

**SYNTHESIS OF LIQUID CRYSTALLINE
CONTAINING MALEIMIDE COPOLYMERS**

**M.Sc. Thesis by
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Department: Polymer Science and Technology

Programme: Polymer Science and Technology

AUGUST 2006

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İSTANBUL TEKNİK ÜNİVERSİTESİ « FEN BİLİMLERİ ENSTİTÜSÜ

**SIVI KRİSTAL İÇEREN MALEİMİD
KOPOLİMERLERİNİN SENTEZİ**

YÜKSEK LİSANS TEZİ

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July, 2006

Mevzun YÜKSEL

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ABBREVIATIONS

FRP	: Free Radical Polymerization
CRP	: Controlled / “Living” Radical Polymerization
ATRP	: Atom Transfer Radical Polymerization
ATRA	: Atom Transfer Radical Addition
LC	: Liquid Crystal
LCP	: Liquid Crystalline Polymers
PMDETA	: N,N,N,N',N''pentamethyldiethylenetriamine
LC6	: 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate
MI	: Maleimide
NCMI	: N-Cyclohexylmaleimide
DMSO	: Dimethyl sulfoxide
DSC	: Differential Scanning Calorimetry
¹H-NMR	: Nuclear Magnetic Resonance
GPC	: Gel Permeation Chromatography
TGA	: Thermogravimetric Analysis

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SYMBOLS

M_n	: Number average molecular weight
M_w	: Weight average molecular weight
M_w/ M_n	: Molecular weight distribution
DP_n	: Degree of polymerization
k_a, k_d	: Rate constants of activation and deactivation steps of the initiation in radical polymerization
K_{eq}	: Equilibrium rate constant in radical polymerization
k_p, k_t	: Rate constant of propagation and rate constant of termination
T_g	: The glass transition temperature
T_i	: The initial decomposition temperature
T_{50}	: The half-weight loss temperature

SYNTHESIS OF LIQUID CRYSTALLINE CONTAINING MALEIMIDE COPOLYMERS

SUMMARY

In the last decade, the ability to synthesize macromolecules with complex and controlled architectures is becoming an increasingly important aspect of polymer science by being able to control the radical polymerization. It is seen a considerable increase in new controlled radical polymerization techniques. Specifically, controlled architectures possess some characteristics which are molecular weight control, low polydispersity, end group control and a living nature.

In 1995, Matyjaszewski et al. developed an alternative living radical polymerization process using a copper (I)-catalyzed atom transfer process (ATRP). Meanwhile, N-substituted maleimides have become interesting monomers because of the superiority of their polymers or copolymers in thermal stability.

In this thesis, free radical polymerization (FRP) and atom transfer radical polymerization (ATRP) was applied to copolymerize liquid crystalline acrylate monomer and N-substituted maleimide monomer. Spectral and thermal properties of resultant copolymers were investigated.

SIVI KRİSTAL İÇEREN MALEİMİD KOPOLİMERLERİNİN SENTEZİ

ÖZET

Son yıllarda radikal polimerizasyon üzerinde kontrol sağlanmasıyla kompleks ve kontrollü mimariye sahip makromoleküllerin sentezi üzerine yapılan çalışmalar, polimer biliminde gittikçe artan bir öneme sahiptir. Yeni kontrollü radikal polimerizasyon tekniklerinin gelişmesinde gözle görülür bir artış gözlenmektedir. Kontrollü mimari denilince, molekül ağırlığı kontrolü, düşük polidispersite, uç grup kontrolü ve yaşayan karakter akla gelmektedir.

1995 yılında Matyjaszewski ve grubu atom transfer radikal polimerizasyonu'nu (ATRP) gerçekleştirmişlerdir. ATRP, Cu(I) / Ligand sistemi ile katalizlenen yaşayan serbest radikal polimerizasyon sistemidir. Termal kararlılığa sahip polimer ve kopolimerlerinin üstünlüğünden dolayı, N-süstitüe maleimid'lerin radikal kopolimerizasyonları şimdiye kadar pek çok kez uygulanmıştır.

Bu çalışmada; N-süstitüe maleimid monomeri ile bir sıvı kristal akrilat monomerin, serbest radikal polimerizasyon (FRP) ve atom transfer radikal polimerizasyon (ATRP) yöntemleri ile kopolimerizasyonu gerçekleştirilmiş, sonuç kopolimerlerin termal ve yapısal özellikleri incelenmiştir.

1. INTRODUCTION

Free radical polymerizations are generally poorly controlled, producing high molecular weight polymers at the early stages of polymerization and ultimately poorly defined polymers with high polydispersity. Recently Matyjaszewski and coworkers [1] reported an efficient way of performing radical polymerization [atom transfer radical polymerization (ATRP)] in a living controlled manner to overcome the disadvantages of classical radical polymerization. The latest developments in the area of controlled radical polymerization have opened new synthetic possibilities for the synthesis of vinyl polymers with controlled molecular weights and narrow molecular weight distributions.

ATRP has been used to copolymerize monomers that will undergo radical homopolymerization as well as combinations of these monomers with olefins that will not undergo radical homopolymerization such as N-Cyclohexylmaleimide [2-4].

Maleimide and its N-substituted derivatives are 1,2-disubstituted ethylenes. N-substituted maleimides have become interesting monomers that can be either radically copolymerized with other vinyl monomers [5,6] or homopolymerized [7] by radical and anionic initiators despite their 1,2-disubstituted ethylene structure. Many works on their radical polymerization and copolymerization have been performed so far because of the superiority of their polymers or copolymers in thermal stability [8]. The incorporation of rigid polar maleimide units in the backbones increases the backbone rigidity and molecular interactions, so the glass transition temperature of the copolymer is increased greatly.

Liquid crystals (LCs) signify a state of aggregation that is intermediate between the crystalline solid and the amorphous liquid. A substance in this state is strongly anisotropic in some of its properties as crystals and yet exhibits a certain degree of fluidity like liquids. Polymer liquid crystals are a class of material that combines the properties of polymers with those of LCs. Liquid crystalline polymers are excellent structural materials for engineering applications because of their excellent chemical

and heat resistance, high mechanical properties, high dimensional stability, low viscosity during processing, low thermal shrinkage, and electro optic and rheological properties [9].

In this study, to get thermally stable alternating copolymers, radical copolymerization of liquid crystalline acrylate monomer (LC6) with N-Cyclohexylmaleimide has been performed via ATRP and FRP mechanisms.

2. THEORETICAL PART

2.1 Free Radical Polymerization (FRP)

Free radical polymerization has been a very important industrial process because of its distinct advantages over other polymerization methods, such as tolerance to trace impurities, less stringent conditions, and also to be able to polymerize a wide range of monomers [10]. The polymers obtained via this method are used in the manufacture of numerous products such as fabrics, surface coatings, plastics, paints, packaging, and contact lenses [11].

