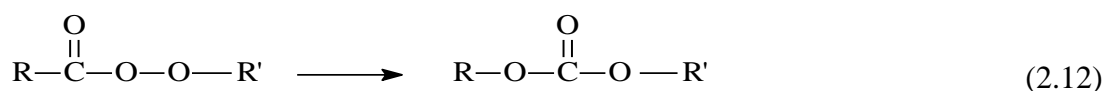
- **Peresters**

The peresters are sources of alkoxy and acyloxy radicals. Most commonly encountered peresters are derivatives of t – alkyl hydroperoxides (e.g. cumyl, t – butyl, t – amyl). Aryl peresters are generally unsuitable as initiators of polymerization owing to the generation of phenoxy radicals which can inhibit or retard polymerization [1,21].

Thermal decomposition

The rates of decomposition of peresters (**9**) are very dependent on the nature of the substituents R and R'. The variation in the decomposition rate with R follows the same trends as have been discussed for the corresponding diacyl peroxides (see thermal decomposition of the diacyl peroxides).

Peresters may undergo non-radical decomposition via the Criegee rearrangement [1].



Photochemical decompositions

Peresters seldom find use as photoinitiators since photodecomposition requires light of 250 – 300 nm, a region where many monomers also absorb. This situation may be improved by the introduction of a suitable chromophore into the molecule or through the use of sensitizers [22].

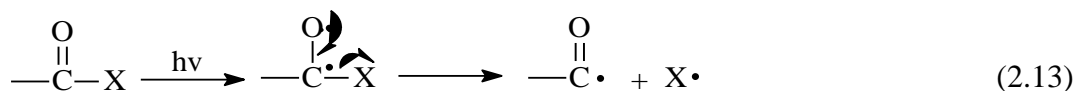
III. Photochemical Initiators

Photoinitiation is most commonly used in curing or crosslinking processes and in initiating graft copolymerizations.

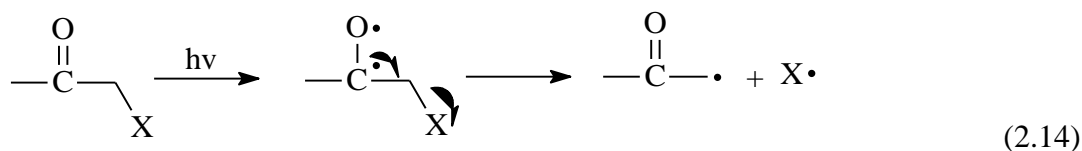
- **Aromatic Carbonyl Compounds**

Primary radicals are generated by one of the following processes [1,23,24]:

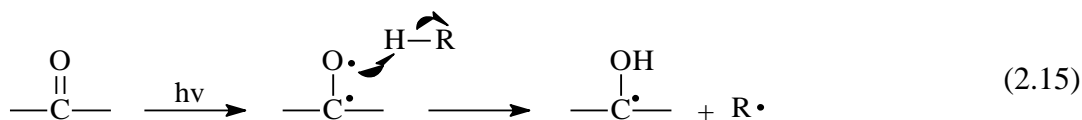
- a) A unimolecular fragmentation involving, most commonly, either α – scission (e.g. benzoin ethers, acyl phosphine oxides)



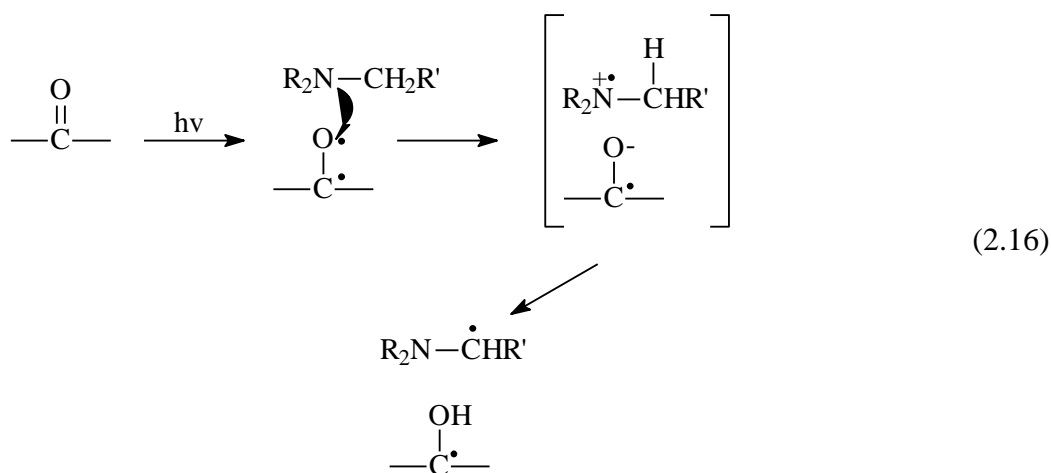
or β – scission (e.g. α – haloketones).



- b) A bimolecular process involving direct abstraction of hydrogen from a suitable donor (e.g. with hydrocarbons, ethers, alcohols),

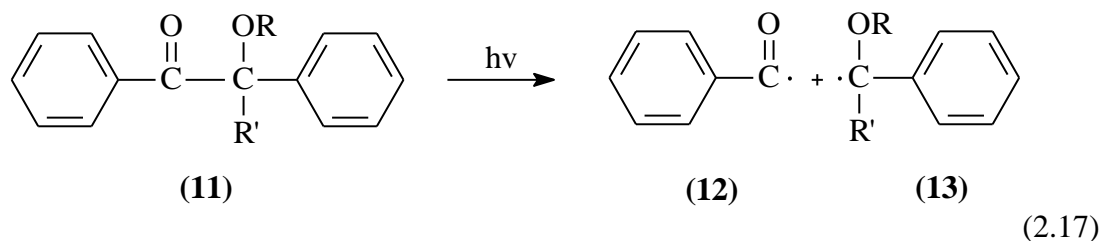


or sequential electron and proton transfer (e.g. with amines, thiols).



Benzoin derivatives

Benzoin and a variety of derivatives (**11**) have been extensively studied both as initiators of polymerization and in terms of their general photochemistry [25]. The mechanism of radical generation is usually depicted as excitation to the $S_1(n, \pi^*)$ state followed by intersystem crossing to the $T_1(n, \pi^*)$ state and fragmentation; usually by α – scission (2.17) [1].

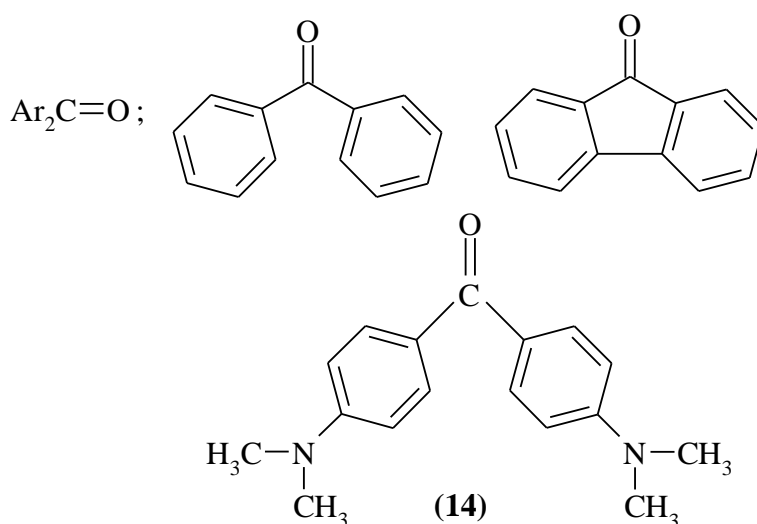
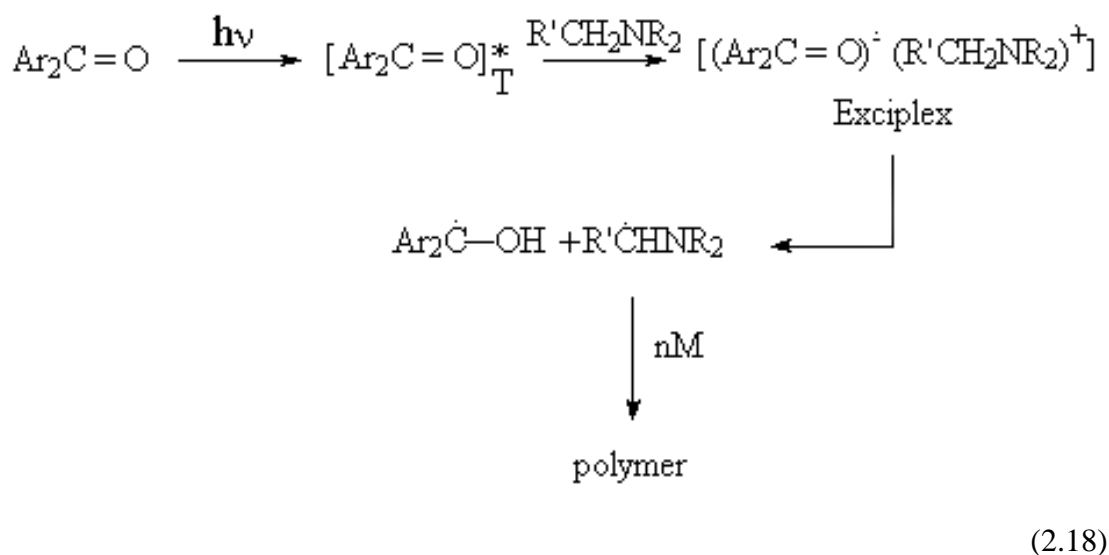


Those benzoin derivatives most used as initiators are the benzoin ethers (**11**, R = alkyl; R' = H) and the α – alkyl benzoin derivatives (**11**, R = H, alkyl; R' = alkyl). The α – scission process is extremely facile and is not quenched by oxygen or conventional triplet quenchers [26]. This means that the initiators can be used for UV – curing in air. The products of α – scission of benzoin derivatives (see (2.17)) are a benzoyl radical (**12**) and an α – substituted benzyl radical (**13**) both of which may, in principle, initiate polymerization [26,27].

It should be pointed out that not all benzoin derivatives (**11**) are suitable for use as photoinitiators. Benzoin esters (**11**, R = acyl) undergo a side reaction leading to furan derivatives. Benzoin derivatives with α – hydrogens (**11**, R' = H) are readily autoxidized and consequently have poor shelf lives [27].

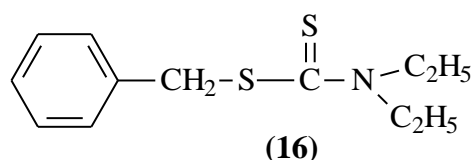
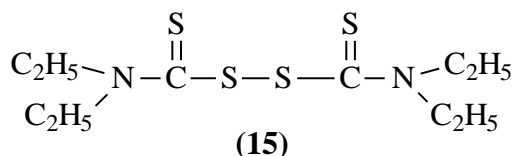
Carbonyl compound – tertiary amine system

Photoinitiators of this type include benzophenone and derivatives such as Michler's ketone (**14**), thioxanthenes, benzyl and quinones. In contrast to cleavage type photoinitiators, which are capable of generating radicals independently, this type of initiators must undergo a bimolecular reaction with hydrogen donors. Tertiary amines with abstractable hydrogen atoms are particularly effective H-donors for UV curing of acrylate monomers [28,29].



- Sulfur Compounds**

The S – S linkage of disulfides and the C – S linkage of certain sulfides can undergo photoinduced homolysis. The disulfides may also be extremely susceptible to transfer to initiator. However, these features are used to advantage when the disulfides are used as initiators in the synthesis of telehelics [30] or in living polymerizations. The most common initiators in this context are the dithiuram disulfides **(15)**, which are both thermal and photochemical initiators. The corresponding monosulfides [e.g. **(16)**] are thermally stable but can be used as photoinitiators [1].



IV. Redox Initiators

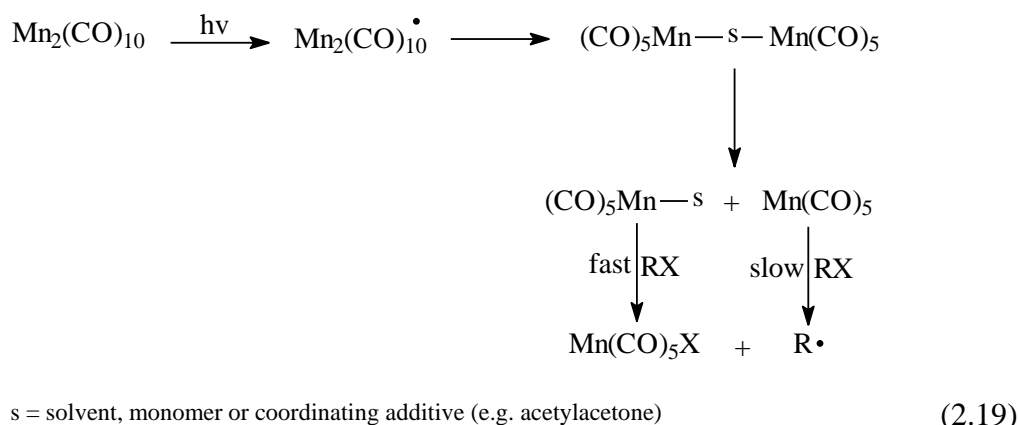
Redox initiation systems are in common use when initiation is required at or below ambient temperature and they are frequently used for initiation of emulsion polymerization.

Common components of many redox systems are a peroxide and a transition metal ion or complex. The following two sections describe redox systems based on the use of metal complexes and simple organic molecules.

- **Metal complex – organic halide systems**

One system which has seen extensive use comprises a transition metal in a low, typically zero, oxidation state (e.g. $\text{Mo}(\text{CO})_6$, $\text{Re}(\text{CO})_6$) and an organic halide. Radical production involves single electron transfer from the metal to the halogen substituent of the alkyl halide which then fragments to form a halide ion and an alkyl radical [31]. The use of polymeric halo compounds allows this chemistry to be used in the preparation of block and graft copolymers [32].

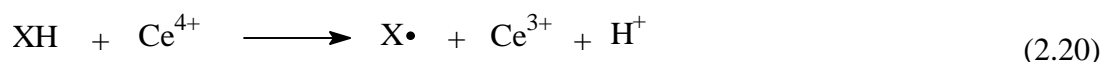
The metal complexes most commonly used in these photoredox systems are manganese and rhenium carbonyls. The proposed mechanism of the photoredox reaction involving $\text{Mn}_2(\text{CO})_{10}$ is represented schematically as follows (2.19). Quantum yields for photoinitiation are high [33].



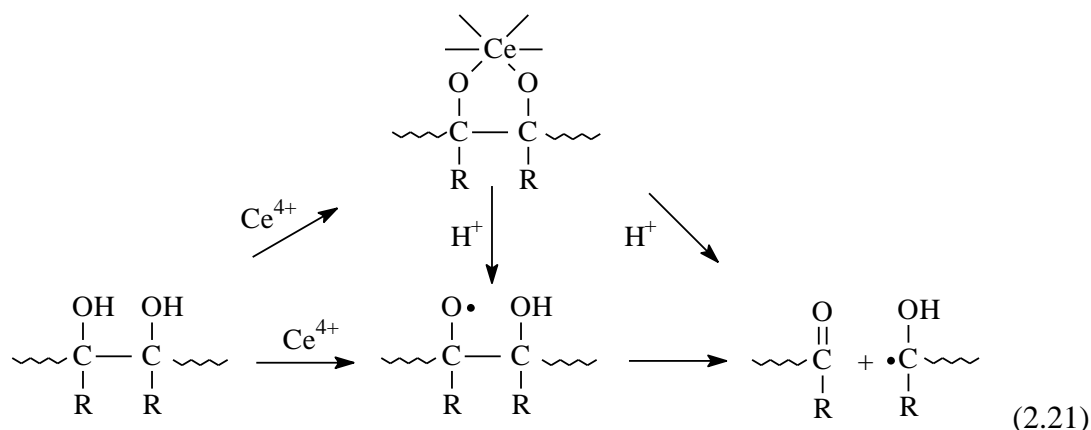
- **Ceric ion systems**

Ceric ions oxidize various organic substrates and the mechanisms typically involve free radical intermediates [34]. When conducted in the presence of a monomer these radicals may initiate polymerization.

The reaction of ceric ion with alcohols, amides and urethanes is thought to involve single electron transfer to the ceric ion and loss of a proton to give the corresponding oxygen – or nitrogen – centered radical (2.20). The reaction may involve ligation of cerium. Mechanisms for ceric ion oxidation of alcohols which yield α – hydroxyalkyl radicals as initiating species have also been proposed [1].



Ceric ions react rapidly with 1, 2 diols. There is evidence for chelation of cerium and these complexes are likely intermediates in radical generation [35]. The overall chemistry may be understood in terms of an intermediate alkoxy radical which undergoes β – scission to give a carbonyl compound and a hydroxyalkyl radical (2.21). However, it also possible that there is concerted electron transfer and bond – cleavage.

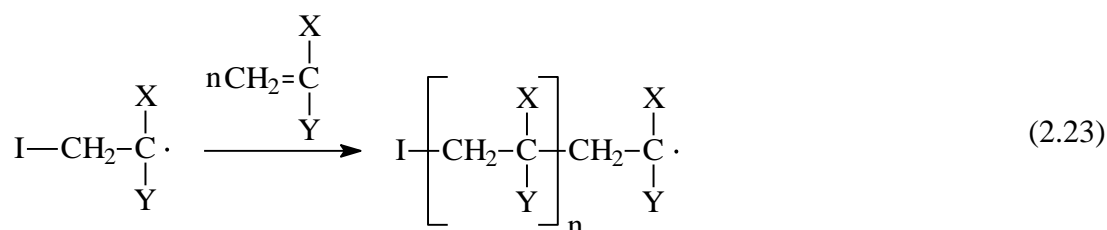


The reaction of ceric ions with polymer – bound functionalities gives polymer – bound radicals. Thus, one of the major applications of ceric ion initiation chemistry has been in grafting onto starch, cellulose [35], polyurethanes and other polymers [36]. The ceric ion also traps carbon – centered radicals (initiator – derived species, propagating chains) by single electron transfer (2.22) [1].

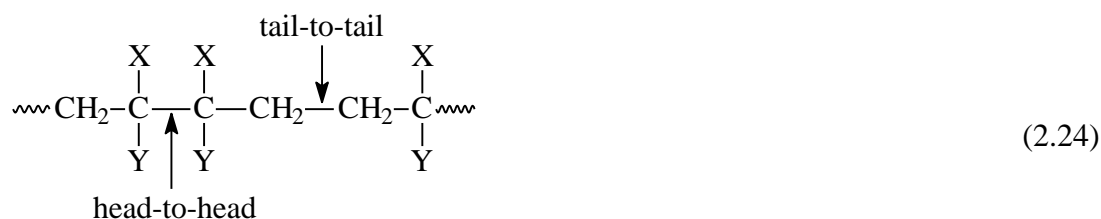


2.1.1.3 Propagation

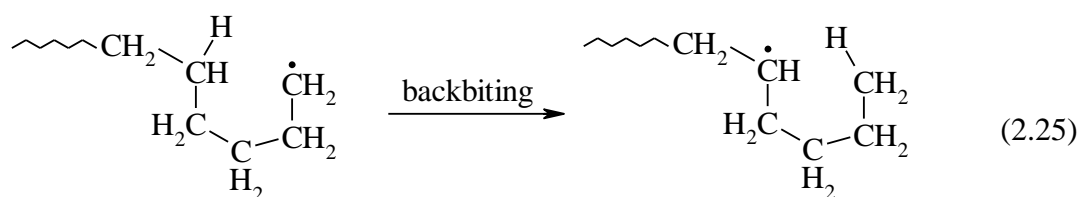
The propagation step of radical polymerization comprises a sequence of radical additions to carbon – carbon double bonds (2.23). In order to produce high molecular weight polymers, a propagating radical must show a high degree of specificity in its reactions with unsaturated system. It must give addition to the exclusion of side reactions which bring about the cessation of growth of the polymer chain. Despite this limitation, there is considerable scope for structural variation in homopolymers.



Addition to double bonds may not be completely regiospecific. The predominant head – to – tail structure may be interrupted by head – to – head and tail – to – tail linkages.



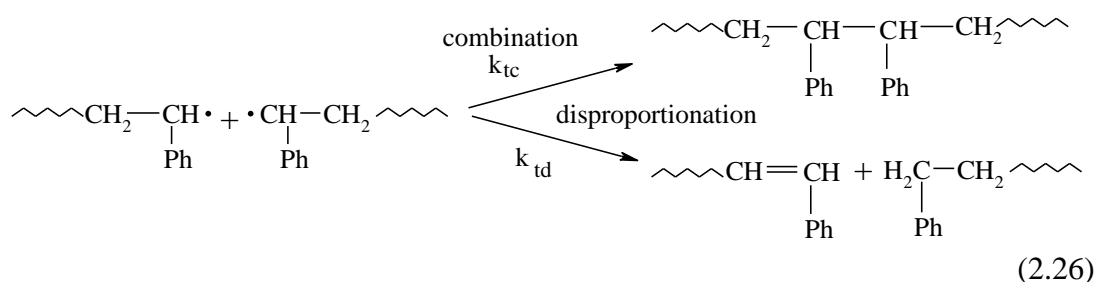
Intramolecular rearrangement of the initially formed radical may occur occasionally (e.g. backbiting – see (2.25)) or even be the dominant pathway (e.g. cyclopolymerization, ring – polymerization) [1].



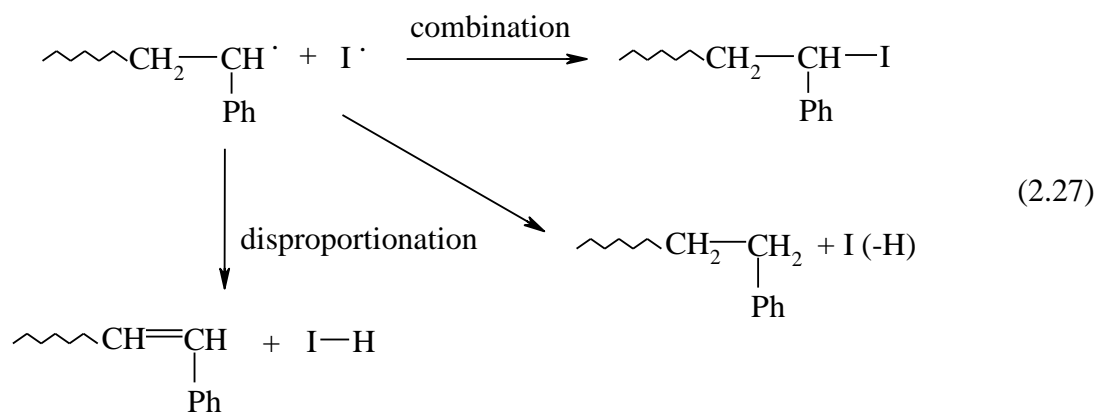
2.1.1.4 Termination

a) Radical – Radical Termination

(i) The self – reaction of propagating radicals by combination and / or disproportionation.



(ii) Primary radical termination; the reaction of a propagating radical with a radical derived from the initiator or transfer agent (e.g. $\text{I}\cdot$, see (2.27)). This process is highly dependent on the structure of the initiator – derived radical.



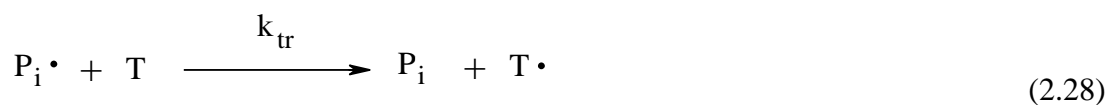
Disproportionation vs. Combination

It is possible to make some generalizations [1]:

- Termination of polymerizations involving vinyl monomers involves predominantly combination.
- Termination of polymerizations involving α – methylvinyl monomers always involves a measurable proportion of disproportionation.
- During disproportionation of radicals bearing an α – methyl substituent (for example, those derived from MMA), there is a strong preference for transfer of a hydrogen from the α – methyl group rather than the methylene group.
- Within a series of vinyl or α – methylvinyl monomers, k_{td} / k_{tc} appears to decrease according to the ability of the substituent to stabilize a radical center in the series $\text{Ph} > \text{CN} \gg \text{CO}_2\text{R}$.

b) Chain Transfer

The overall process involves a propagating chain (P_i^\cdot) reacting with a transfer agent (T) to terminate one polymer chain and produce a radical (T^\cdot) which initiates a new chain (P_1^\cdot) [1,37].



Even in the absence of added transfer agents, all polymerization are likely to be complicated by transfer to initiator, solvent, monomer, polymer, etc. the significance of transfer reactions is dependent upon the exact nature of the species involved and the polymerization conditions.

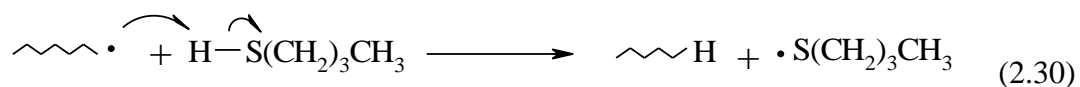
The presence of the transfer agent reduces the molecular weight of the polymer without directly influencing the rate of polymerization. If, however, $k_s < k_p$ then polymerization will be retarded and the likelihood that the transfer agent derived radical ($T\cdot$) will undergo side reactions is increased. Thus, retardation is much more likely in polymerizations of high k_p monomers (e.g. MA, VAc) than it is with low k_p monomers (e.g. Styrene, MMA) [1].

There are at least two basic mechanisms for chain transfer which should be considered in any discussion of chain transfer:

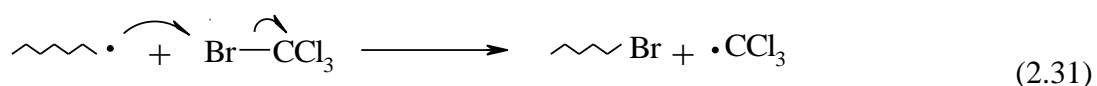
- **Atom or group transfer**

Chain transfer most commonly involves transfer of an atom or group from the transfer agent to the propagating radical by a homolytic substitution (S_H2) mechanism [1].

The moiety transferred will most often be a hydrogen atom, for example, when the transfer agent is a thiol, a hydroperoxide, the solvent, etc.

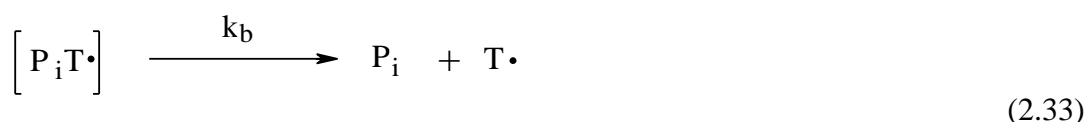


It also possible to transfer a heteroatom (e.g. hallogen atom from bromotrichloromethane).



- **Addition – elimination**

Some transfer agents react with radicals by an addition – elimination mechanism. This involves the formation of a short – lived intermediate $[P_iT]^\bullet$:



The reactivity of the transfer agent (T) towards the propagating species and the properties of the adduct $[P_iT]^\bullet$ are both important in determining the effectiveness of the transfer agent: if the lifetime of the intermediate $[P_iT]^\bullet$ is significant (k_b slow), it may react by other pathways than β – scission; if it $[P_iT]^\bullet$ undergoes coupling or disproportionation with another radical species it will inhibit or retard polymerization; if it adds to monomer (T copolymerizes) it will be an inefficient transfer agents [1].

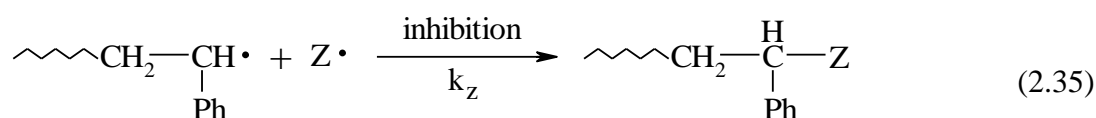
The most commonly used transfer agents in radical polymerization are presented in Table 2.2.

Table 2.2. Transfer Agents Commonly Used in Radical Polymerization

Transfer Agent Class	Example	Structure	Ref.
Thiols	Mercaptoethanol	$HO-CH_2-CH_2-SH$	[38]
Disulfides	Dithiauram disulfide	$ \begin{array}{c} H_3C \quad S \quad S \quad S \quad CH_3 \\ \diagdown \quad \quad \quad \quad / \\ N-C-S-S-C-N \\ \diagup \quad \quad \quad \quad \diagdown \\ H_3C \quad S \quad S \quad S \quad CH_3 \end{array} $	[39]
Halocarbons	Trichlorometane	$CHCl_3$	[40]
Solvents	Acetone	$ \begin{array}{c} H_3C \\ \diagdown \\ C=O \\ \diagup \\ H_3C \end{array} $	[1]

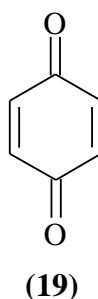
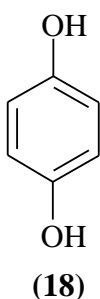
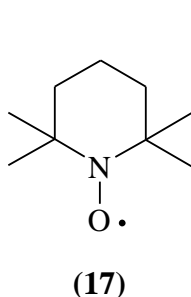
c) Inhibition and Retardation

An inhibitor is a species which is able to rapidly and efficiently scavenge propagating and / or initiator derived radicals and thus prevent polymer chain formation (2.35). Inhibitors which stop all polymerization until such time as they are completely consumed (i.e. during the induction period) and then allow polymerization to proceed at the normal rate, are called ideal inhibitors [1].



Common inhibitors include stable radicals [e.g. TEMPO (2, 2, 6, 6 – tetramethyl –1– piperidinyloxy) (17)] , captodative olefins, phenols [e.g. hydroquinone (18)], quinones [e.g. p – benzoquinone (19)], oxygen and certain transition metal salts [41].

Whether a given species functions as an inhibitor, retarder, or transfer agent in polymerization is dependent on the monomer(s) and the reaction conditions.



2.1.2 Controlled / “Living” Radical Polymerization

Radical polymerization is a very important commercial process for preparing high molecular weight polymers because it can be used for many vinyl monomers under mild reaction conditions, requiring the absence of oxygen but tolerant to water, and large temperature ranges (-20 to 200 °C). In addition, many monomers can easily copolymerize radically leading to an infinite numbers of copolymers with properties dependent on the proportions of the comonomers. The only disadvantage to conventional radical polymerization is the poor control of macromolecular structures

including degrees of polymerization, polydispersities, end functionalities, chain architectures and compositions. Thus, it is desirable to prepare by radical polymerization, new well – defined block and graft copolymers, stars, combs and networks that have not been previously prepared using ionic living polymerizations. Therefore, controlled – “living” radical polymerizations allow for the synthesis of new well – defined and functional materials from a larger range of monomers under simpler reaction conditions than are appropriate for ionic processes [42].

Living polymerizations are chain growth polymerizations that proceed in the absence of irreversible chain transfer and chain termination [43]. Provided that initiation is complete and exchange between species of various reactivities is fast, one can adjust the final average molecular weight of the polymer by varying the initial monomer–to–initiator ratio ($DP_n = \Delta[M] / [I]_0$), while maintaining a narrow molecular weight distribution ($1,0 < M_w / M_n < 1,5$). also, one has control over the chemistry and the structure of the initiator and active endgroup, so polymers can be end-functionalized and block copolymerized with other monomers [44].

There are two caveats for “living” radical polymerizations. The first is that irreversible termination is only minimized in these polymerizations and not excluded from the mechanism. Therefore, these polymerizations do not meet the strict definition of a living polymerization and are more properly termed controlled / “living” polymerizations to reflect the uncertainty regarding the contribution of unavoidable irreversible termination. Second, above some molecular weight value specific to the polymerization of each monomer, all controlled / “living” radical polymerizations can no longer be considered controlled, because slower termination, transfer and other side reactions become significant [44].

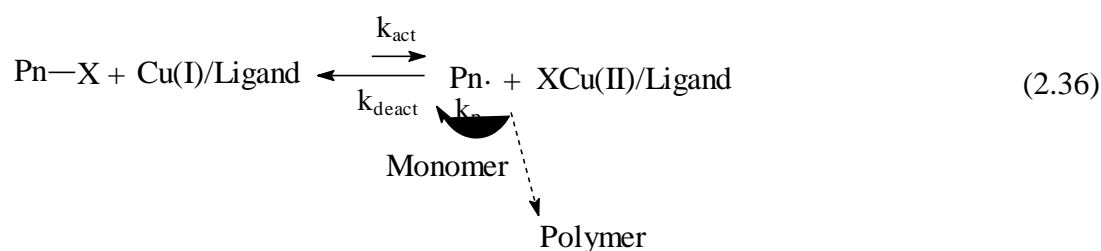
2.1.2.1 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well – defined low molecular weight polymers [42,45,46].

Previously, radical reactions had found limited application in organic synthesis due to the low yields of desired addition and substitution products caused by radical termination reactions. The usefulness of these reactions increased dramatically after

discovery that persistent radicals could be used to reduce the stationary concentration of reacting radicals and thereby minimize the contribution of termination. Of the methods developed based on this concept, one of the most useful is atom transfer radical addition (ATRA), so named because it employs atom transfer from an organic halide to a transition- metal complex to generate the reacting radicals, followed by back- transfer from the transition metal to a product to a product radical to form the final product [42,44-46].

Atom transfer radical addition can be extended to ATRP if the conditions can be modified such that more than one addition step is possible. Thus, if the radical species before and after addition of the unsaturated substrate (monomer) possess comparable stabilization, then the activation – addition – deactivation cycle will repeat until all of the unsaturated substrate present is consumed. This process results in a chain – growth polymerization (2.36) [44-46].

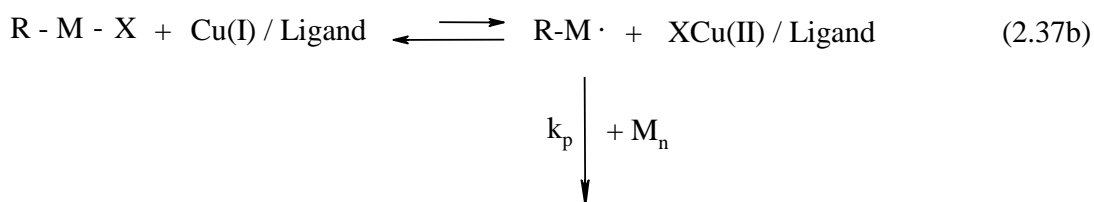
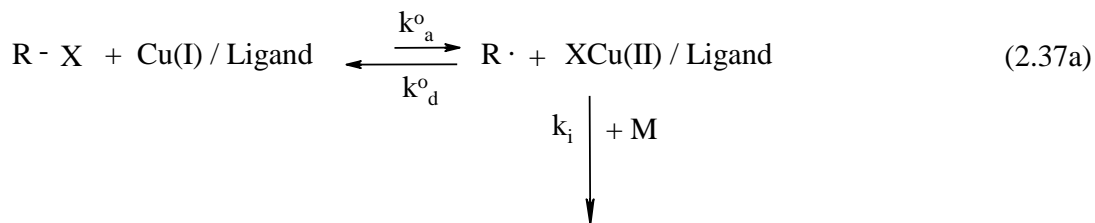


• Mechanism and Kinetics of ATRP

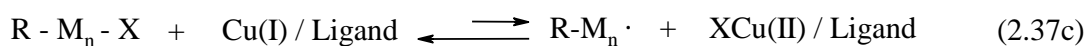
An ATRP system consists of an initiator, a copper(I) halide, ligand(s), and of course, monomer. The general mechanism of ATRP which is schematically represented in (2.37a-d), involves the abstraction of a halogen from the dormant chain by a metal center, such as complexes of Cu^{I} , in a redox process [42]. Upon halogen abstraction, the free radical formed (the active species) can undergo propagation. However, the free-radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of free radicals is quite low, resulting in a reduced amount of irreversible radical-radical termination. The final result is that degrees of polymerization (DP) can be predetermined ($\text{DP} = \Delta[\text{M}]/[\text{I}]_0$).

and M_w/M_n is quite low (1,05-1,5), and good control of functionalities is achieved [47].

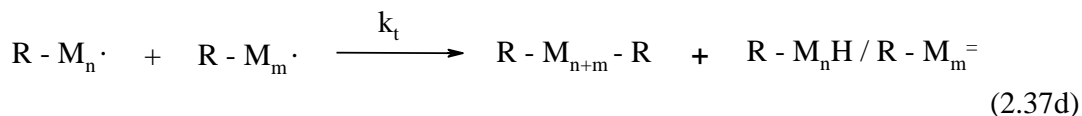
Initiation



Propagation



Termination



The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator ($\text{CuX}_2 / \text{Ligand}$).

$$R_P = k_{app}[M] = k_p [P\cdot] [M] = k_p K_{eq} [I]_o \frac{[\text{Cu(I)}]}{[\text{Cu(II)X}]} [M] \quad (\text{Eq:2.3})$$

The equilibrium constant (K_{eq}) depends on the monomer used, for example, in the bulk polymerization of styrene at 110 °C using R-Br and $\text{CuBr} / \text{dNbipy}$ the equilibrium constant is approximately $K_{eq} = k_{act} / k_{deact} = 4 \times 10^{-8}$ [48,49].