In step-growth polymerization reactions it is often necessary to use multifunctional monomers if polymers with high molar masses are to be formed; this is not the case when addition reactions are employed. Long chains are readily obtained from monomers such as vinylidene compounds with the general structure $\text{CH}_2=\text{CR}_1\text{R}_2$. These are bi-functional units, where the special reactivity of π -bonds in the carbon to carbon double bond makes them susceptible to rearrangement if activated by free radical initiators. The active center created by this reaction then propagates a kinetic chain which leads to the formation of a single macromolecule whose growth is stopped when the active centre is neutralized by a termination reaction. The complete polymerization proceeds in three distinct stages: (i) Initiation, when the active center which acts as a chain carrier is created; (ii) Propagation, involving growth of the macromolecular chain by a kinetic chain mechanism and characterized by a long sequence of identical events, namely the repeated addition of a monomer to the growing chain; (iii) Termination, whereby the kinetic chain is brought to a halt by the neutralization or transfer of the active center. Typically the polymer formed has the same chemical composition as the monomer, i.e. each unit in the chain is a complete monomer and not a residue as in most step-growth reactions. [12]

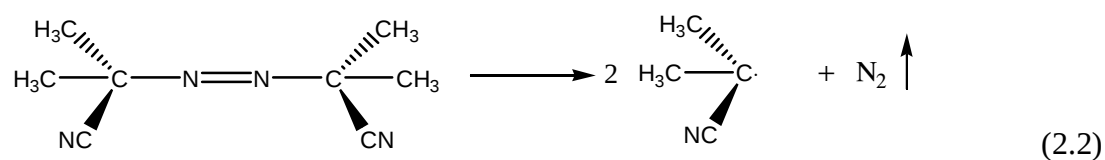
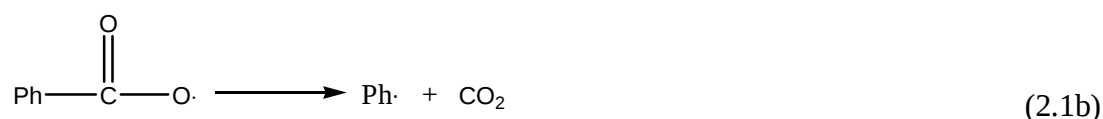
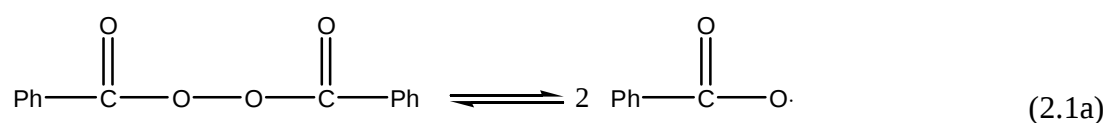
2.1.1 Initiators and Monomers Fitted for Free Radical Polymerization

2.1.1.1 Initiators

An effective initiator is a molecule which, when subjected to heat, electromagnetic radiation, or chemical reaction, will readily undergoes homolytic fission into radicals of greater reactivity than the monomer radical. These radicals must also be stable long enough to react with a monomer and create an active centre. Particularly useful for kinetic studies are compounds containing an azonitrile group as the decomposition kinetics is normally first order and the rates are unaffected by the solvent environment.

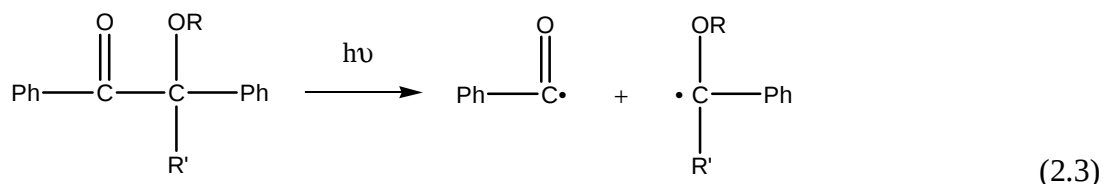
Typical radical producing reactions are [12-14]:

(1) Thermal decomposition can be usefully applied to organic peroxides or azo compounds, e.g. benzoyl peroxide when heated eventually forms two phenyl radicals with loss of CO_2 (2.1) and azobisisobutyronitrile (AIBN) is decomposed by giving cyanoisopropyl radicals (2.2).

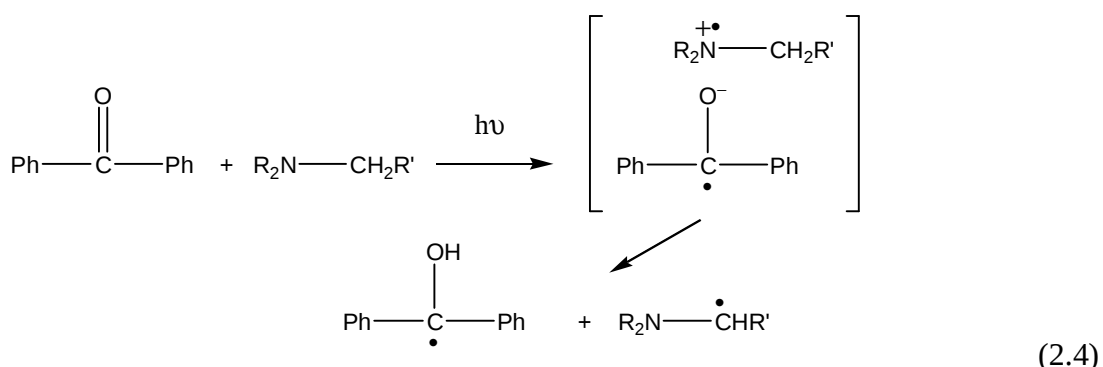


(2) Photoinitiators are usually classified as type I and type II initiators according to the mechanism by which primary radicals are generated. Photoinitiators of type I decompose via a direct unimolecular photofragmentation process, usually α -fragmentation (i.e., bond breakage occurs at a bond adjacent to the carbonyl group, as for benzoin ethers and acyl phosphine oxides) or β -fragmentation (α -haloketones).

Examples of type I photoinitiators include benzoin derivatives such as benzoin ethers, α -aminoalkylphenones, and acyl phosphine oxides. Benzoin ethers readily undergo α -fragmentation on exposure to near UV light (2.3) in a process that is not quenched by oxygen, thereby making them suitable for curing in air.



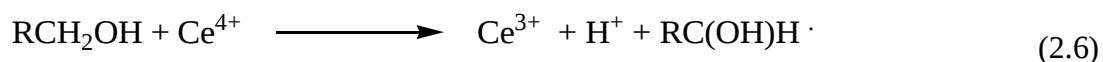
Aromatic ketones such as benzophenone and thioxanthone are typical photoinitiators of type II. Type II photoinitiators normally generate radicals by abstracting hydrogen from the environment or undergoing photoinduced electron and hydrogen transfer with a coinitiator resulting in radical ions that fragment to generate radicals (2.4). The most commonly employed coinitiators for aromatic ketones are tertiary amines.



(3) Redox reactions, e.g. the reaction between the ferrous ion and hydrogen peroxide in solution produce hydroxyl radicals (2.5).