ATRP is a multi-component system, so concentrations and the structures of all these compounds affect the polymerization rate and the properties of the resulting polymer. For each particular ATRP, a specific initiator, metal, ligands, deactivator, temperature, reaction time and solvent should be selected [42].

- **Components Used in ATRP**

- a) Monomers**

ATRP can be used for many vinyl monomers including styrenes, acrylates, methacrylates, acrylonitrile and dienes. The currently used catalyst systems are not sufficient to polymerize less reactive monomers that produce non – stabilized, reactive radicals such as ethylene, α – olefins, vinyl chloride and vinyl acetate, though copolymerization is sometimes succesful [42].

The most commonly used monomers in ATRP are styrenes and MMA.

(i) Styrenes: Styrene ATRP is usually conducted at 110 °C for bromide – mediated polymerizaiton and 130 °C for the chloride – mediated polymerization [2]. Generally, bulk system is preferred. Solvents may be used for styrene ATRP and nonpolar solvents are recommended.

Well – defined polystyrenes can be prepared with the molecular weight range of 1000 to 90000. In the region from 1000 to 30000, polydispersities (M_w / M_n) are less than 1.10 and above 30000 polydispersities increase to within the range of 1.10 to 1.50 due to some side reactions, predominantly HX elimination. These side reactions can be reduced at lower polymerization temperatures [42].

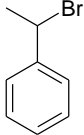
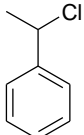
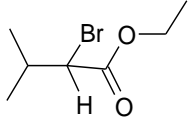
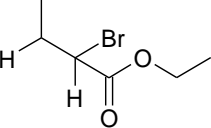
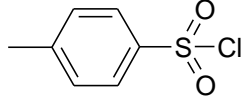
(ii) Methyl Methacrylate: The standart conditions for MMA ATRP are similar to those of styrene ATRP except that less copper(I) catalyst is needed and the polymerizations are conducted in 50% solution in diphenyl ether or dimethoxy benzene at 90 °C. The use of copper bromide instead of copper chloride leads to more rapidly decreasing polydispersities. This is due to the better efficiency of bromine in the deactivation step. The polymerization also is less controlled when bipy is used instead of dNbipy due to the correspondingly smaller concentration of deactivator.

Well – defined poly(methyl methacrylate) has been prepared within the molecular weight range of 1000 to 180000. In the region from 1000 to 90000 the polydispersities are less than 1.10 and above 90000 the polydispersities fall within the range of 1.10 to 1.50 [42].

b) Initiators

The most frequently used initiator types in ATRP systems are given in Table 2.3.

Table 2.3 Types of initiators used in ATRP systems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethylisobutyrate	Methylmethacrylate
 2-Bromo ethyl propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

In general, any alkyl halide with activating substituents on the α – carbon, such as aryl, carbonyl and allyl groups, potentially can be used as ATRP initiators. Polyhalogenated compounds (CCl_4 and CHCl_3) and compounds with a weak $\text{R} - \text{X}$ bond, such as $\text{N} - \text{Y}$, $\text{S} - \text{X}$ and $\text{O} - \text{X}$ presumably also can be used as ATRP initiators. There is however, an upper limit to the stability of the initiating radicals beyond which it also becomes an inefficient initiator. For example, trityl halides are poor initiators for ATRP [44].

c) Transition Metals

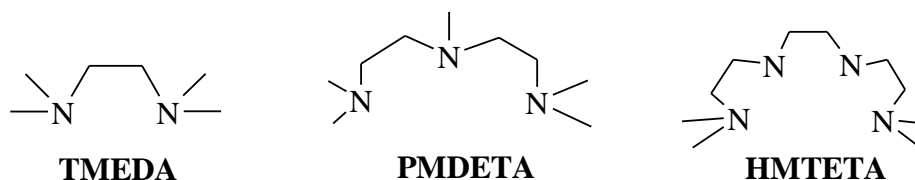
Basic requirements for the good catalyst are high selectivity towards atom transfer process and high lability of the resulting $X-M_t^{n+1}$ species (higher oxidation state of metal). The metal should participate in a one-electron process which would result in oxidative addition / reductive elimination but not in atom transfer process. Additionally, the metal should have a high affinity for atom / group X, but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β -hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control (livingness) of process. The most important factors in selecting good ATRP catalyst are the equilibrium position, dynamics of exchange between dormant and active species. These parameters are related to the redox cycle M_t^n / M_t^{n+1} but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus, the inner coordination sphere of M_t^n must expand to accommodate a new X (halide) ligand. Expansion from tetra to pentacoordinated structure $Cu(I) / 2 \text{ ligand} \rightarrow X-Cu(II) / 2 \text{ ligand}$ or pentacoordinated structure $X_2Fe(II) / 3PR_3 \rightarrow X_3Fe(III) / 3PR_3$ must be possible. The most important catalysts used in ATRP are; $Cu(I)Cl$, $Cu(I)Br$, $Ni(II)$, $Ru(II) / Al(OR)_3$ and $Fe(II) / 3 PR_3$ [48,49].

d) Ligands

The position of the atom transfer equilibrium depends upon the nature of the metal and ligands. Generally, more electron donating ligands stabilize better the higher oxidation state of the metal and accelerate the polymerization [44].

Ligands that sterically crowd the metal center prevent the approach of the alkyl halide initiator or endgroup and therefore are poor ligands for ATRP [42].

The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N',N'',N''' pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimethylamino) ethyl]amine ($Me_6\text{-TREN}$) and Alkylpyridylmethaneimines are also used.



e) Deactivators

The deactivator plays a vital role in ATRP in reducing the polymerization rate and the polydispersity of the final polymer. In the limit that the rate of deactivation is too slow or does not occur, then ATRP simply becomes a redox – initiated polymerization. For copper – catalyzed ATRP, the deactivator is the corresponding copper(II) halide complex (e.g. 2 dNbipy / CuX₂) [44].

In most systems the concentration of deactivator continuously, but slowly, increases due to slow termination by radical coupling [44].

As a conclusion, ATRP is robust polymerization system that can polymerize a wide variety of monomers including styrenes, methacrylates, acrylates and acrylonitrile. The reaction conditions are not stringent because only the absence of oxygen is required to conduct the polymerizations. The polymer endgroups can be transformed to other functional groups, such as amines and a range of polymers with different architectures and compositions can be prepared by relatively simple means. The combination of synthetic versatility and simplicity makes ATRP a powerful technique for use in designing and preparing new and unusual materials [44].

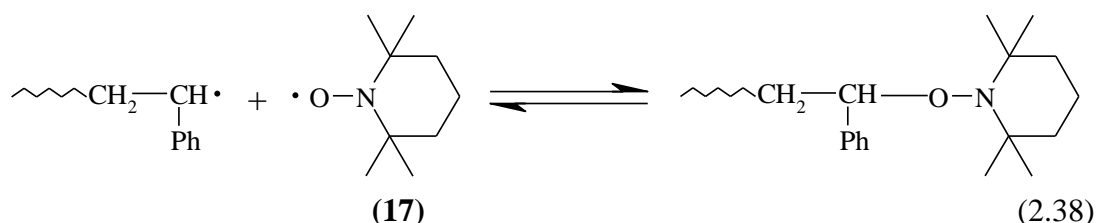
2.1.2.2 Stable Free Radical Polymerization (SFRP)

The concept of reversible termination by using a stable free radical has recently been shown to control growing free radical chains [50-52]. The stable nitroxide radicals such as 2, 2, 6, 6 – tetramethyl – 1 – piperidinyloxy (TEMPO) (**17**) are known to act as strong polymerization inhibitors [50,53].

The main advantage of the TEMPO – mediated systems is that they are metal – free. However, one relatively expensive nitroxide molecule per chain is needed: it is difficult to displace nitroxide from the chain end and introduce useful functional

groups. At present TEMPO can be used only for preparation of polystyrene and copolymers, though substituted nitroxides can expand the range of monomers. Polymerization rates in TEMPO – mediated polymerization are usually quite low and there have been several reports describing the acceleration by destroying excess nitroxide with acids and simple radical initiators [42].

The success of this method can be related to the ability of stable nitroxide free radicals, such as TEMPO, to react at near diffusion controlled rates with the carbon – centered radical of the growing polymer chain end in a thermally reversible process. This dramatically lowers the concentration of free radicals in the polymerization system and, coupled with the inability of the nitroxide free radicals to initiate new chain growth, leads to controlled polymerization [54].



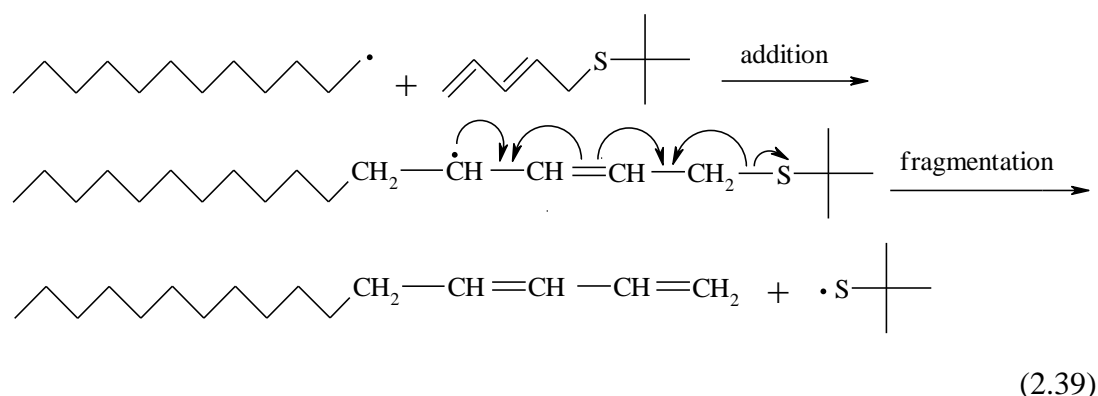
Consequently, the stable free radicals are not capable of initiating new chains late in the polymerization process, as they reversibly react with a propagating chain. This polymerization system contains a monomer or monomer mixtures, free radical initiator, and a stable free radical and requires only heating at elevated temperatures [50].

These features have been exploited in the preparation star and graft polymers, hyperbranched systems and low – polydispersity random and block copolymers. The living nature of this process also permits the molecular weight and chain ends of the macromolecules to be accurately controlled [54].

2.1.2.3 Addition – Fragmentation Reactions

Free radical addition – fragmentation has, of late, been identified as an effective means for controlling the molecular weight of vinyl polymers avoiding the use of conventional S – based chain transfer agents. The intermediate radical formed by the addition of the propagating radical on the transfer agent, undergoes fragmentation,

generating another radical which enters into the polymerization cycle. Compounds of these types include allylic sulfides, allylic peroxides, α – benzyloxy styrenes, alkyl thiomethyl acrylates, thiohydroxamic esters, α – bromomethyl acrylates, etc. One attractive feature of this technique is the concomitant incorporation of a terminal functional group, following fragmentation, the functional groups being of the type allyl, epoxy, styrenic, acrylic, keto, carboxy, amino etc., depending on the system. When the functional groups are polymerizable, this method appears to be a viable route for the single – step synthesis of macromonomers [55].



It has however been noted that the unsaturation produced at polymer terminal by the hitherto reported addition – fragmentation reactions are acrylates and styrene derivatives bearing bulky substituents at the α – position, whose polymerizability is known to be very poor. In these cases propagation is competed by the fragmentation of the polymer radical leading to premature chain termination [56,57].

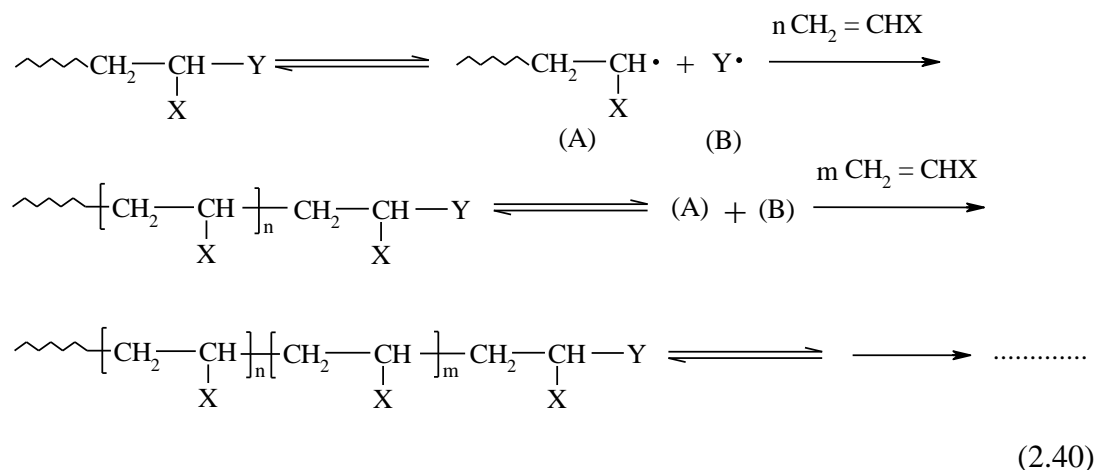
A whole range of new addition – fragmentation agents (AFA) in radical polymerization were investigated. Different combinations of leaving radicals (alkyl – thiyl, benzylic, captodative carbon radicals) and olefin pattern [allyl, α – (substituted methyl)acrylate, pentadienyl] to generate the corresponding AFAs were used [55].

2.1.2.4 Iniferters

The disulfides were discussed as chain transfer agents before. These compounds also play a major role in iniferter reactions. The S – S bond present in the molecule generates thiyl radicals, which act as both initiators and terminators. Disulfides are

properly termed iniferters to reflect their roles in initiation, transfer and termination reactions.

The mechanism of the iniferter process can be shown as follows [58]:



If the propagating chain end which can dissociate thermally or photochemically into a propagating radical (A) and small radical (B), which must be stable enough to initiate a new polymer chain, and can recombine easily with a propagating radical. In the event that these dissociation, monomer addition, and recombination processes repeats as a cycle, such a radical polymerization proceeds apparently via a living mechanism [58].

This kind of controlled radical polymerization can be classified by their initiation mechanisms and reaction conditions:

- (a) Iniferter reactions by photo - irradiation,
- (b) Ultrasonic irradiation,
- (c) Thermal and Redox systems.

2.2 Photopolymerization

Polymerization can also be induced by supplying the initiation energy through irradiation with visible or ultraviolet light. The conversion of a monomer to a polymer occurs through the normal propagation, termination and chain transfer

reactions. Only the initiation processes are unusual. Perhaps the most obvious advantage of photopolymerization in laboratory research is the avoidance of chemical contamination by initiator residues [59].

Photoimaging, UV curing technology or photocrosslinking processes are mainly based on photopolymerization. These kinds of processes utilize photoinitiators, photocross-linking agents and photocrosslinkable polymers which contain a photo – reactive group.

The advantage of photopolymerization is that the initiation process may take place over a wide range of temperatures and with a greater specificity than is found in chemically initiated systems [59].

2.2.1 Photoinitiators and Quantum Yield

Photoinitiators for free-radical polymerization are classified into two groups: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which when photoexcited abstract hydrogen atoms from H – donors and so form radicals. Photoinitiators were previously considered in more details (see initiators section in 2.1.1.2).

The quantum yield of a simple photochemical reaction is defined as the number of molecules of the product formed, or reactant consumed, per quantum of light absorbed. In photopolymerization the quantum yield for initiation is defined by the number of chains initiated per quantum of light absorbed. This may be written in terms of rates as:

$$\phi_i = \frac{\text{rate of initiation}}{\text{rate of light absorption}} \quad (\text{Eq:2.4})$$

When a simple photoinitiation occurs and absorbing compound dissociates directly to two monoradicals, Φ_i must lie between zero and 2 [59].

2.3 Different Ways To Synthesize Block Copolymers

Various methods have been proposed and used for the synthesis of block copolymers. These methods are generally based on the use of either telehelics oligomers in polycondensation reactions or living polymerization techniques [60]. In this section the methods for block copolymer synthesis are described.

2.3.1 Transformation Reactions

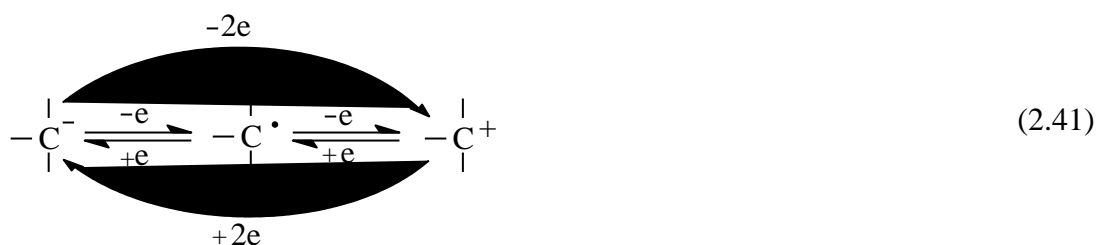
Transformation reactions involve the preparation of polymeric species by some mechanism which leaves a terminal functionality that allows polymerization to be continued by another mechanism [1].

Transformation reactions may be outlined in two main categories which are divided in subcategories within themselves as follows:

2.3.1.1 Direct Transformation Reactions

- Cation to Anion Direct Transformation
- Radical to Cation Direct Transformation

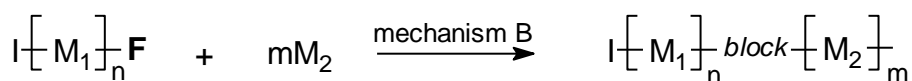
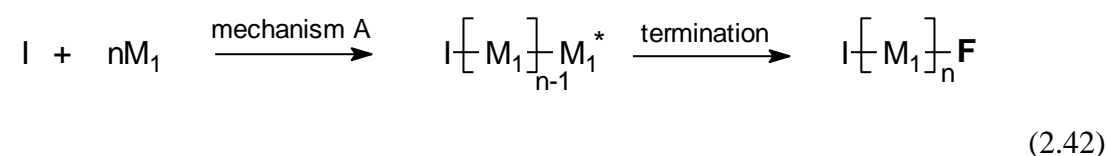
The mechanism of the first monomer's polymerization may be changed to another mechanism of the second one by a redox process without termination and isolation (2.41) [61].



2.3.1.2 Indirect Transformation Reactions

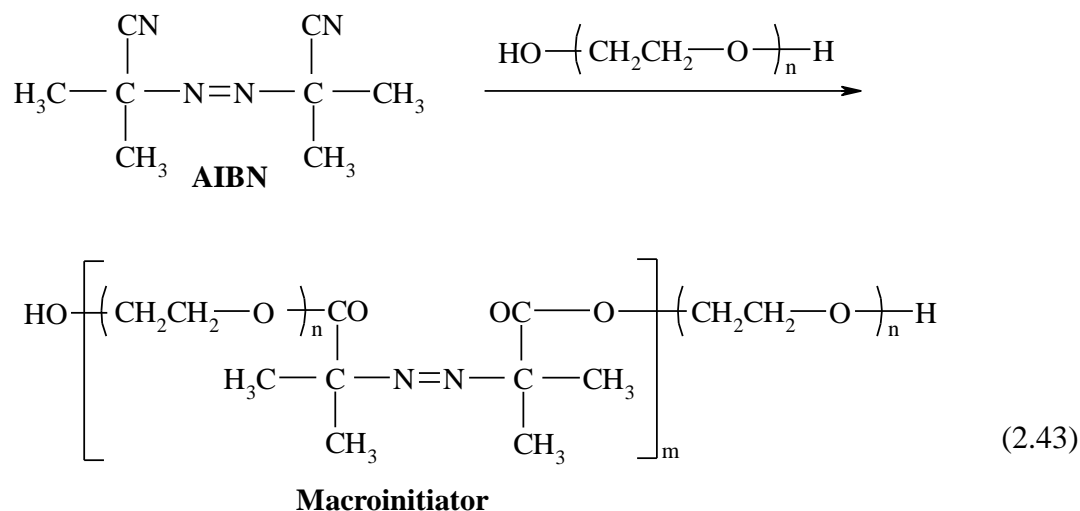
- Transformations Involving Condensation Polymerization
- Transformation of Anionic Polymerization to Radical Polymerization
- Transformation of Cationic Polymerization to Radical Polymerization
- Transformation of Radical Polymerization to Anionic Polymerization
- Transformation of Radical Polymerization to Cationic Polymerization
- Transformation of Anionic Polymerization to Cationic Polymerization
- Transformation of Cationic Polymerization to Anionic Polymerization
- Transformation Involving Activated Monomer Polymerization
- Transformation Involving Ziegler – Natta Polymerization
- Transformation Involving Group Transfer Polymerization
- Transformation Involving Metathesis Polymerization

In these methods, multistep reactions are generally required. During the first monomer's polymerization, a functional group which is reactive for only the second polymerization step is introduced into the chain ends either at initiation or termination process. After obtaining this functional ended polymer which is consist of first monomer, It is used as macroinitiator for the second monomer's polymerization according to the functionality of the macroinitiator [61].



• Macroinitiators via Multifunctional Initiators

Multifunctional initiators contain two or more different types of functional groups within the one molecule in order to achieve block copolymer. These initiators can then be used to form polymers that contain initiator moieties either at the end or on the backbone (macroinitiators). These end groups can be subsequently utilized to afford higher molecular weight polymers. For example, block copolymers may be synthesized from a α, ω – diol and AIBN (2.43) [1].



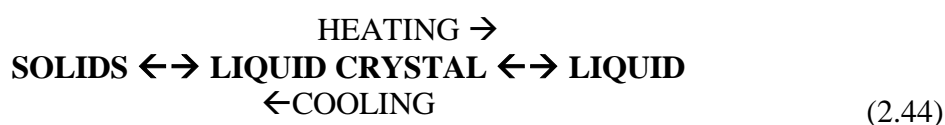
Also, some of bifunctional initiators are presented in Table 2.1.

2.4. Liquid Crystals

Liquid crystals are a state of order between crystals and liquids (2.44). They can be fluid like a liquid and they can have anisotropic properties like crystals. The study of liquid crystals began in 1888 when an Austrian botanist named Friedrich Reinitzer observed that a material known as cholesteryl benzoate had two distinct melting points. Because of this early work, Reinitzer is often credited with discovering a new phase of matter - the liquid crystal phase [62].

The main reasons for the formation of liquid crystalline phases are:

- A simple geometrical form of the molecule: rods, discs or ball, which allow a closer packing in a mesophase (monophilic liquid crystals).
- An intramolecular contrast, which cases microseparation of different parts of the molecules (amphiphilic liquid liquid crystals).



In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state (Figure 2.1). Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic liquid has no orientational order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals [62].

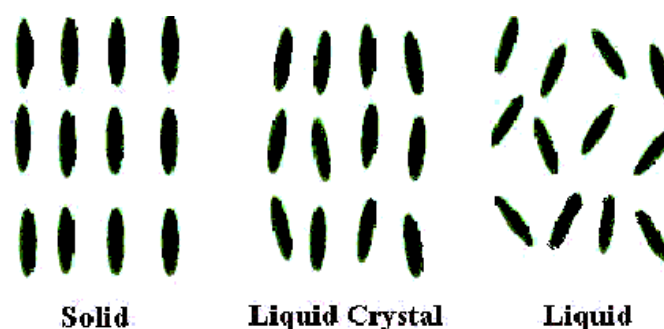


Figure 2.1 The illustration of the average alignment of the molecules for each phase.

Liquid crystals can roughly be divided into two areas:

- a) *Lyotropic liquid crystals* which are formed from compounds with amphiphilic properties and solvents (commonly water). Common examples of such lyotropic liquid crystals are those produced from soaps and other detergent systems and water.
- b) *Thermotropic liquid crystals* which are formed from compounds (predominantly organic, but also organometallic) whose molecules are mainly either rod – shaped or disc – shaped, either by heating the crystalline solid or by cooling the isotropic liquid, i.e. by thermal effects [63].

2.4.1 Liquid Crystal Phases

There are many types of liquid crystal states, depending upon the amount of order in the material. The most well known liquid crystal phases are discussed below.

2.4.1.1 Nematic Phases

The nematic phase is an anisotropic liquid [63]. The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction (along the director).

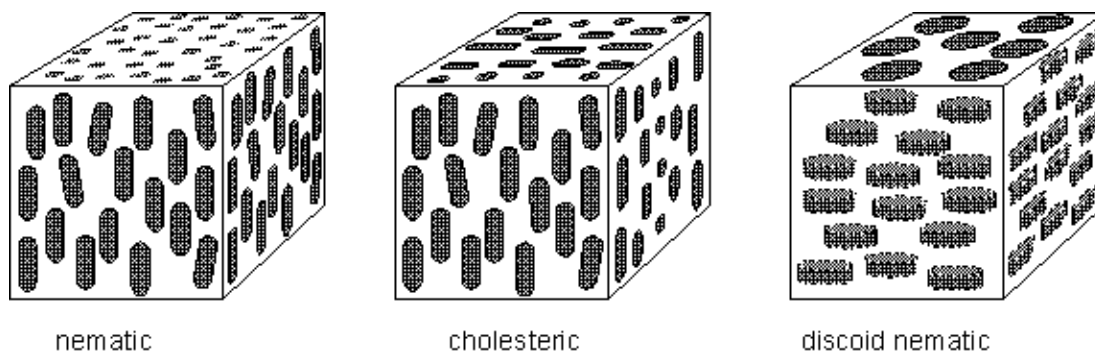


Figure 2.2 The schematic representation of nematic phases.

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 [60]. A special class of nematic liquid crystals is called chiral nematic. The term chiral nematic is used interchangeably with cholesteric [62].

2.4.1.2 Smectic Phases

The smectic state is another distinct mesophase of liquid crystal substances. Molecules in this phase show a degree of translational order not present in the nematic.

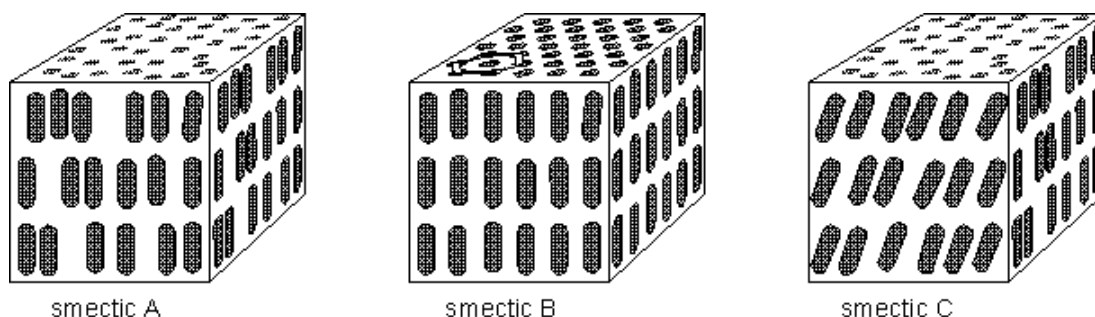


Figure 2.3 The schematic representation of smectic phases.

In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted to within these planes, and separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic (Figure 2.3) [62]. Many compounds are observed to form more than one type of smectic phase. As many as 12 of these variations have been identified, however only the most distinct phases are discussed here.

In the smectic-A mesophase, the director is perpendicular to the smectic plane, and there is no particular positional order in the layer. Similarly, the smectic-B mesophase orients with the director perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer. In the smectic-C mesophase, molecules are arranged as in the smectic-A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane (Figure 2.3).

2.4.2 Applications of Liquid Crystals

Liquid crystal technology has had a major effect many areas of science and engineering, as well as device technology. Applications for this special kind of material are still being discovered and continue to provide effective solutions to many different problems. Typical applications are:

- LCD displays
- dyes (cholesterics)
- advanced materials
- membrans
- temperature measurement
- solvents for GC, NMR, etc.

2.4.3 Liquid Crystalline Polymers (PLC)

PLCs are a class of materials that combine the properties of polymers with those of liquid crystals.

In order for normally flexible polymers to display liquid crystal characteristics, rod-like or disk-like elements (called mesogens) must be incorporated into their chains. The placement of the mesogens plays a large role in determining the type of PLC that

is formed. *Main-chain polymer liquid crystals* or MC-PLCs are formed when the mesogens are themselves part of the main chain of a polymer. Conversely, *side chain polymer liquid crystals* or SC-PLCs are formed when the mesogens are connected as side chains to the polymer by a flexible "bridge"(called the spacer) (Figure 2.4) [62].

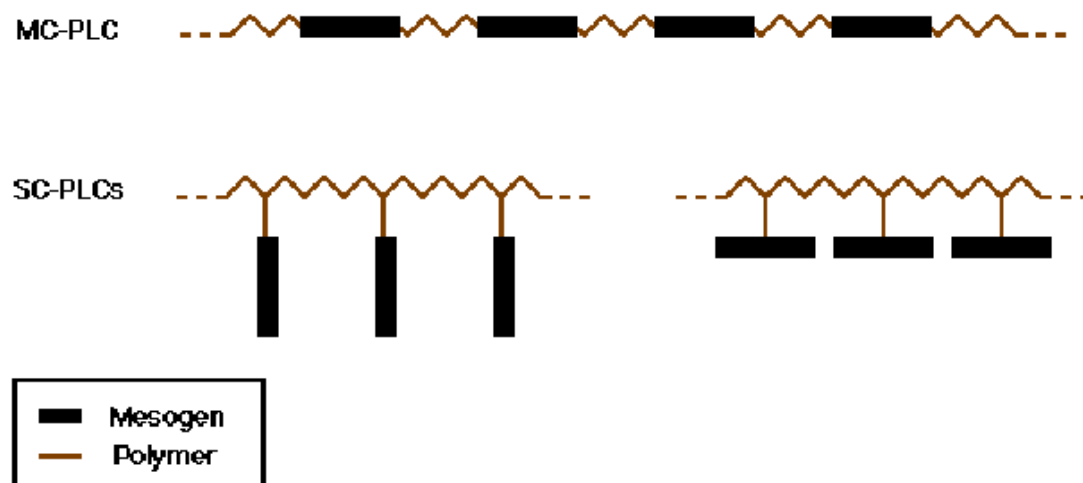


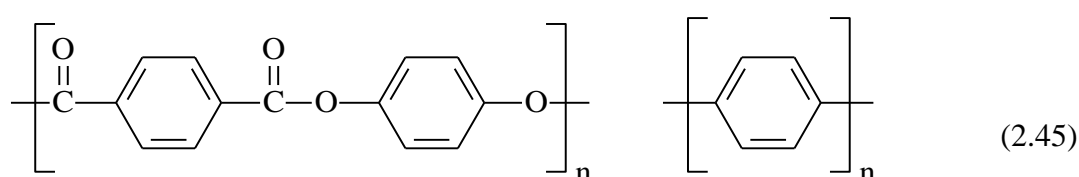
Figure 2.4 The structures of MC – PLCs and SC – PLCs.

Other factors influencing the mesomorphic behavior of polymers include the presence of long flexible spacers, a low molecular weight, and regular alternation of rigid and flexible units along the main chain [62,63].

2.4.3.1 Main Chain Polymer Liquid Crystals

Main chain polymer liquid crystals are formed when rigid elements are incorporated into the backbone of normally flexible polymers. These stiff regions along the chain allow the polymer to orient in a manner similar to ordinary liquid crystals, and thus display liquid crystal characteristics.

The basic structure in MC – PLCs are benzene rings interlinked of parapositions (2.45):



MC – PLCs of the ester type have been the most widely synthesized because they can be prepared by the traditional methods of condensation polymerization. Examples are polyesteramides, polyaminoesters, polyetheresters, polythioesters [60].

2.4.3.2 Side Chain Polymer Liquid Crystals

It has been demonstrated that main chain polymer liquid crystals often cannot show mesogenic behavior over a wide temperature range. Side chain polymer liquid crystals, however, are able to expand this scale. These materials are formed when mesogenic units are attached to the polymer as side chains.

Side chain polymer liquid crystals have three major structural components: the backbone, the spacer, and the mesogen.

The backbone of a side chain polymer liquid crystal is the element that the side chains are attached to. The structure of the backbone can be very important in determining if the polymer shows liquid crystal behavior. Polymers with rigid backbones typically have high glass transition temperatures, and thus liquid crystal behavior is often difficult to observe.

Perhaps the most important part of a side chain polymer liquid crystal is the mesogen. It is the alignment of these groups that causes the liquid crystal behavior. Usually, the mesogen is made up of a rigid core of two or more aromatic rings joined together by a functional group.

Mesogens attached as side groups on the backbone of side chain polymer liquid crystals are able to orient because the spacer allows for independent movement. The structure of the spacer is an important determining factor in side chain polymer liquid crystals. The spacer length has a profound effect on the temperature and type of phase transitions. Short spacers tend to lead to nematic phases, while longer spacers lead to smectic phases [62,63].

3. EXPERIMENTAL WORK

3.1 Materials

3.1.1 Purification of Materials

3.1.1.1 Monomer

Styrene (St) (Fluka)

Washed with aq. 5% NaOH to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure (50 °C / 25 mm Hg). Middle fraction was collected and immediately used.

3.1.1.2 Solvents

Tetrahydrofuran (THF) (J.T. Baker)

Dried and distilled over CaH_2 , then it was let mixing over sodium/benzophenone ketyl, and was distilled prior to use.

Dimethyl sulfoxide (DMSO) (Merck)

Refluxed over CaH_2 then distilled under reduced pressure (75,6 – 75,8 °C / 12 mm Hg).

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 °C / 760 mm Hg).

N, N – Dimethyl Formamide (DMF) (J.T. Baker)

Dried over MgSO_4 then distilled under reduced pressure.

Chloroform (J.T. Baker)

Shaken with several portions of conc. H_2SO_4 washed thoroughly with water and dried with CaCl_2 before filtering and distilling ($61\text{ }^\circ\text{C}$ / 760 mm Hg).

Diphenyl ether (DPE) (Aldrich)

It was used without further purification.

3.1.1.3 Other Chemicals and Reagents

3 Acetyl – 1 – propanol (Aldrich)

It was used without further purification.

2 – Bromopropionyl bromide (Aldrich)

It was used without further purification.

Acryloyl chloride (Aldrich)

Distilled over P_2O_5 ($72\text{ }^\circ\text{C}$ / 760 mm Hg).

4' – Hydroxy – 4 – biphenylcarbonitrile (Aldrich)

It was used without further purification.

6 – Chloro 1 – hexanol (Aldrich)

It was used without further purification.

Triethylamine (TEA) (J.T. Baker)

Distilled with fractionation under CaH_2 .

Copper (I) bromide (Aldrich)

It was used without further purification.

N,N,N',N'',N'' pentamethyldiethylenetriamine (PMDETA) (Aldrich)

It was used without further purification.

Other chemicals were used as received.

3.2 Equipments

3.2.1 Photo Reactor

A merry-go-round type photoreactor, with 16 Philips 8W / 06 lamps, emitting overwhelmingly light at c.370nm was used.

3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

H-NMR analysis were recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.3 Gel Permeation Chromotography (GPC)

GPC analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and three Waters Styragel columns (HR 4, HR 3, and HR 2). THF was used as the eluent at a flow rate of 0,3 mL/min. Molecular weight of the polymers was calculated with the aid of polystyrene standarts.

3.2.4 Differential Scanning Calorimetry (DSC)

The thermal and liquid crystalline properties of the polymers were studied by Perkin Elmer DSC 6 at a scanning rate of 5 and 10 °C.min⁻¹.

3.2.5 Optical Microscopy (OM)

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

3.3 Synthesis of Chemical Compounds

3.3.1 Preparation of 4-((E)-2-{4-[(2-bromopropanoyl)oxy]-1-cyano-1-methylbutyl}-1-diazenyl)-4-cyanopentyl 2-bromopropanoate (AI)

3.3.1.1 Synthesis of 4, 4'-Azobis(4-cyano pentanol) (ACP)

14,32 g (0,11 mol) hydrazine sulphate was dissolved in 150 ml of water contained into a round bottom baloon. 22,5 g (0,22 mol) 3 Acetyl – 1 – propanol was added, followed by slow addition of a solution of 10,8 g (0,22 mol) NaCN in 100 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 $2\text{ }^{\circ}\text{C}$. The addition took all day and continued untill a yellow coloration appears in the solution. Excess bromine was removed by adding NaHSO_3 . 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 [60,64].

3.3.1.2 Synthesis of AI

AI was prepared according to the modified method of Paik et al. [65]. Under nitrogen, 1,78 ml (16,91 mmol) 2 – Bromopropionyl bromide was added dropwise to a stirring mixture of 1,7 g (6,74 mmol) 4, 4' – Azobis(4 – cyano pentanol) (ACP) and 2,34 ml (16,91 mmol) triethylamine in 150 ml of CHCl_3 in an ice bath for 1 h. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 h. The reaction mixture was washed with water (3 x 150 ml) and then dried over MgSO_4 after filtration, evaporation of CHCl_3 gave a greasy product. It was

dissolved in CHCl_3 again and precipitated in cold hexane then filtered and dried under vacuum (yield 49%).

^1H NMR (CDCl_3): δ (ppm) = 1,6 – 1,8 (s, 6H, $-\text{CCN}(\text{CH}_2)\underline{\text{CH}_3}$), 1,8 – 2,0 (d, 6H, $-\text{CH}(\text{Br})\underline{\text{CH}_3}$), 2,0 – 2,3 (m, 8H, $-\text{CH}_2\text{CH}_2-$), 4,1 – 4,3 (q, 2H, $-\text{CH}$), 4,3 – 4,5 (m, 4H, $-\text{OCH}_2$) (Figure 3.1).