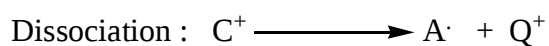
Alkyl hydroperoxides may be used in place of H_2O_2 . A similar reaction is observed when cerium (IV) sulphate oxidizes an alcohol (2.6):



(4) Persulphates (2.7) are useful in emulsion polymerizations where decomposition occurs in the aqueous phase and the radical diffuses into a hydrophobic, monomer containing, droplet.

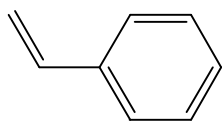


(5) Ionizing radiation such as α , β , γ or X-rays (2.8) may be used to initiate a polymerization, by causing the ejection of an electron followed by dissociation and electron capture to produce a radical.

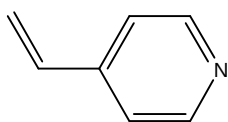


2.1.1.2 Monomers

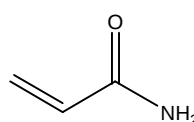
Most of the vinylic, acrylic and dienic monomers (2.9) can undergo free radical polymerization [13].



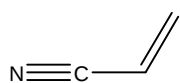
Styrene



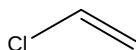
4-Vinyl pyridine



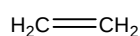
Acrylamide



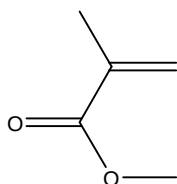
Acrylonitrile



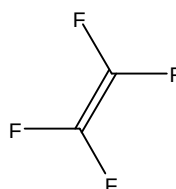
Vinyl chloride



Ethylene



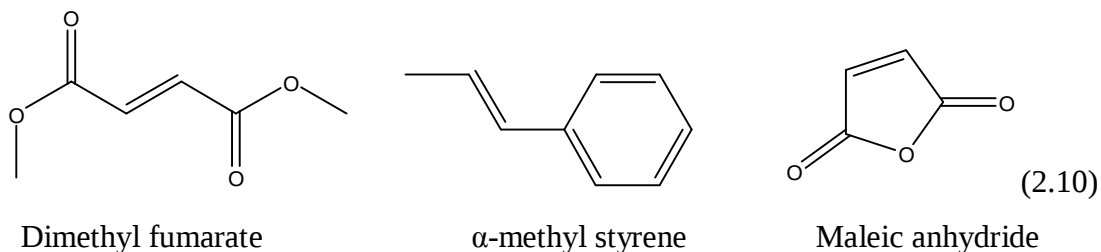
Methyl methacrylate



Tetrafluoro ethylene

(2.9)

Some potential monomers (2.10) do not form polymers under usual free radical polymerization conditions. Such as α -methyl styrene is involved in polymerization-depolymerization equilibrium above a ceiling temperature. Maleic anhydride and dimethyl fumarate are symmetrically substituted ethylenes therefore; they can not be polymerized by free radical polymerization. [13]



2.1.2 Mechanism of Free Radical Polymerization

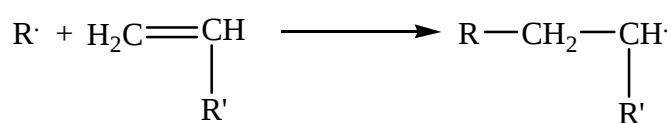
2.1.2.1 Initiation

The initiation reaction is the attack of a monomer molecule by a primary radical originating from the initiator. This process involves two reactions (2.11):

- Decomposition of the initiator to form primary radicals:



- The actual initiation reaction:



Not all primary radicals formed react with the monomer. In the above possible fates of initiator radicals are summarized (2.12):

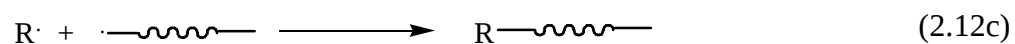
- Primary combination (within the cage):



- Secondary combination (outside the cage):



- Reaction with polymeric radicals:



- Reaction with initiator:



- Radical abstraction:



- Reaction with solvent:



- Chain initiation:



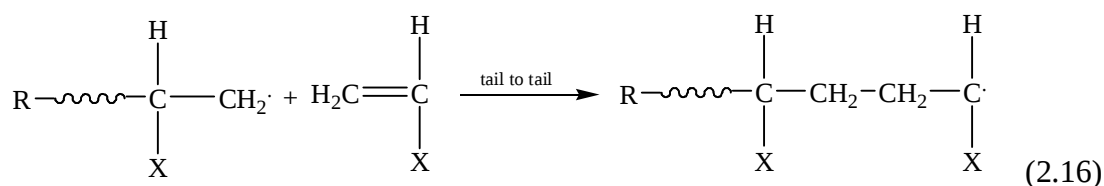
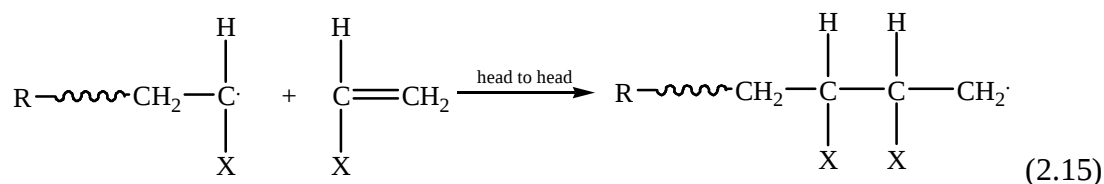
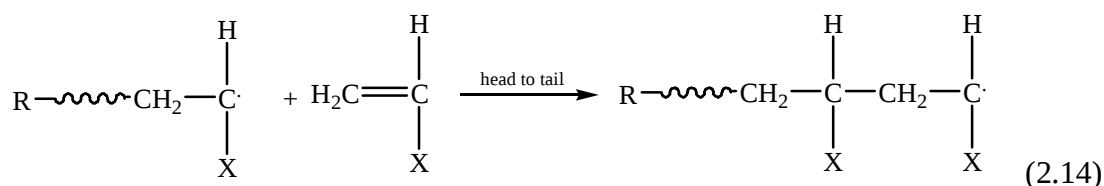
The initiator efficiency factor f is defined as the probability for a primary radical to react with a monomer and to initiate a chain; thus $(1-f)$ is the probability that it will react with another primary radical, to form a dead product. [13]

2.1.2.2 Propagation

This reaction is repeated many thousands of times for each chain formed, as already stated; it can be written as (2.13):



The most likely form of monomer addition is head to tail addition (2.14). Alternatively head to head (2.15) and tail to tail (2.16) additions are possible. [14]



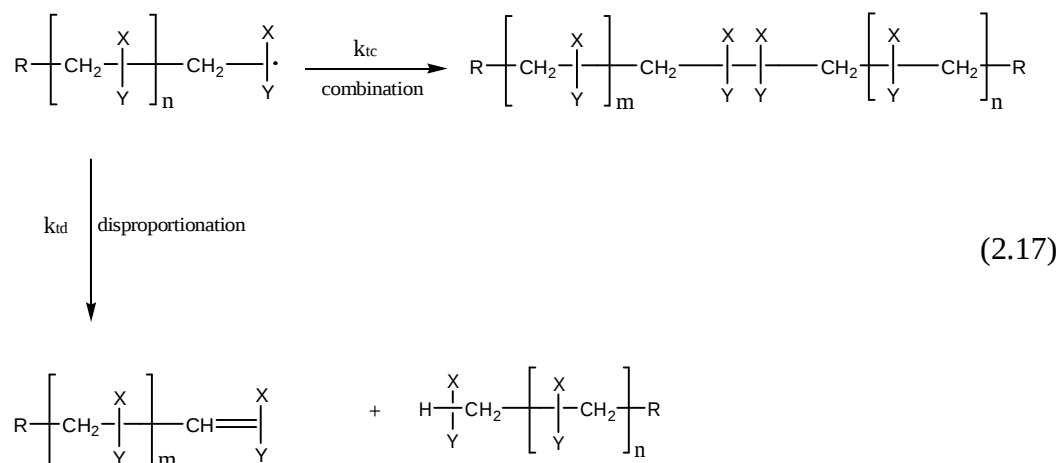
2.1.2.3 Termination

In theory the chain could continue to propagate until all the monomer in the system had been consumed but for the fact that free radicals are particularly reactive species and interact as quickly as possible to form inactive covalent bonds. This means that short chains are produced if the radical concentration is high, because the probability of radical interaction is correspondingly high, and the radical should be kept small if long chains are required. Termination of chains can take place in several ways [12]:

- (1) the interaction of two active chain ends;
- (2) the reaction of an active chain end with an initiator radical;
- (3) termination by transfer of the active center to another molecule which may be solvent, initiator, or monomer;
- (4) interaction with impurities (e.g. oxygen) or inhibitors.

The most important termination reaction is the first, a bimolecular interaction between two chain ends. Two routes are possible (2.17):

- (a) Combination where two chain ends couple together to form one long chain.
- (b) Disproportionation with hydrogen abstraction from one end to give an unsaturated group and two dead polymer chains.



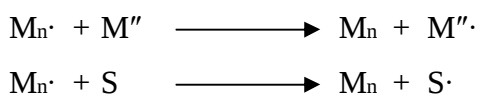
One or both processes may be active in any system depending on the monomer and polymerizing conditions. Experimental evidence suggests that polystyrene terminates predominantly by combination whereas poly(methyl methacrylate) terminates exclusively by disproportionation when the reaction is above 333 K but both mechanisms below this temperature. The mechanism can be determined by

measuring the number of initiator fragments per chain using a radioactive initiator. One fragment per chain is counted when disproportionation is operative and two when combination occurs. [12]

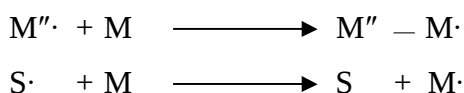
2.1.2.4 Chain Transfer Reactions

Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would be expected, is important in free radical polymerization. It leads to the chain-transfer process, which brings about the cessation of growth of a propagating radical and at the same time produces a new small radical which may propagate. A great variety of species can participate in chain transfer, act as transfer agents. Chain transfer, therefore, occurs widely; it commonly involves reaction of growing chains with monomer or solvent (2.18) or other additive and is well established for polymers and some initiators. Atoms other than hydrogen, notably halogens (except fluorine), may be transferred. Transfer to carbon tetrachloride is illustrated in 2.19.

Chain transfer to monomer or solvent: (2.18a)



Reinitiation by transfer radicals: (2.18b)



2.2 Free Radical Chain Copolymerization

The demand for new and improved materials often can be achieved as a result of altering the properties of existing polymeric materials. For example, the use of additives can incorporate desirable properties into an existing polymer material that is to be used for specialized applications. Common additives include plasticizers, stabilizers, flame retardants, fillers, colorants, processing aids, and impact modifiers [15]. Another approach is to combine the beneficial properties of different known polymer structures. One known technique to achieve this is to simply blend two individual blend components (*i.e.* synergism). A few advantages of blending include

reducing the cost of expensive high performance polymers, improving the process ability of a high temperature material, and improving impact resistance of materials. However, because few polymers are miscible, their blends form immiscible phase separated materials. These immiscible blends often have poor physical properties due to inadequate interfacial strength between the phases [16]. A desirable alternative is to copolymerize different monomer structures into a single polymeric material (Figure 2.1) [17]. Prime examples include the important commercial materials produced from vinyl chloride/vinyl acetate and styrene/butadiene copolymers. Careful consideration of such factors as the selection of the comonomers and the copolymerization reaction conditions allows one to precisely tailor the properties of the resulting copolymer and provides a useful method of synthesizing an almost unlimited number of polymeric structures with a wide range of properties and applications.

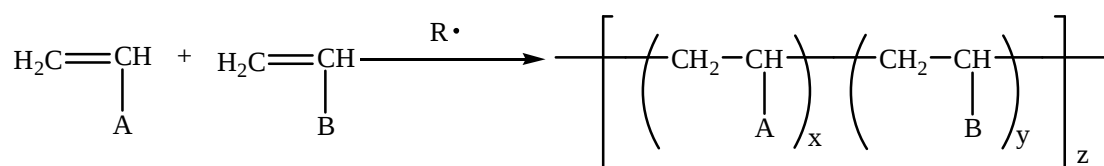


Figure 2.1: Generalized free radical chain copolymerization reactions

Copolymer structures can be described in a variety of ways. Different types of copolymers include random, alternating, block, and graft copolymers (Figure 2.2). Random copolymers result from a single process where the incorporation of the comonomers follows some statistical law that is due solely to kinetic factors [18]. Alternating copolymerization is an example of chain copolymerization where each of the monomers adds preferentially to the other and homopropagation is effectively nonexistent [19]. Block and graft copolymers differ in that they contain long sequences of each comonomer either along the backbone or as side chains (grafts) and are often the result of multi-step process [20].