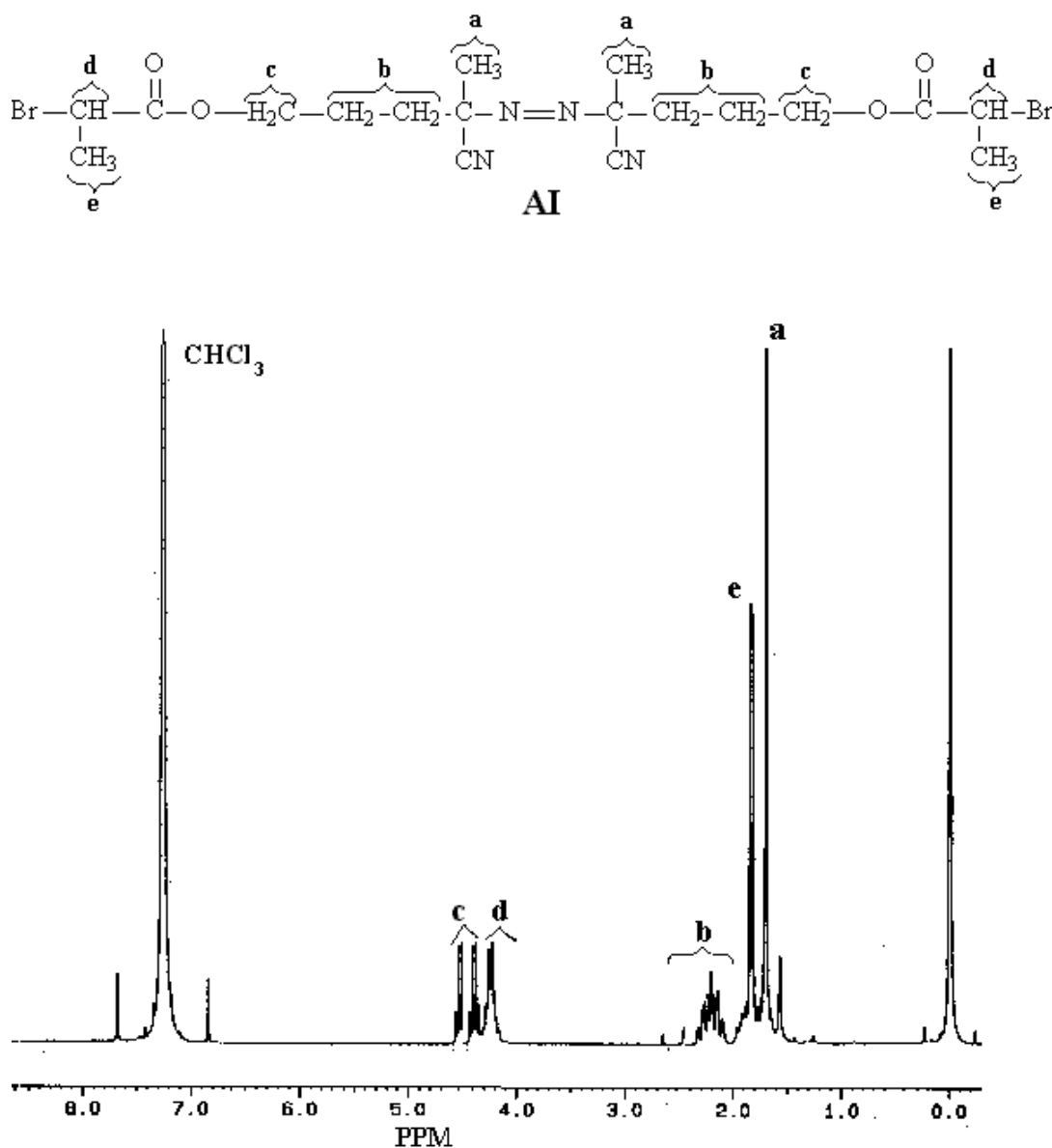


Figure 3.1. ^1H NMR spectrum of AI in CDCl_3 .

3.3.2 Preparation of 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate (LC6)

3.3.2.1 Synthesis of 6-(4-Cyanobiphenyl-4'-oxy)hexan-1-ol

Under nitrogen, 2,25 ml (20 mmol) 6-chloro 1-hexanol was added dropwise to a stirring mixture of 3 g (15,1 mmol) 4'-hydroxy-4-biphenylcarbonitrile and 2 g (14,5 mmol) anhydrous K_2CO_3 in 200 ml of anhydrous DMSO. The reaction mixture was heated at 110 °C for 2 hours. After this process, the reaction mixture was added dropwise to 400 ml 10% NaOH solution at room temperature and filtered. The resulting solid product was dried at 70 °C in vacuum. It was recrystallized from benzene. White crystalline product was obtained and dried under vacuum (m.p. = 90 – 92, yield 68%) [61,66].

3.3.2.2 Synthesis of LC6

Under nitrogen, 1,36 ml (16,69 mmol) fresh acryloyl chloride in 20 ml of dry THF was added dropwise to a stirring mixture of 2,93 ml (21,03 mmol) triethylamine and 2,99 g (10,12 mmol) 6-(4-Cyanobiphenyl-4'-oxy)hexan-1-ol in 20 ml of dry THF at 0 °C. The reaction mixture was stirred for 15 hours at room temperature. Then it was added dropwise to 300 ml 5% HCl solution. After neutralizing the mixture, it was filtered and dried in vacuum. The resulting product was recrystallized from ethanol. White crystals were obtained and dried under vacuum (m.p. = 69 – 71 °C, yield 71%) [61,66].

1H NMR ($CDCl_3$): δ (ppm) = 1,9 – 2,0 (m, 8H, $-(CH_2)_4$), 3,9 – 4,1 (t, 2H, $-OCH_2$), 4,1 – 4,3 (t, 2H, $ArO-\underline{CH_2}$), 5,8 – 5,9 (d, 1H, $=CH_2$), 6,0 – 6,2 (m, 1H, $=CH$), 6,3 – 6,5 (d, 1H, $=CH_2$), 6,9 – 7,0 (d, 2H, 3' and 5' aromatic protons), 7,5 – 7,6 (d, 2H, 3 and 5 aromatic protons), 7,6 – 7,8 (q, 4H, 2, 6 and 2', 6' aromatic protons) (Figure 3.2).

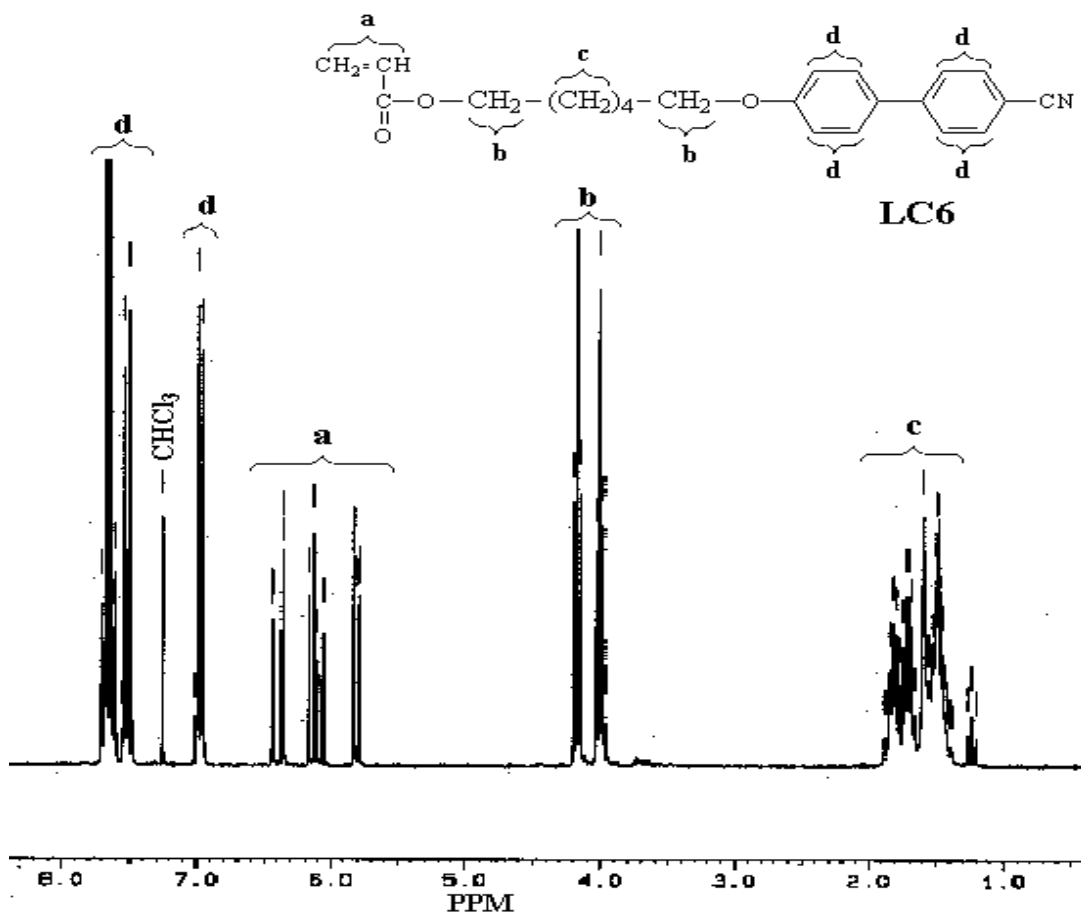


Figure 3.2. ¹H NMR spectrum of LC6 in CDCl₃.

3.3.3 General Polymerization Procedure for CFRP of LC6 and St by using AI

In a typical polymerization reaction, the required amounts of monomer LC6 or St, macroinitiator AI were dissolved in solvent. The reaction mixture was introduced in a Pyrex glass ampoule, thoroughly freeze-thaw degassed and the sealed under vacuum. After reacting for variable time periods at 80 °C or 110 °C, the polymer was precipitated by addition of a ten-fold excess of methanol, filtered and purified by reprecipitation into methanol. The polymer was then dried in vacuo for 18 h. The amounts of monomer LC6 or St and initiator AI, reaction times and conversions for the different preparations of macroinitiators MI-1-3 and MI-4 are collected in Table 4.1.

3.3.4 General Copolymerization Procedure for ATRP of St and LC6

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied three or four times, then certain amounts of styrene or LC6, solvent, ligand (PMDETA), CuBr and macroinitiator were added in the order mentioned under nitrogen. Solvent, diphenyl ether was only used with LC6 monomer. The reaction solution was bubbled by nitrogen to remove dissolved gases and then tube was immersed in an oil bath and held by a thermostat at 110 °C., with rigorous stirring. The copolymerization was performed for a determined time and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The polymer was dried under vacuum. The conversion was determined by gravimetrically. Copolymerization conditions are given in Table 4.2.

3.3.5 Preparation of 2-methoxy-3-oxo-2,3-diphenylpropyl 2-bromopropanoate (PI)

3.3.5.1 Synthesis of α – Methylol Benzoin Methyl Ether (MBME)

MBME was prepared according to the modification method of Ahn et al. [67]. 1,66 g of paraformaldehyde was added to a stirred solution of 10,3 g (45,6 mmol) benzoin methyl ether dissolved in 50 ml DMSO containing 0,1 g (1,8 mmol) KOH dissolved in 5 ml ethanol. The reaction was performed under nitrogen at 40 °C for 3 h. The reaction mixture was cooled to room temperature, neutralized with dilute HCl and then diluted to 120 ml by addition of a saturated NaCl solution. The mixture was then extracted with ethyl acetate and the extract was washed three times with saturated NaCl solution and dried over anhydrous MgSO₄. the solution was concentrated under reduced pressure to give a pale yellow oil, which was crystallized slowly in a refrigerator to give colorless crystals of α – methylol benzoin methyl ether (m.p. = 70 – 73 °C, yield 55%).

3.3.5.2 Synthesis of PI

PI was prepared according to the modified method of Paik et al. [65]. Under nitrogen, 1,66 ml (15,68 mmol) 2 – Bromopropionyl bromide was added dropwise to a stirring mixture of 1,6 g (6,25 mmol) MBME and 2,19 ml (15,68 mmol) triethylamine in 150 ml of CHCl_3 in an ice bath for 30 mins. After complete addition of the acid bromide, the reaction was stirred at room temperature for 3 h. The reaction mixture was washed with water (3 x 150 ml) and then dried over MgSO_4 . after filtration, evaporation of CHCl_3 gave a yellowish greasy product. It was dissolved and crystallized in ethanol then filtered and dried under vacuum (m.p. = 84 – 87 °C, yield 45%). UV: λ_{max} =338 nm, $\epsilon_{338\text{nm}}$ = 224 l. mol⁻¹ cm⁻¹.

¹HNMR (CDCl_3): δ (ppm) = 1,5 – 1,7 (d, 3H, -CH₃), 3,3 – 3,4 (s, 3H, -OCH₃), 4,2 – 4,3 (q, 1H, -CH), 4,7 – 4,8 (d, 1H, -CH₂), 5,0 – 5,1 (d, 1H, -CH₂), 7,2 – 7,5 (m, 8H, aromatic protons), 7,9 – 8,0 (d, 2H, aromatic protons) (Figure 3.3).

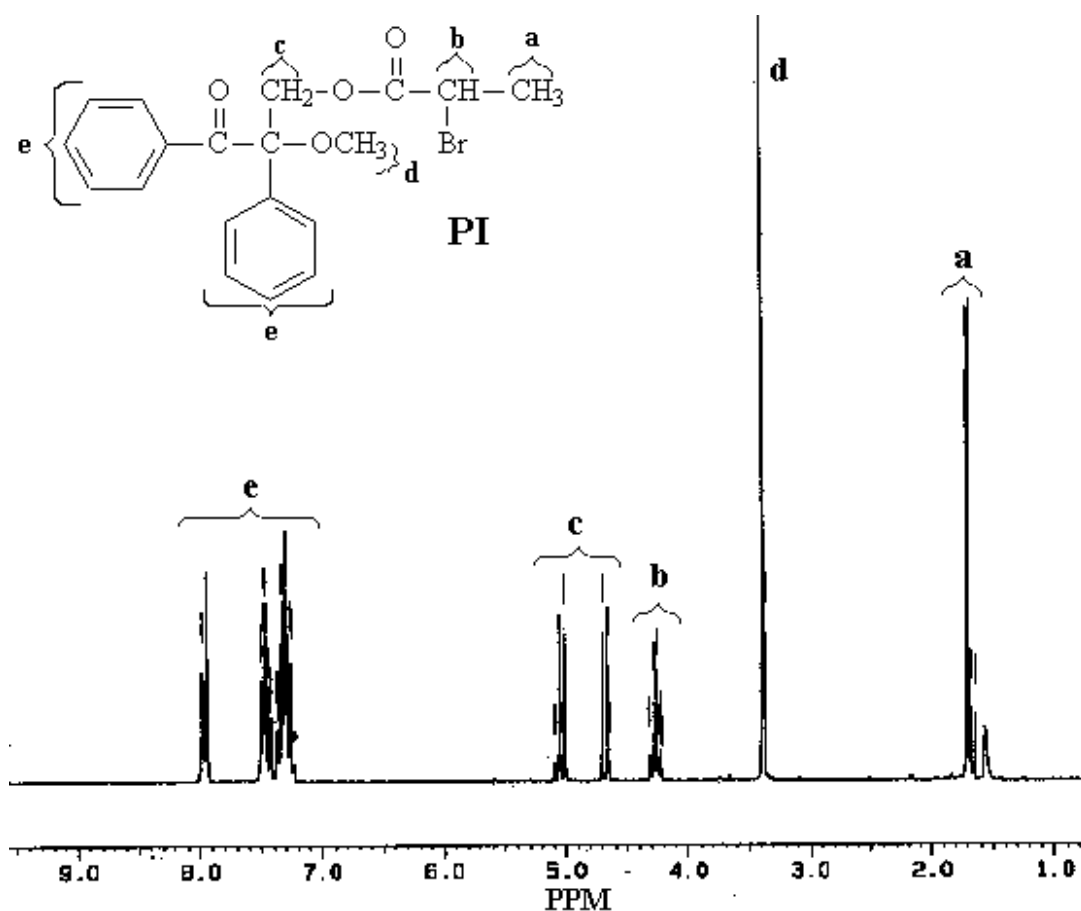


Figure 3.3. ¹HNMR spectrum of PI in CDCl_3 .

3.3.6 General Polymerization Procedure for ATRP of St and LC6 by using PI

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied three times, then certain amounts of styrene or LC6, solvent, ligand (PMDETA), CuBr and PI were added in the order mentioned under nitrogen. Solvent, diphenyl ether was only used with LC6 monomer. The reaction solution was bubbled by nitrogen to remove dissolved gases and then tube was immersed in an oil bath and held by a thermostate at 110 °C, with rigorous stirring. The polymerization was performed for a determined time and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipitated into excess methanol and filtered. The polymer was dried under vacuum. The conversion was determined by gravimetrically (Table 4.5).

3.3.7 General Polymerization Procedure for PIRP of LC6 and St

Appropriate solutions of above obtained prepolymers, solvent and a monomer were placed in Pyrex tubes. The mixtures were degassed with nitrogen in the usual manner prior to irradiation with an merry go round type photoreactor equipped with 16 Philips 8W/06 lamps emitting light at about 367 nm at 25⁰C. At the end of a given reaction time polymers were obtained from the reaction mixture by precipitation into methanol, filtered and dried in vacuo. The conversion of polymerization was determined by gravimetrically (Table 4.6) and block copolymers were purified by successive extraction in boiling cyclohexane.

4. RESULTS and DISCUSSION

In this thesis, we mainly present, two different synthetic routes for the obtaining liquid crystalline-amorphous block copolymers combination conventional free radical polymerization (CFRP) - atom transfer radical polymerization (ATRP) and photo-induced free radical polymerization (PIRP) - ATRP.

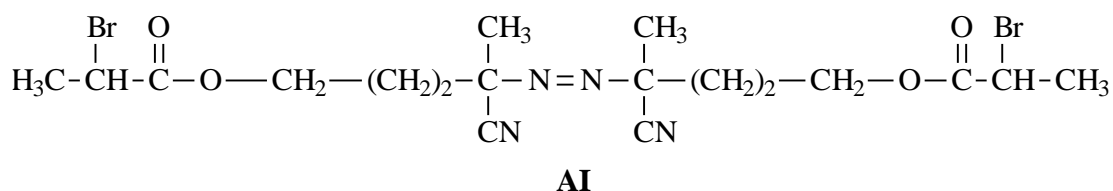
In the first part, using a difunctional initiator containing an ATRP initiator and a decomposable azo functionality (AI), block copolymerization was performed by applying first either CFRP or ATRP [68].