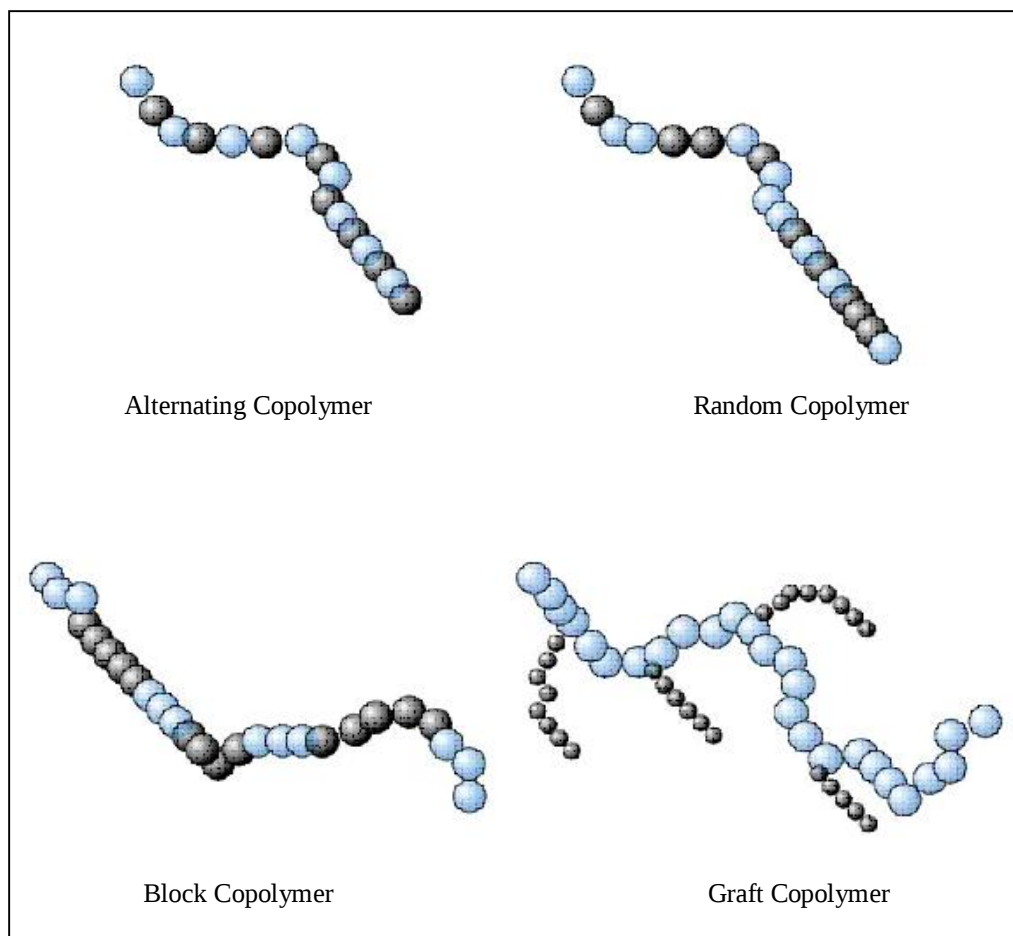


Figure 2.2: Types of copolymer topologies.

The manner in which comonomer repeat units are incorporated into the polymer backbone is determined from the reactivities of the monomers and radicals involved in the reaction. Reaction conditions such as solvent and temperature can also have a marked effect on the monomer reactivities and will contribute to the copolymer composition.

2.2.1 Copolymer Equation

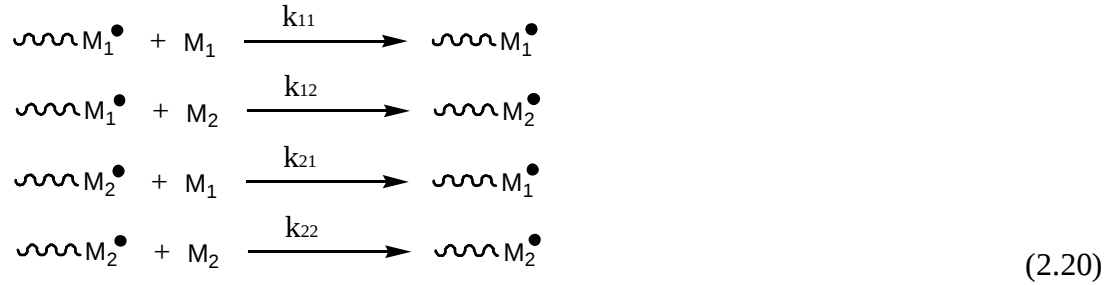
Some observations are relevant to the consideration of copolymerization kinetics are:

- The number of reactions involved in copolymerization of two or more monomers increases geometrically with the number of monomers. Consequently, the propagation step in the copolymerization of two monomers involves four reactions.
- The number of radicals to be considered equals the number of monomers. The terminal monomer unit in a growing chain determines almost exclusively the reaction

characteristics; the nature of the preceding monomers has no significant influence on the reaction path.

- There are two radicals in the copolymerization of two monomers. Consequently, three termination steps need to be considered.
- The composition and structure of the resulting copolymer are determined by the relative rates of the different chain propagation reactions.

By designating the two monomers as M_1 and M_2 and their corresponding chain radicals as $M_1^\bullet$ and $M_2^\bullet$, the four propagation reactions and the associated rate equations in the copolymerization of two monomers may be written as follows (2.20) [21]:



The Mayo-Lewis equation (2.21), which is derived from the terminal model using the assumption of the steady-state radical approximation, can be used to describe the instantaneous copolymer composition:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \tag{2.21}$$

Where r_1 and r_2 are the respective monomer reactivity ratios defined by $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The quantity $r_1 r_2$ represents the ratio of the product of the rate constants for the reaction of a radical with its own kind of monomer to the product of the rate constants for the cross-reactions. Copolymerization may therefore be classified into three categories depending on whether the quantity $r_1 r_2$ is unity, less than unity, or greater than unity. In the case of $r_1 r_2 = 1$; ideal copolymerization, $r_1 = r_2 = 0$; alternating copolymerization, $r_1 > 1$ $r_2 > 1$; block copolymerization. [21]

2.2.2 Alternating Copolymerization

Monomers that are difficult to homopolymerized are often found to be capable of alternating copolymerization. When $r_1 = r_2 = 0$ (or $r_1 r_2 = 0$), each radical reacts exclusively with the other monomer; that is neither radical can regenerate itself. Consequently, the monomer units are arranged alternately along the chain irrespective of the feed composition.

Polymerization continues until one of the monomers is used up and then stops. Perfect alternation occurs when both r_1 and r_2 are zero. As the quantity $r_1 r_2$ approaches zero, there is an increasing tendency toward alternation. This has practical significance because it enhances the possibility of producing polymers with appreciable amounts of both monomers from a wider range of feed compositions.

An alternating copolymer can easily be obtained by copolymerization of an electron-rich monomer and an electron-deficient monomer through the formation of charge transfer complexes. Extensively studied systems of this type are maleic anhydride (MA) / styrene or maleimide (MI) / styrene. [22]

2.3 Controlled/ “Living” Radical Polymerization (CRP)

Conventional free radical polymerization (FRP) has many advantages; the procedure can be used for the (co)polymerization of a very large range of vinyl monomers under undemanding conditions; requiring the absence of oxygen, but tolerant to water, and can be conducted over a large temperature range (-20 to 250°C). Many additional vinyl monomers can be copolymerized via a radical route leading to an infinite number of copolymers with properties dependent on the proportion of incorporated comonomers. The major limitation of FRP is poor control over some of the key structural elements that allow the preparation of well defined macromolecular architectures such as molecular weight, polydispersity, end functionality, chain architecture and composition. [23]