In the second part, using another difunctional initiator having an ATRP initiator and a decomposable photo-active group (PI), block copolymerization was carried out by applying first either ATRP or PIRP [69].

Moreover, each sythetic route was succesfully performed in the presence of liquid crystalline LC6 and styrene (St) monomer.

4.1. Preparation of Block Copolymers By Combination of CFRP and ATRP Mechanisms Using AI

In this part, ABA type amorphous-liquid crystalline block copolymers were synthesized via two-step procedure involving CFRP and ATRP methods [68]. This successive CFRP and ATRP initiation processes started from a difunctional azo alkyl halide low molar mass initiator containing one azo group and two bromine end groups. AI is highly efficient in initiating the CFRP and ATRP for the suitable monomers.

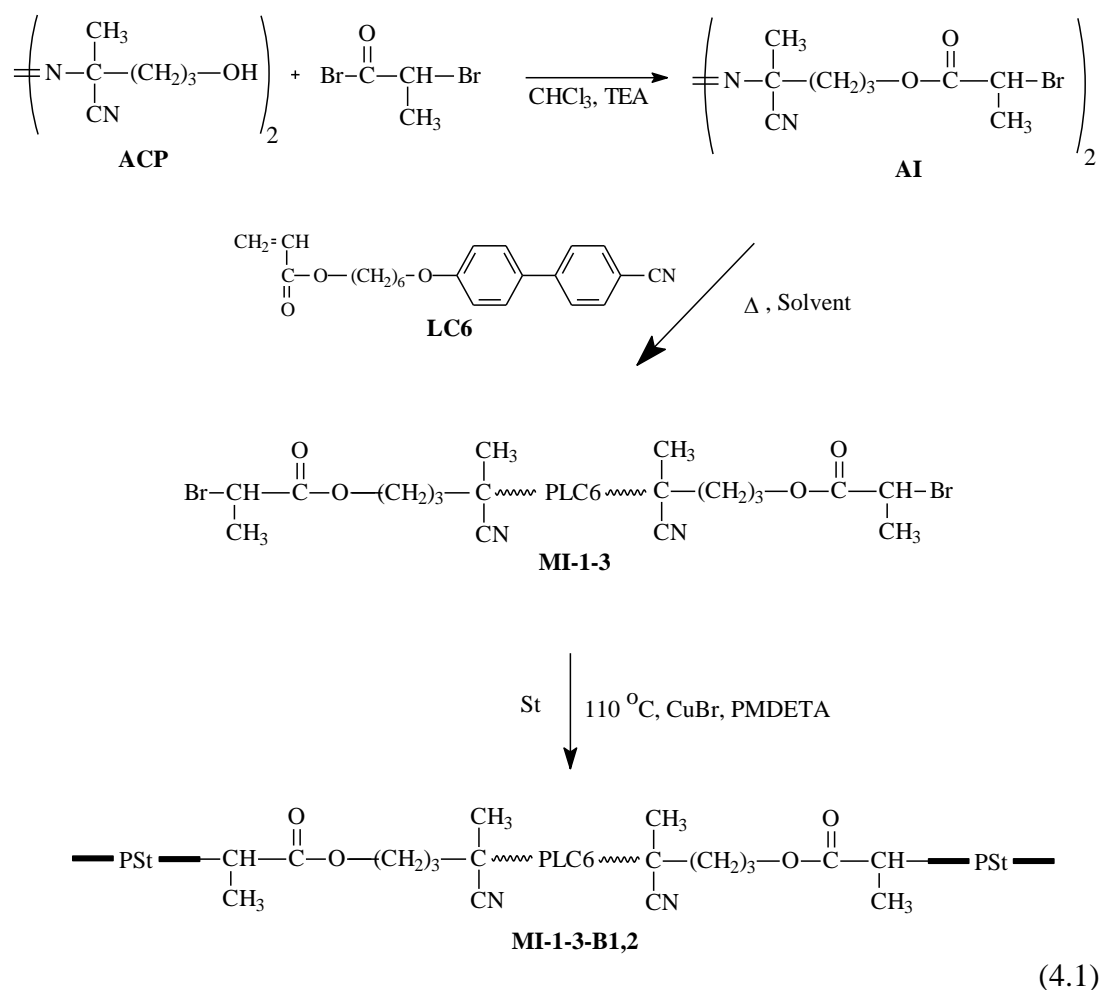


AI was prepared by esterification of the hydroxyl-azo compound with the acid halides and then polymerized in the presence of liquid crystalline or styrene monomer by the thermal decomposition of the azo moiety at 80 or 110 °C. Consequently, PLC6 or PSt homopolymers possessing two reactive bromine end groups in the main chain was obtained.

These macroinitiators PLC6 or PSt having bromine end groups was then isolated and subsequently used to initiate ATRP of the second monomer in the presence of copper catalyst.

4.1.1. Synthesis of PSt-*b*-PLC6-*b*-PSt Copolymers by CFRP and ATRP

In the first synthetic route, AI was first used for the polymerization of LC6 by CFRP as shown in Eq 4.1:



Polymerization conditions and results are collected in Table 4.1. Acrylic liquid crystalline segment which was obtained via this initiation method contained liquid crystalline macromolecular chain of the block copolymers. Since termination occurred predominantly by coupling, then macroinitiators MI-1-3 would have two functional bromine end groups for ATRP process (4.1).

$^1\text{H-NMR}$ spectrum prove the expected structure of the macroinitiator MI-1. According to the spectrum, the signals originating from esterificated Br end group of MI-1 were discerned at 1,8-2,0 ppm, ($-\text{CH}(\text{Br})\underline{\text{CH}_3}$), 2,0-2,3 ($-\underline{\text{CH}_2}-\underline{\text{CH}_2}$) and 3,9-4,2 ppm ($-\text{O}\underline{\text{CH}_2}$) (Figure 4.1).

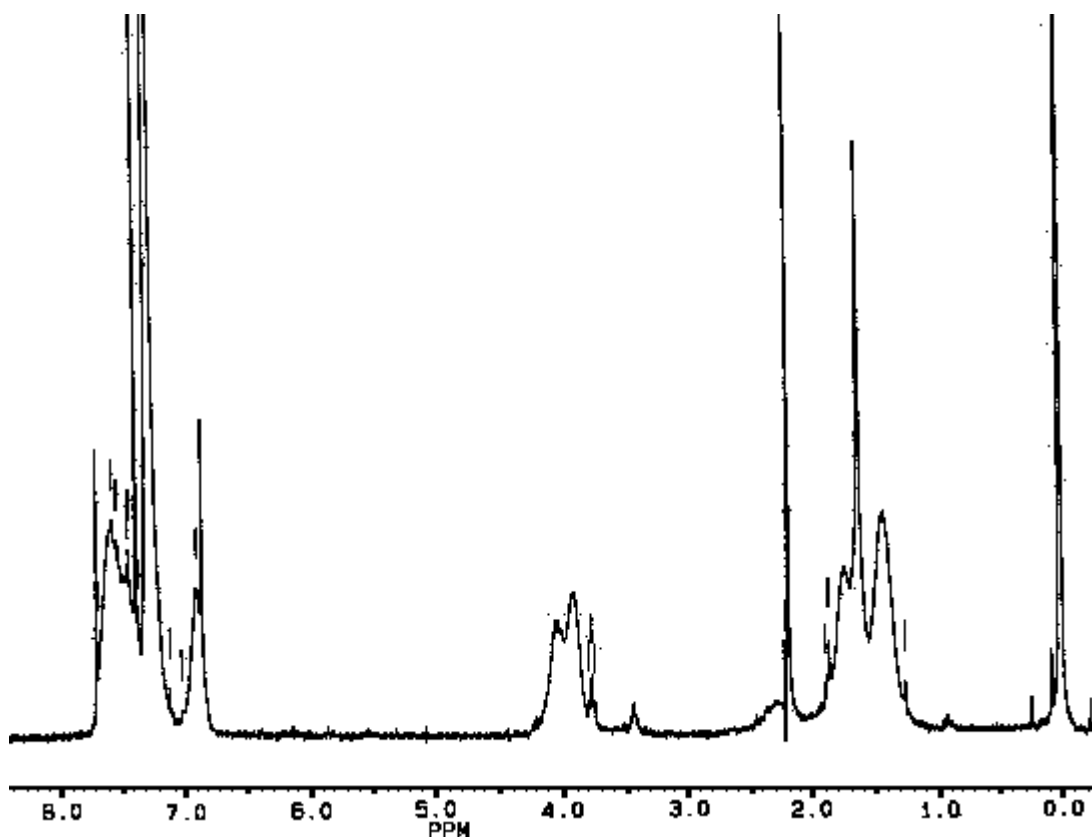


Figure 4.1. ^1H -NMR spectrum of MI-1 in CDCl_3 .

Table 4.1. CFRP of LC6 and St by using AI

Run No	[AI] (mol / l)	Solvent	Temperature (° C)	Time (h)	Conv. (%)	M_n^c	M_w / M_n^c
MI-1 ^a	$2,6 \times 10^{-3}$	Benzene	80	100	75	11100	1,63
MI-2 ^a	$7,7 \times 10^{-4}$	DMF	110	100	94	5200	1,32
MI-3 ^a	$2,6 \times 10^{-3}$	Benzene	80	100	88	7850	1,92
MI-4 ^b	$6,4 \times 10^{-2}$	Benzene	80	1	47	7300	1,55

^a [LC6] = $3,5 \times 10^{-1}$ mol / l.

^b [St] = 4,4 mol / l.

^c Determined from GPC, based on PSt standards.

Macroinitiators were isolated and subsequently used to initiate ATRP of styrene in the presence of a copper catalyst at the different reaction conditions (Table 4.2). The results of ATRP of styrene are presented in Table 4.3.

Table 4.2. ATRP of St and LC6 initiated by bromine terminated MI^a

Run No	Initiator No	[MI] (mol / l)	Solvent	[I ₀] ^b / [Cu ⁺] / [PMDETA] / [M ₀] ^c	Time (h)
MI-1-B1	MI-1	3,7 x 10 ⁻³	Bulk	1 / 21 / 42 / 2589	9
MI-2-B1	MI-2	8,7 x 10 ⁻³	Bulk	1 / 8 / 16 / 1000	6
MI-3-B1	MI-3	3,7 x 10 ⁻³	Bulk	1 / 21 / 42 / 2589	16
MI-3-B2	MI-3	1,7 x 10 ⁻³	Benzene	1 / 21 / 42 / 2589	11
MI-4-B1	MI-4	9,2 x 10 ⁻⁴	Diphenyl ether	1 / 64 / 128 / 500	96
MI-4-B2	MI-4	3,7 x 10 ⁻⁴	Diphenyl ether	1 / 21 / 42 / 2589	96

^a Temperature = 110 °C.

^b [I₀] = initial [MI].

^c [M₀] = initial [St] or [LC6].

Table 4.3. Results of ATRP of St and LC6 initiated by bromine terminated MI

Run No	Conv. (%)	M_n^a	$M_{n(\text{Theo})}^b$	$M_{n(\text{NMR})}^c$	M_w/M_n^a	% LC6 in copolymer ^c
MI-1-B1	22	79000	72000	82000	1,20	14
MI-2-B1	19	15500	25200	24000	1,11	22
MI-3-B1	39	99200	112500	113000	1,12	7
MI-3-B2	15	76500	49000	56000	1,10	14
MI-4-B1	2	10500	10200	70000	1,39	88
MI-4-B2	9	11100	88000	80000	1,29	90

^a Determined from GPC, based on PSt standards.

^b Calculated by $[M_o] / [I_o] \times \text{conv.} \times \text{MW}_{\text{monomer}} + M_n(\text{macroinitiator})$.

^c Calculated by ^1H – NMR.

Block copolymerization reached low conversions even yielding high molecular weight. On the other hand, polydispersities of the related block copolymers (MI-3-B2) decreased very sharply from 1,9 to 1,1 (Table 4.3).

These copolymers were purified by extraction with boiling cyclohexane which is selective solvent for PSt.

Block copolymer composition has been determined by ^1H -NMR and GPC measurements. The NMR spectrum of MI-1-B1 (Figure 4.2) displays signals at 1,2 - 2,1 ppm $-\text{CH}-\text{CH}_2$ (PSt) and $-\text{CH}-\text{CH}_2$, $(-\text{CH}_2)_4$ (PLC6), 3,6 - 4,0 ppm $-\text{OCH}_2$ (PLC6), 6,2 - 7,5 ppm (aromatic protons of PSt and PLC6).

The structure of the block copolymers was established by ^1H -NMR spectroscopy. Integration of the signals in ^1H -NMR spectrum of MI-1-B1 displays signals aromatic protons of St at 6,5 ppm and 3,9-4,0 ppm $-\text{OCH}_2$ groups of PLC6.

The clear indication of the block copolymer formation was determined by GPC with detection by refractive index recording. The GPC traces of the samples MI-1-B1, MI-3-B1, MI-3-B2 obtained using refractive index is reported in Figure 4.3 and 4.4 as a typical example.

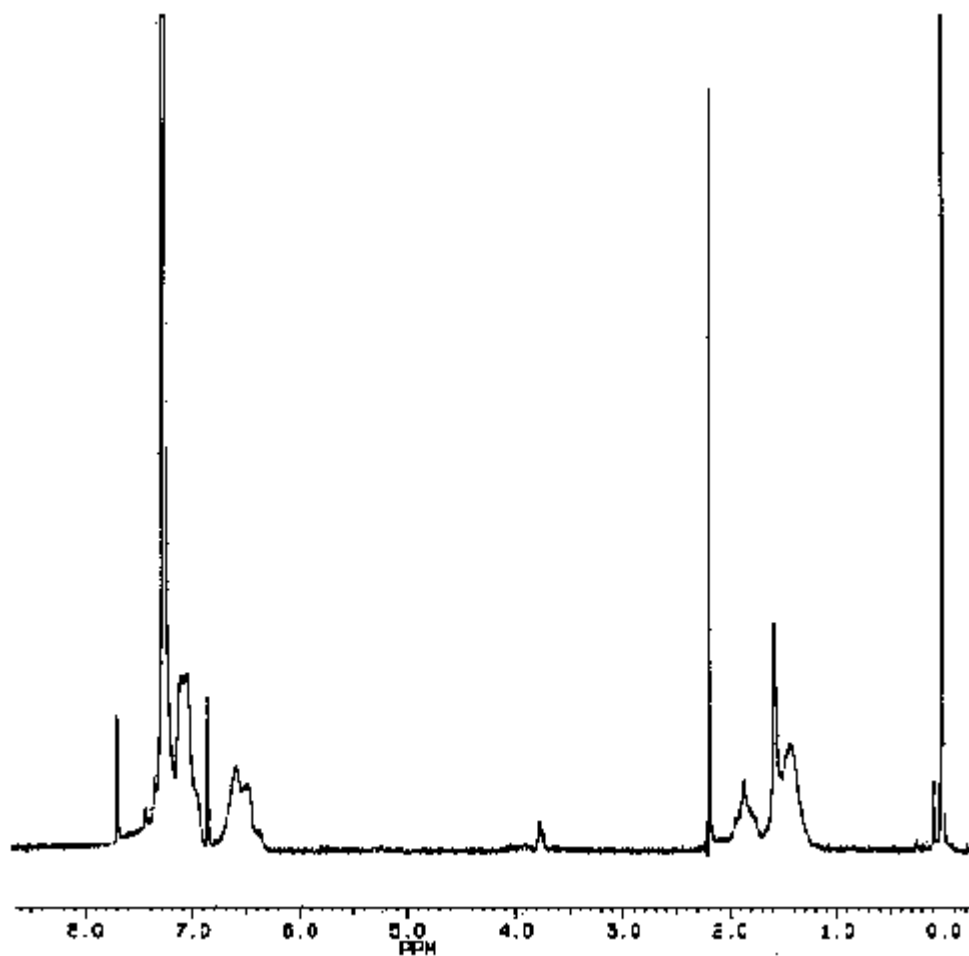


Figure 4.2. ^1H -NMR spectrum of MI-1-B1 in CDCl_3 .

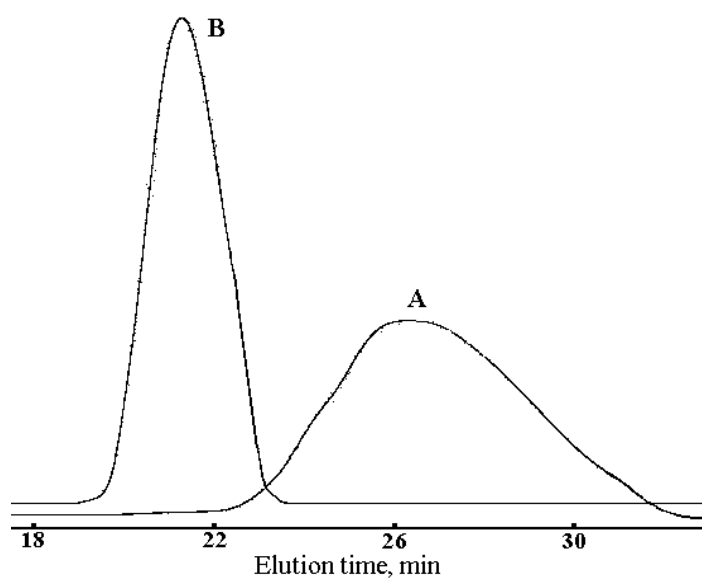


Figure 4.3. GPC traces of MI-1 (A), MI-1-B1 (B).

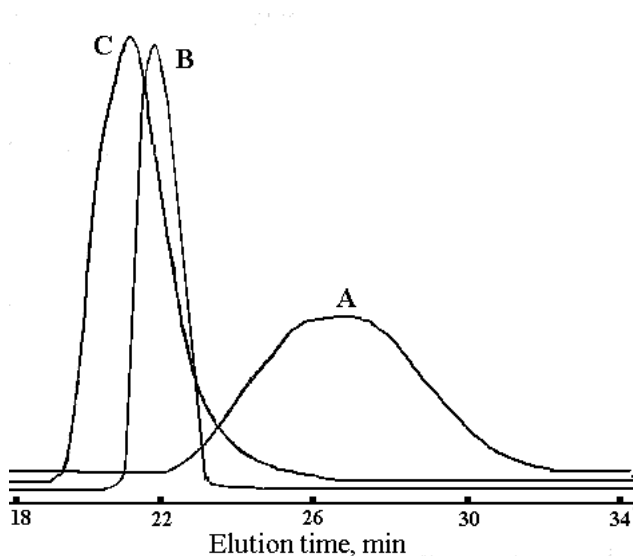


Figure 4.4. GPC traces of MI-3 (A), MI-3-B2 (B), MI-3-B1 (C).