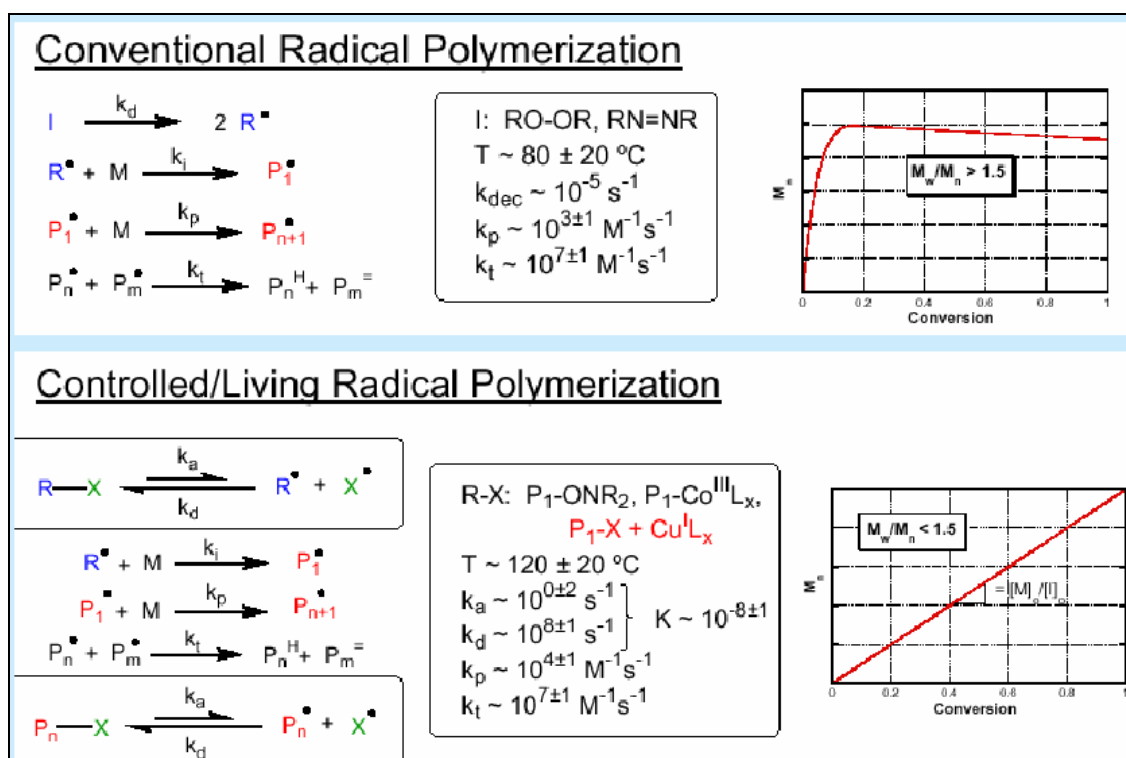


Figure 2.3: Comparisons between FRP and CRP

In all of the CRP processes developed to date there is a low occurrence of side reactions (e.g., termination or chain transfer) due to creation of a dynamic equilibrium between a dormant species present in large excess and a low concentration of active radical sites. By reducing the instantaneous concentration of active radicals, and hence the number of side reactions, polymerization is able to proceed in a controlled manner. This results in the formation of (co)polymers having predictable molecular weight and controllable polydispersity with molecular weight increasing as a function of time in a batch polymerization process, all the while maintaining a narrow polydispersity. CRP is also able to produce materials with well-defined block lengths, complex architecture, and functionalized chain ends. [23]

A major difference between conventional radical and controlled radical polymerizations is the lifetime of the propagating radical during the course of the reaction (Figure 2.3). In conventional radical processes, radicals generated by decomposition of the initiator undergo propagation and bimolecular termination reactions within a second. In contrast, the lifetime of a growing radical can be extended to several hours in a CRP, enabling the preparation of polymers with well-defined properties as shown Figure 2.4 [24,25].

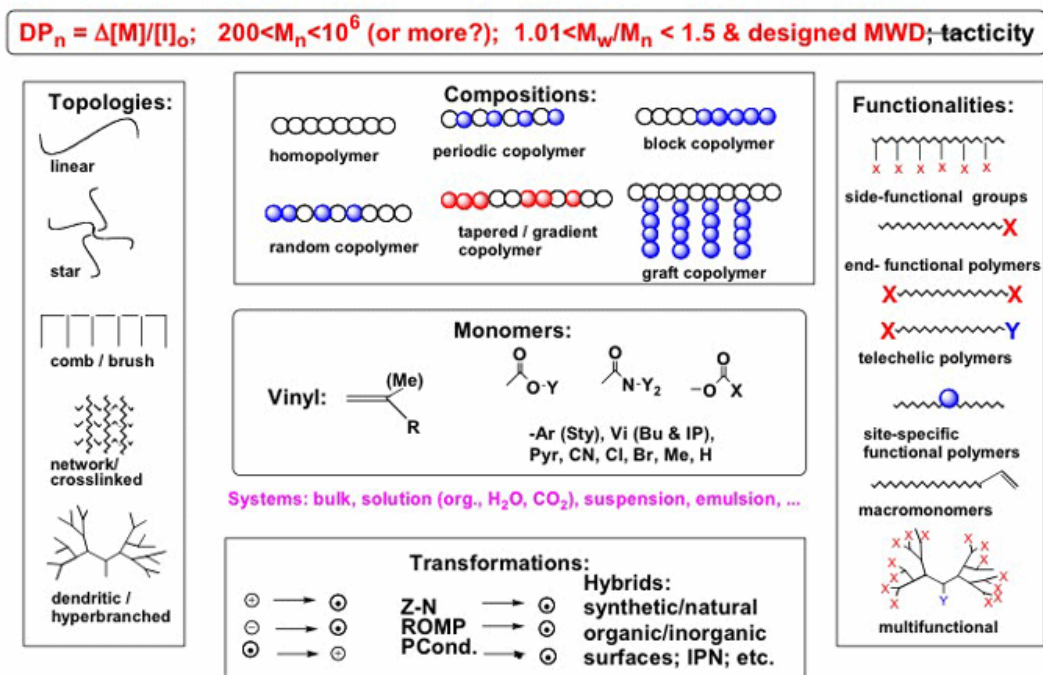
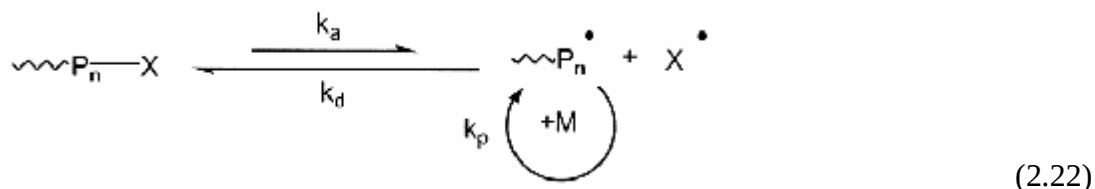


Figure 2.4: The general features of controlled radical polymerization

2.3.1 Classification of CRP

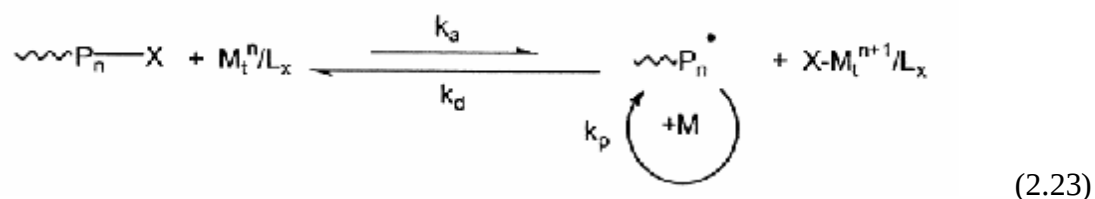
Currently three approaches generally appear to be successful at controlling radical polymerization and the major processes will be discussed in historical order [23].

(1) Thermal homolytic cleavage of a weak bond in a covalent species which reversibly provides a growing radical and a less reactive radical (a persistent or stable free radical) (2.22). There are several examples of persistent radicals but it seems that the most successful are nitroxides, triazoliny radicals, bulky organic radicals, e.g., trityl or compounds with photolabile C–S bonds and some organometallic species.

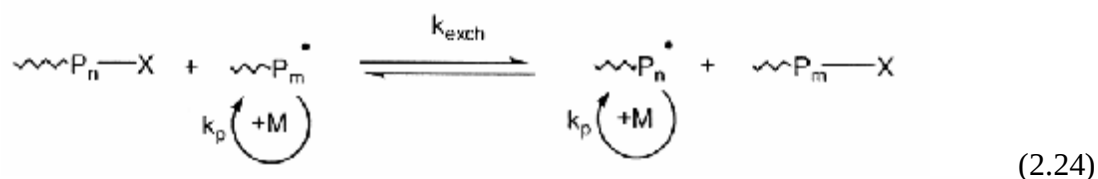


A subset of this process is the transition metal catalyzed, reversible cleavage of the covalent bond in the dormant species via a redox process (2.23). Since the key step in controlling the polymerization is transfer of an atom (or group) between a dormant chain and a transition metal catalyst in a lower oxidation state forming an active

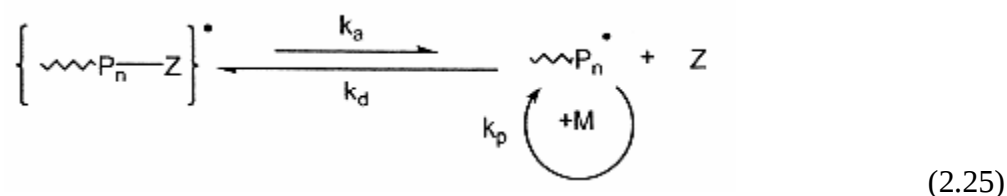
chain end and a transition metal deactivator in a higher oxidation state, this process was named atom transfer radical polymerization (ATRP).



(2) The second approach to CRP is based on a thermodynamically neutral exchange process between a growing radical, present at very low concentrations, and dormant species, present at much higher concentrations (generally three to four orders of magnitude) (2.24). This degenerative transfer process can employ alkyl iodides, unsaturated methacrylate esters, or thioesters. The latter two processes operate via addition-fragmentation chemistry.



(3) Finally, there is a third approach that has not yet been as extensively examined as the above systems. This process is the reversible formation of persistent radicals, by reaction of the growing radicals with a species containing an even number of electrons, which do not react with each other or with monomer (2.25). Here, the role of a reversible radical trap may be played by phosphites or some reactive, but non-polymerizable alkene, such as tetrathiofulvalenes, stilbene or diphenylethylene.



2.3.2 Atom Transfer Radical Polymerization (ATRP)

As a novel precision polymerization, atom transfer radical polymerization (ATRP) has received rapidly increased interest recently, since it furnishes control over the resulting polymers, which possess narrower molecular weight distributions. The merit of the ATRP system is that it can be performed by an ordinary polymerization procedure. The name atom transfer radical polymerization (ATRP) comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of polymeric chains. ATRP originates in atom transfer radical addition (ATRA) reactions. 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 radical to form the final product. The general mechanism of ATRA can be seen in Figure 2.5. [26]

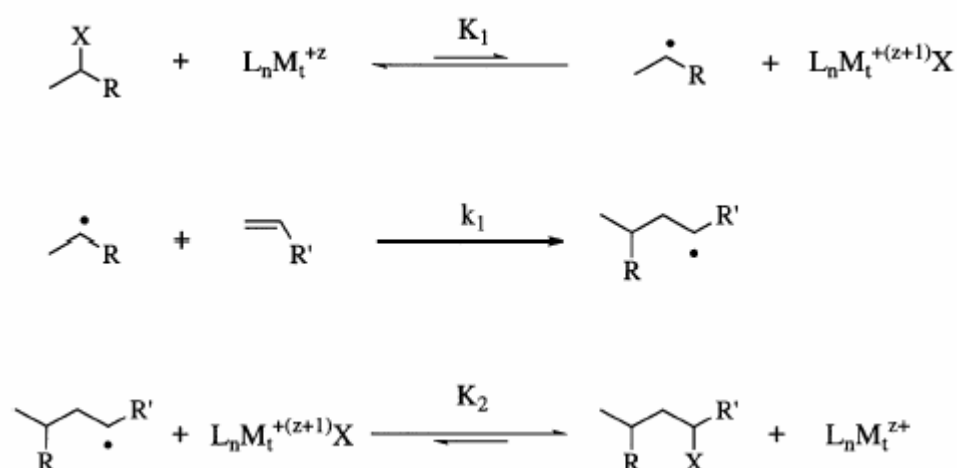


Figure 2.5: The general mechanism of ATRA

ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process. This allowed for an unprecedented control over the chain topology, the composition and the end functionality for a large range of radically polymerizable monomers [14].

2.3.2.1 Mechanism and Kinetics of ATRP

An ATRP system consist of an initiator, a copper(I) halide complexed with some ligand(s), and of course, monomer. ATRP occurs as a repetitive addition of a monomer to a growing radicals generated from dormant alkyl (pseudo) halides by a reversible redox process catalyzed by transition metal compounds complexed by amine ligand. A general mechanism for ATRP is shown in Figure 2.6 [1].

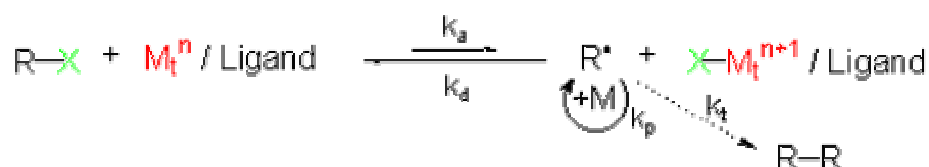


Figure 2.6: A general mechanism for ATRP

This process occurs with a rate constant of activation, k_a , and deactivation k_d , respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to conventional radical polymerizations, with the rate constant of propagation, k_p .

Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.

Higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control may be observed at higher temperatures.