They are practically superposable in the terms of shape and peak position, thus indicating the formation of a copolymer in which both PLC6 and PSt blocks of different lengths are uniformly distributed over whole macromolecular species determining the molecular weight dispersion curve. The number-average molecular weight $M_n = 79.000$ and 72.000 g/mol was calculated by GPC and theoretically for the MI-1-B1 sample respectively. Almost the same M_n values were obtained from $^1\text{H-NMR}$ analyses. Polydispersity of the related copolymer sample was decreased from 1,63 to 1,20. Conversion of the styrene monomer was ranged from 15 % to 39 %.

The narrow molecular weight distributions were also obtained for MI-3-B1, MI-3-B2 block copolymer samples (Figure 4.4).

The thermal behaviour of block copolymers MI-1-B1, MI-2-B1, MI-3-B1, MI-3-B2 and macroinitiators MI-1, MI-2, MI-3 was studied by DSC and polarizing microscopy. The phase transition temperatures are given in Table 4.4.

Table 4.4. Thermal and Liquid Crystalline properties of macroinitiators and block copolymers

Run No	T _g ^{a,b} (°C)	T _g ^{a,c} (°C)	T _{N-I} ^{a,d} (°C)
MI-1	39	-	120
MI-2	37	-	117
MI-3	38	-	123
MI-4	-	97	-
MI-1-B1	38	105	120
MI-2-B1	39	102	122
MI-3-B1	36	105	121
MI-3-B2	36	103	122
MI-4-B1	36	nd ^e	119
MI-4-B2	36	nd ^e	119

^a Detected by DSC.

^b Referred to PLC6 segment of polymer.

^c Referred to PSt segment of polymer.

^d Observed by polarizing microscopy.

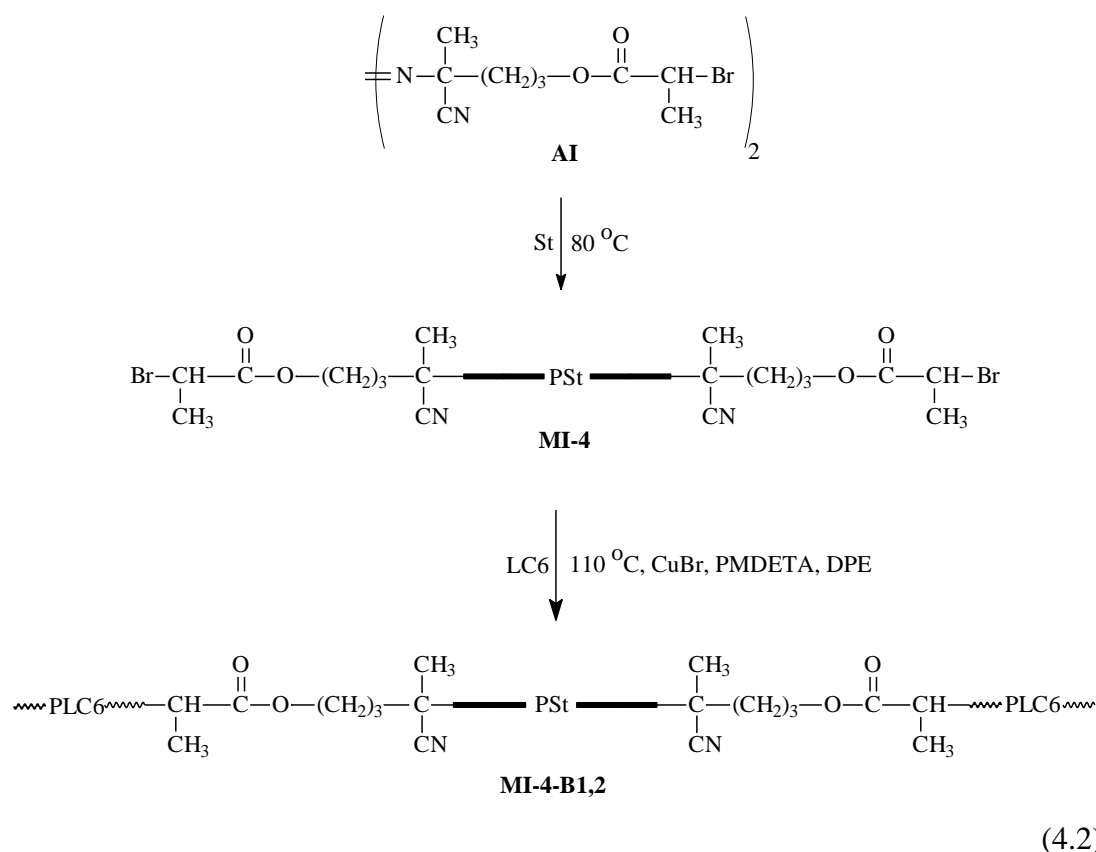
^e not detected.

Copolymers MI-1-B1, MI-2-B1, MI-3-B1, MI-3-B2 gave rise to two phases in the thermal range between the glass transition temperature (T_g) and the isotropization temperature (T_{N-I}) (Table 4.4). Their mesophase behavior is compared to that of the corresponding LC6 homopolymers [70]. For each copolymer sample the mesophase transition temperatures were relatively same of the corresponding LC6 homopolymer. Block copolymer samples show the glass transition temperatures of liquid crystalline block at the range of 36-38 °C and polystyrene block at the range of 102-105 °C depending on block compositions. Nematic-Isotropic transition temperatures were also observed between 117 to 123 °C under optical microscopy by different heating rates.

4.1.2. Synthesis of PLC6-*b*-PSt-*b*-PLC6 Copolymers by CFRP and ATRP

The different sequence of the same procedure may be employed as an alternative way to incorporate liquid crystalline segment into a block copolymer [68].

In this approach, styrene monomer was firstly polymerized by CFRP and then copolymerized by ATRP in the presence of liquid crystalline monomer (4.2).



The conditions and results of polymerization of styrene by CFRP are presented in Table 4.1.

Unfortunately the preparation of block copolymers using ATRP mechanism was not successful with liquid crystalline acrylate monomer.

In contrast, the polymerization of styrene using AI successfully produced a polystyrene macroinitiator (MI-4). This different behaviour was attributed to transfer of the bromine of AI to the propagating liquid crystalline acrylate radical. Since the styryl radical has relatively lower reactivity than LC acrylate radical [1].

The conditions and the results of ATRP of LC6 are given in Table 4.2 and Table 4.3.

The copolymerization obtained only low conversions and yielded low molecular weight polymers by GPC analyses. Polydispersity of the related copolymers (MI-4-B1,2) was remained roughly same with the precursor polymers (Table 4.3).

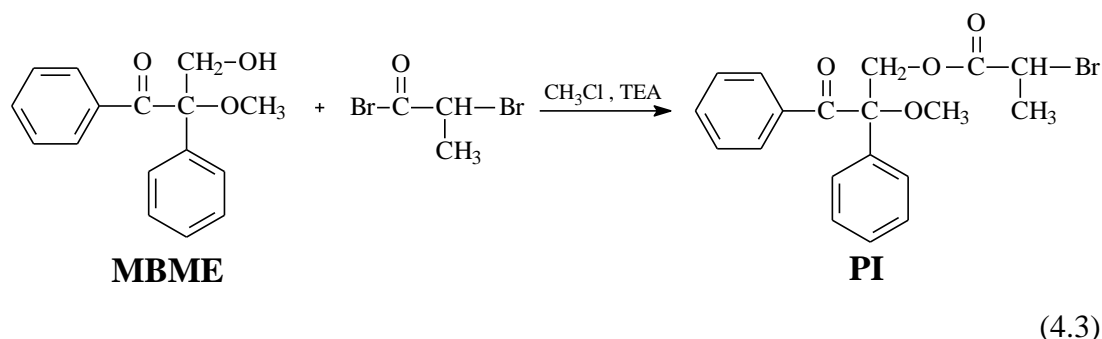
The observed molecular weights were found higher than the GPC values for the polymerization of LC6. This could be explained with the differences obtained by GPC when comparing the PLC6 to linear polystyrene standards.

ATRP of the liquid crystalline monomer require additional adjustments to the reaction conditions. Especially, the free radical polymerization difficulties for bulky LC6 monomer can be achieved by choosing specific ligand and copper catalyst concentration values in ATRP.

Thermal behaviour of the MI-4-B1, MI-4-B2 was observed quite similar transition temperatures with the related homopolymers and copolymers (Table 4.4).

4.2. Preparation of Block Copolymers By Combination of ATRP and PIRP Mechanisms Using PI

In this part, ABA type amorphous-liquid crystalline block copolymers were synthesized via two-step procedure involving ATRP and PIRP mechanisms [69]. For this purpose a bifunctional initiator having benzoin and halide groups in the same structure was synthesized by esterification of the α -methylol benzoin methyl ether with 2-bromopropanoyl bromide (4.3).



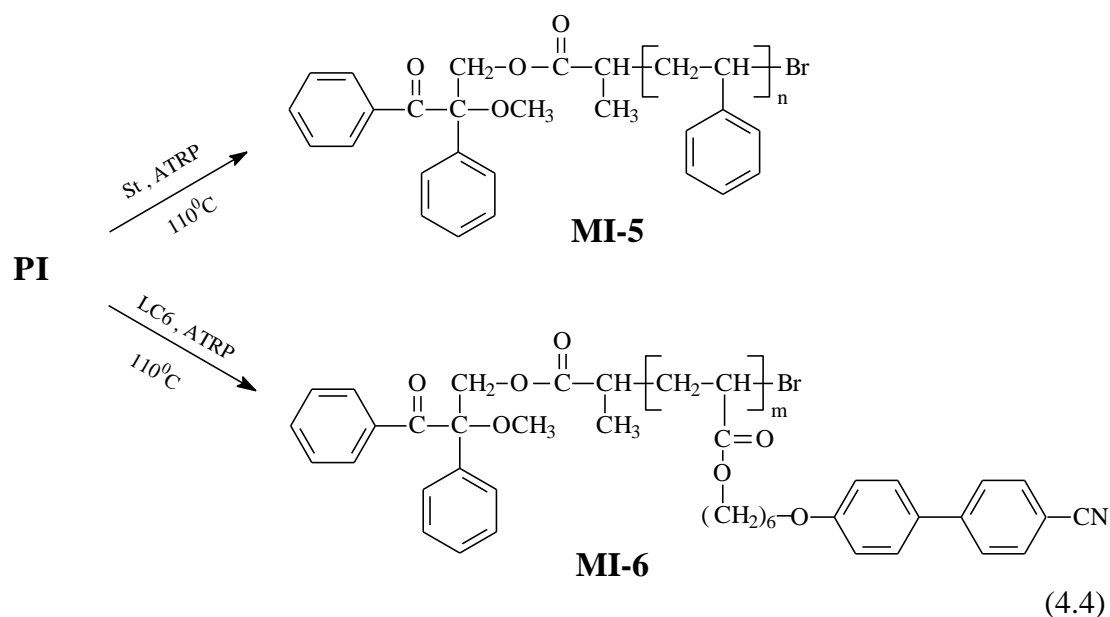
The structure of the new initiator was confirmed by spectroscopic investigations. The IR spectrum contain the characteristic CO ester band and the CO keto group of benzoin at 1725 and 1680 cm^{-1} , respectively. The $^1\text{H-NMR}$ spectrum recorded in CDCl_3 evidenced resonance signals of protons of relative intensities corresponding to the number and type of protons (Figure 3.3).

In the first stage this initiator was used in the ATRP of styrene at 110°C to obtain photoactive polymers having benzoin methyl ether moiety at the end of the polymer chain. In the second stage, photochemical polymerization of LC6 was performed by

utilizing the obtained photoactive polystyrenes as an initiator. The different sequence of the same procedure was also studied.

4.2.1 Preparation of Photoactive PSt/PLC6 by using ATRP Mechanisms

St or LC6 monomers were polymerized according to ATRP by utilizing PI in the presence of copper catalyst and yielded polymers having photoactive benzoin methyl ether group at the end of the polymer chain (4.4) [69].



The incorporation of benzoin groups into the polymer was evidenced in the case of polystyrene. Figure 4.5 shows the absorption spectrum of PI together with the absorption spectrum of polystyrene obtained by initiation via PI. It can be seen that both spectra contain an absorption band characteristic of the precursor benzoin group.

Typical results concerning the polymerization of St or LC6 in the presence of PI are presented in Table 4.5. The resulting polymers had $M_n = 4350$ and 6100 , $M_w/M_n = 1.1$ and 1.3 for the related polymers, respectively (Table 4.5).

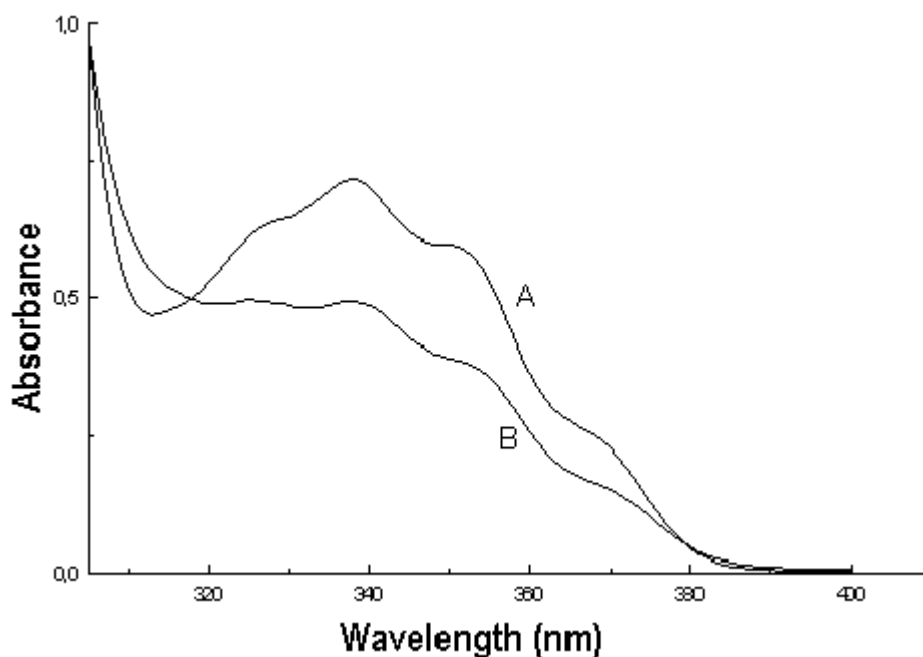


Figure 4.5. Absorption spectra of CH_2Cl_2 solutions containing (A) PI (0,032 mol/l), (B) Polystyrene initiated with PI (MI-5) (100 g/l).

In the case of MI-5, the reaction time was kept short to obtain low molecular weight polymer and unimodal macroinitiators with the narrow polydispersity ($M_w/M_n=1,1$) was obtained.

The increase in the molecular weight, without a significant increase in M_w/M_n , indicates that effective initiation of ATRP of St has taken place. The theoretical molecular weight for MI-6 macroinitiator was found higher than GPC values. This could be explained with the differences between polystyrene standards and poly liquid crystalline segment. In both cases, polymers with unimodal, narrow molecular weight distribution were obtained.

The structure of the MI-5 was confirmed by the ^1H -NMR spectrum that exhibited the signals in the range of 6,6-7,06 ppm corresponding to the two ortho protons of benzene ring and meta and para hydrogens. The methylene and methine protons of the polymer chain give signals at 1,1- 2,4 ppm (Figure 4.6).

Table 4.5. ATRP of St and LC6 by using PI^a

Product Code	Monomer	[PI-Br] (mol L ⁻¹)	Solvent	Time (h)	[I ₀] ^b / [Cu ⁺] / [PMDETA] / [M ₀] ^c	Conv. (%)	M _n (GPC) ^d	M _n (Theo) ^e	M _w / M _n
MI-5	St	1,7 x10 ⁻²	Bulk	4	1 / 1 / 1 / 500	8	4350	3900	1,1
MI-6	LC6	4,3 x 10 ⁻³	Diphenylether	96	1 / 1 / 1 / 75	50	6100	13100	1,4

^a Temperature = 110 °C.

^b Initial initiator concentration.

^c Initial monomer concentration.

^d Determined from GPC, based on PS standarts.

^e Calculated by [M₀] / [I₀] x conv. x MW_{monomer}.

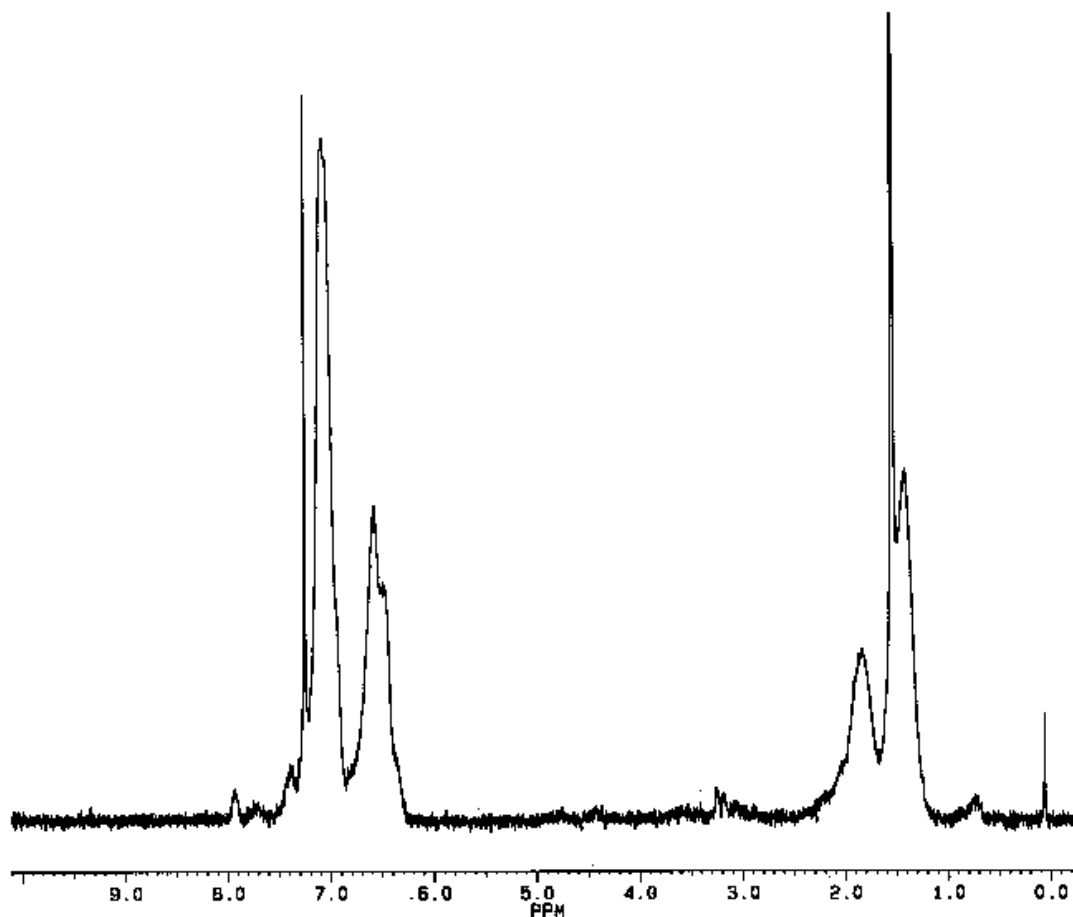


Figure 4.6. ^1H -NMR spectrum of MI-5 in CDCl_3 .

^1H -NMR spectrum of MI-6 prove the expected structure of the liquid crystalline homopolymers. According to the spectrum, the signals 1,2-2,1 ppm $-(\text{CH}-\text{CH}_2)$, $(-\text{CH}_2)_4$, 3,6-4,0 ppm $-\text{OCH}_2$, 6,2-7,5 ppm (aromatic protons) and 7,0-8,0 ppm aromatic protons of the benzoin methyl ether groups (Figure 4.7).

^1H -NMR analyses supported the succesful incorporation of benzoin methyl ether terminal groups at the both ends of the PSt or PLC6 chains.

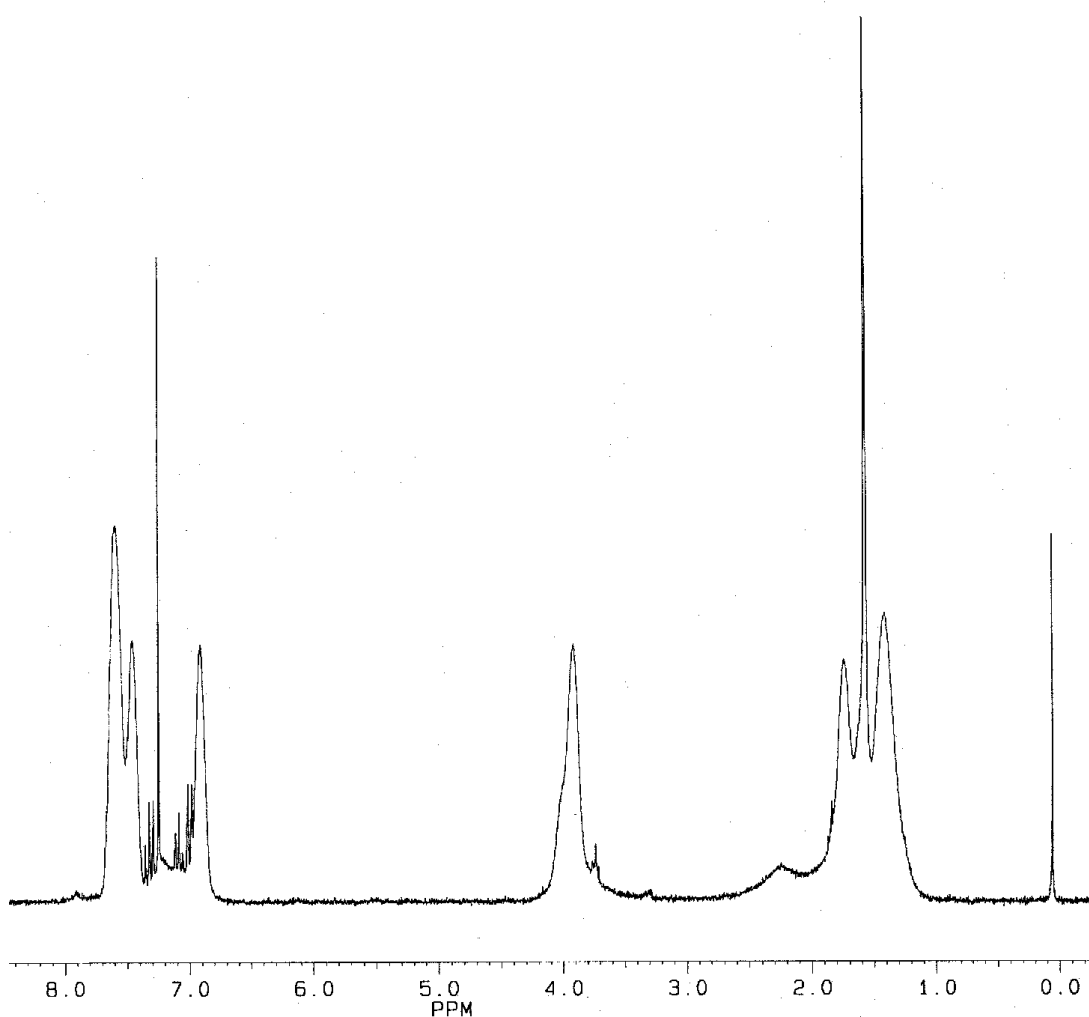
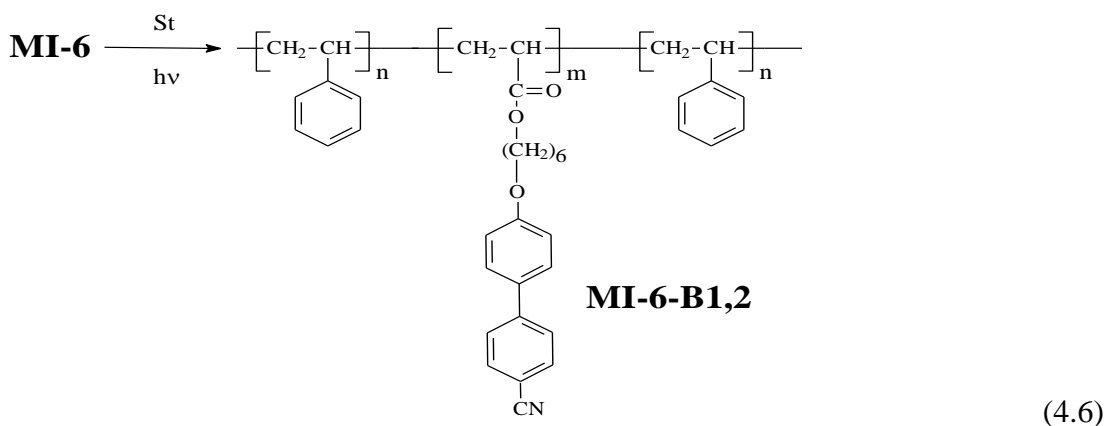
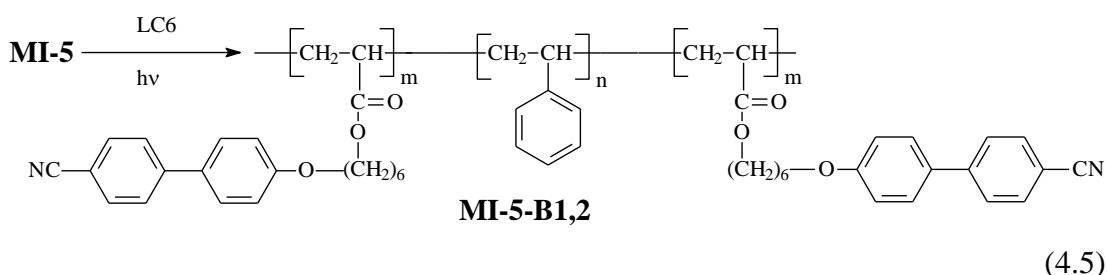


Figure 4.7. ^1H NMR spectrum of MI-6 in CDCl_3 .

4.2.2 Preparation of Block Copolymers

Photolysis of terminal benzoin groups of polymers in the presence of a second monomer is an elegant way to prepare block copolymers. In the second stage block copolymers were synthesized by utilizing the obtained photoactive polymers [69]. The photoactive polymers will decompose on irradiation and form two radicals, namely polymeric alkoxybenzyl radical and low molecular mass benzoyl radical. In this connection we refer the work of Pappas who demonstrated that both radicals are equally effective as initiators in the polymerization of methyl acrylate and methyl methacrylate whereas greater reactivity of benzoyl radical in the polymerization of styrene has been presented [26,71]. In our case it would appear necessary for the polymer bound alkoxy benzyl radical to initiate polymerization for successful block

copolymerization. However, if monomers like St or LC6 which prefer termination mainly by combination are employed, polymer bound alkoxybenzyl radicals can also contribute to the formation of block copolymer in the termination step by coupling with the propagating radicals derived from either benzoyl or alkoxy benzyl radical (4.5,6) [72].



Typical results concerning the block copolymerization of St and LC6 using photoactive macroinitiators are presented in Table 4.6.

MI-5-B1 and MI-5-B2 block copolymers were obtained with the very high yield and in a long reaction time. As can be seen both the monomer concentration (LC6) and solvent affect the conversion, block yield and composition of the block copolymer. Furthermore, the LC6 ratio in the macromolecular chain increases with the increasing monomer (LC6) concentration in the polymerization system. The highest amount of block copolymer formation was obtained by using benzoin methyl ether attached PSt and high concentration of LC6 monomer. The composition of the copolymers was estimated from ^1H -NMR data with the ratio of peak intensities at 6,5 ppm for aromatic protons of PSt and 3,9-4,0 ppm $-\text{OCH}_2$ groups of PLC6.

^1H -NMR spectrum of the block copolymer MI-5-B1 is given in Figure 4.8.

Table 4.6. Block Copolymerization^a by utilizing photoactive macroinitiators, obtained by ATRP

Product Code	[MI] (mol L ⁻¹)	Monomer	[Monomer] (mol L ⁻¹)	Solvent	Time (h)	Conv. (%)	M _n (GPC) ^b	M _n (NMR) ^c	M _w / M _n	Block Copolymer Content of the Reaction Mixture ^d (%)	Block Copolymer Composition ^c PLC6, %
MI-5-B1	6,0 x 10 ⁻⁴	LC6	8,6 x 10 ⁻²	CH ₂ Cl ₂	110	54	6600	5500	1,5	48	21
MI-5-B2	6,0 x 10 ⁻⁴	LC6	2,3 x 10 ⁻¹	DMF	110	92	10000	6400	2,2	85	33
MI-6-B1	3,0 x 10 ⁻³	St	8,7	Bulk	20	7,7	20000	22000	2,6	25	28
MI-6-B2	5,0 x 10 ⁻³	St	8,7	Bulk	20	5,6	16000	14000	3,4	30	43

^a $\lambda > 300$ nm, temperature: 25°C

^b Determined from GPC, based on PS standards.

^c Calculated by ¹H – NMR.

^d After extraction with boiling cyclohexane.

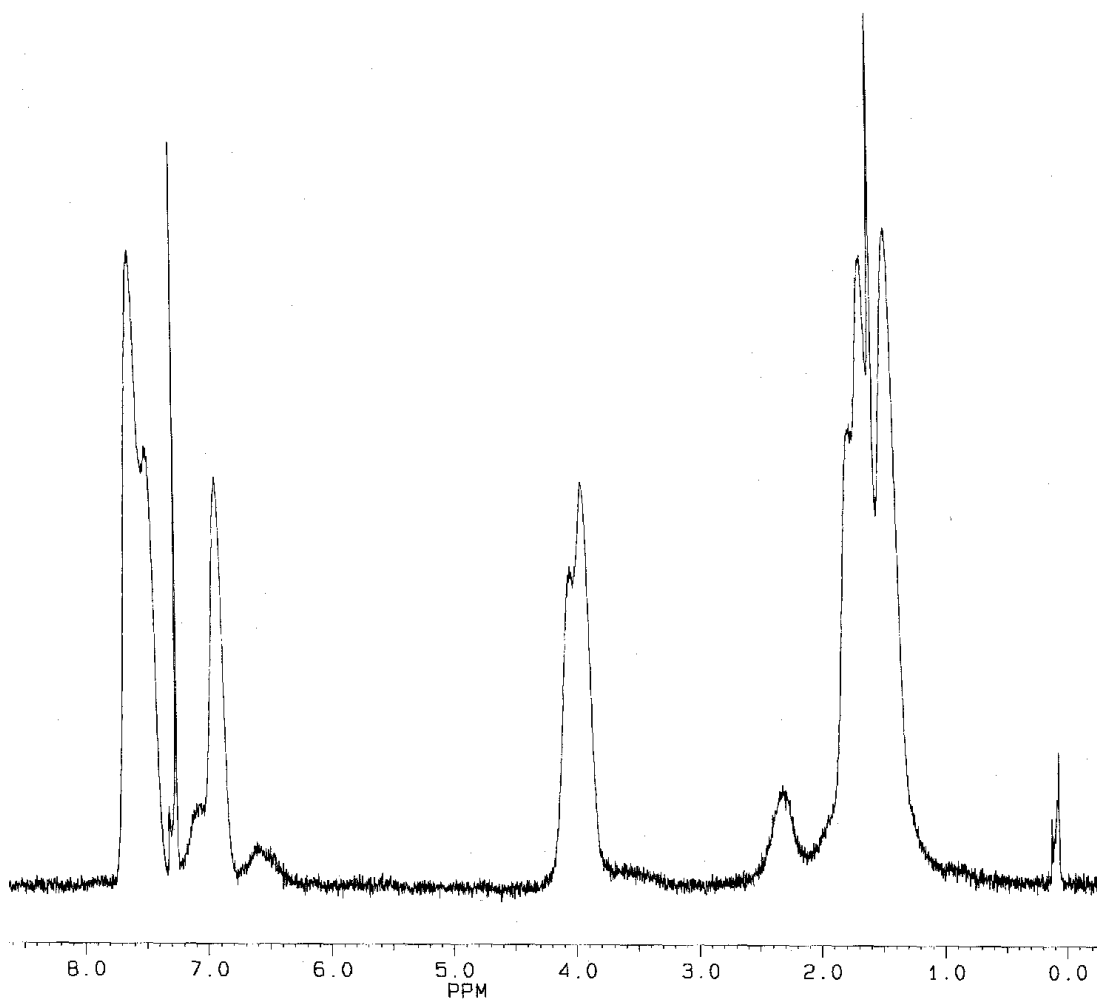


Figure 4.8. ^1H -NMR spectrum of MI-5-B1 in CDCl_3 .

^1H -NMR spectrum of MI-5-B1 (Figure 4.8) displays signals at 1,2 – 2,1 ppm $-\text{CH}-\text{CH}_2-$ (PSt) and $-\text{CH}-\text{CH}_2-$, $(-\text{CH}_2)_4$ (PLC6), 3,6-4,0 ppm $-\text{OCH}_2-$ (PLC6), 6,2 – 7,5 ppm (aromatic protons of PSt and PLC6).

These copolymers were purified by extraction with boiling cyclohexane which is selective solvent for homo PSt. GPC analysis clearly indicates the formation of block copolymer; Figure 4.9 shows the GPC chromatogram recorded with the prepolymer and extracted block copolymer. The new peak at a higher molecular weight is ascribed to the block copolymer.

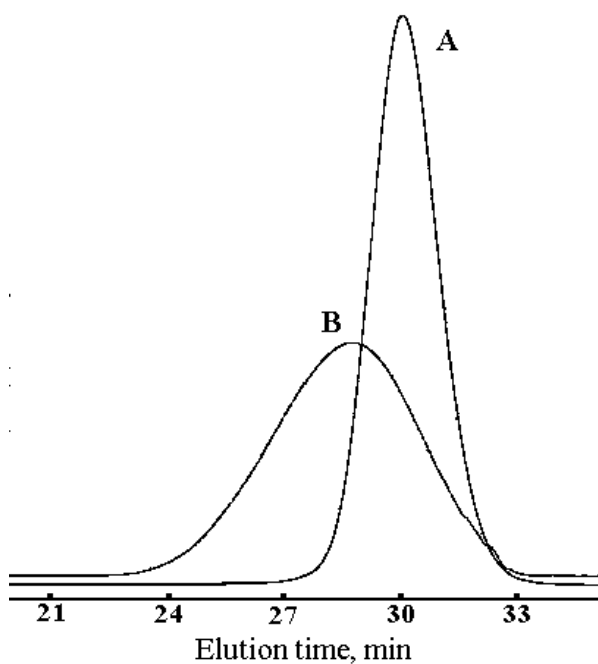


Figure 4.9. GPC traces of MI-5 (A), MI-5-B1 (B).

Photoactive liquid crystalline macroinitiator (MI-6) was also employed in the polymerization of styrene to obtain block copolymers. As shown in Table 4.6, shorter reaction times and lower conversions were obtained compared to polystyrene macroinitiator.

Furthermore a relatively good correlation between the GPC and ^1H -NMR data regarding molecular weights of the block copolymers was also observed. Some measured differences may be due to the differences in the hydrodynamic volumes of the corresponding segments of PLC6 observed in GPC and those of PSt standards.

The thermal behaviour of block copolymers and macroinitiators was studied by DSC and polarizing microscopy. The phase transition temperatures are given in Table 4.7.

Table 4.7. Thermal and Liquid Crystalline properties of macroinitiators and block copolymers.

Run No	T _g ^{a,b} (°C)	T _g ^{a,c} (°C)	T _{N-I} ^{a,d} (°C)
MI-5	-	100	-
MI-6	45	-	117
MI-5-B1	45	101	115
MI-5-B2	46	98	118
MI-6-B1	45	100	nd ^e
MI-6-B2	46	99	117

^a Detected by DSC.

^b Referred to PLC6 segment of polymer.

^c Referred to PSt segment of polymer.

^d Observed by polarizing microscopy.

^e not detected.

Copolymers MI-5-B1, MI-5-B2 gave rise to two phases in the thermal range between the glass transition temperature (T_g) and the isotropization temperature (T_{N-I}) (Table 4.7). Their mesophase behavior is compared to that of the corresponding LC6 homopolymers [70]. Each copolymer sample the mesophase transition temperatures were relatively same of the corresponding LC6 homopolymer. Block copolymer samples show the glass transition temperatures of liquid crystalline block at the range of 43 °C – 45 °C and polystyrene block at the range of 98 °C - 100 °C depending on block compositions. Nematic-Isotropic transition temperatures were also observed between 115 °C to 118 °C under optical microscopy by different heating rates.

5. CONCLUSION

This thesis has described the synthesis and investigation of a novel kind of block copolymers comprising both amorphous and liquid crystalline blocks within the same polymer structure. Block copolymerization via CFRP and ATRP or ATRP and PIRP routes provides a versatile two step method applicable to the vinyl monomers. Synthesis of vinyl polymers with controlled molecular weight and narrow molecular weight distribution were obtained and characterized.

Thermal and spectroscopic data show that two blocks of different chemical composition are at least partly phase-separated in the glassy and LC phase and undergo distinct transitions which are also observed through optical microscopy measurements.

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