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 ($\text{CuX}_2 / \text{Ligand}$). The rate law of ATRP is formulated in discussed conditions and given in equation (2.26) [1].

$$R_p = k_{app} [M] = k_p [P^\bullet] [M] = k_p K_{eq} [In] \frac{[Cu^I]}{[Cu^{II}X]} [M] \quad (2.26)$$

As in typical living polymerization, the average molecular weight of the polymer can be predetermined by the ratio of consumed monomer and the initiator ($DP_n = \Delta[M]/[I_0]$) while maintaining a relatively narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$) [14]. In addition, precise control over the chemistry and the

structure of the initiator and active end group allows for the synthesis of end-functionalized polymers and block copolymers.

The molecular weight distribution or polydispersity M_w/M_n is the index of the polymer chain-length distribution. In well-controlled polymerization, M_w/M_n is usually less than 1.10. [1]

2.3.2.2 Components Used in ATRP

Monomers

ATRP can be used for many vinyl monomers including styrenes, acrylates, methacrylates, acrylonitrile and dienes. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq}=k_a/k_d$) determines the polymerization rate [1].

The most commonly used monomers are styrene (St) and methyl methacrylate (MMA) and acrylates. Also ATRP has been used to copolymerize that will undergo radical homopolymerization as well as combinations of these monomers with olefins that will not undergo radical homopolymerization (such as maleic anhydride, N-cyclohexylmaleimide). [26]

Initiators

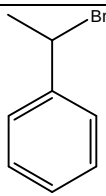
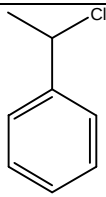
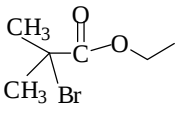
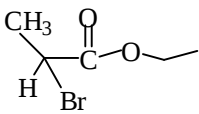
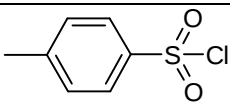
The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group X must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best [26]. Fluorine is not used because the C-F bond is too strong to undergo homolytic cleavage [1].

Initiation should be fast and quantitative with a good initiator and proper selection of group R. Any alkyl halide with activating substituents on the α -carbon, such as aryl carbonyl, or allyl groups, can potentially be used as ATRP initiators, polyhalogenated compounds (CCl_4 and CHCl_3), and compounds with a weak R-X bond, such as N-X, S-X and O-X, can also be used as ATRP initiators.

When the initiating moiety is attached to a macromolecule macroinitiators are formed, and can be used to synthesize block or graft copolymers [27].

Table 2.1: The most frequently used initiator types in ATRP systems

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

Catalysts

Perhaps most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The catalyst is based on a

transition metal which regulates the polymerization rate and polydispersities. There are several prerequisites for an efficient transition metal catalyst. [1]

- a) The metal center must have at least two readily accessible oxidation states separated by one electron
- b) The metal center should have reasonable affinity toward a halogen.
- c) The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo) halogen.
- d) The ligand should complex the metal relatively strongly.
- e) The position and dynamics of the ATRP equilibrium should be appropriate for the particular system.

Ligands

The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRP catalyst. First, fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third, fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth, relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β -H abstraction or reduction/oxidation of the radicals [1].

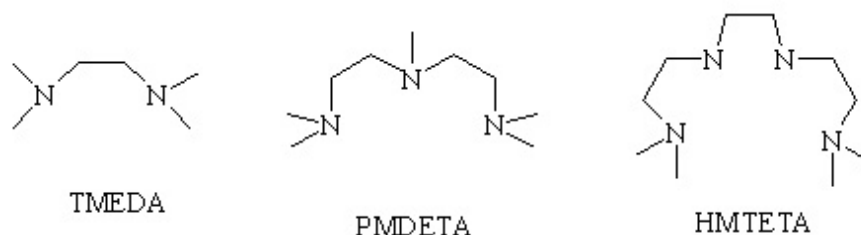


Figure 2.7: Nitrogen based ligands

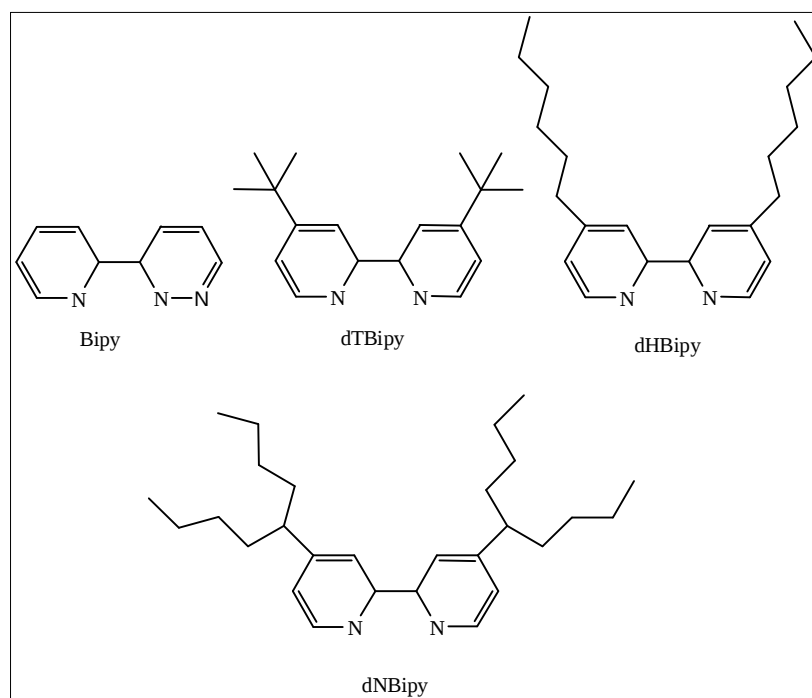


Figure 2.8: Derivatives of 2,2-bipyridine

Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. Solvents are often used to reduce viscosity at high conversion. Chain transfer to solvent should be minimal [1].

Temperature and Reaction Time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant [1]. The energy of activation for radical propagation is appreciably higher than that for termination by radical combination and disproportionation. Consequently, at higher temperatures the ratio k_p/k_t will be higher and therefore better polymerization control will be observed [26].

The most important effect of reaction time in ATRP occurs at high conversions. At high monomer conversions, the rate of propagation is very slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration independent.

2.4 Liquid Crystals

The liquid crystalline (LC) phase is a genuine, thermodynamically stable state of matter, exhibiting the properties of both a crystalline solid and a liquid. The LC state was observed initially by Reinitzer who found that pure cholesteryl benzoate, when melted, produced an iridescent, opaque fluid that on further heating cleared to give an isotropic liquid. These transitions occurred at reproducible temperatures and the phenomenon was found to be present in other systems by Lehmann, who introduced the term 'liquid crystal' to describe this intermediate phase. The nomenclature was further refined by Friedel, who suggested that the generic term, mesophase, should replace 'liquid crystalline phase', and who also introduced nematic and smectic to describe observed differences in the liquid crystal behavior of various compounds [28-30].

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

- A simple geometrical form of the molecule: rods, discs or ball, which allow closer packing in mesophase
- An intramolecular contrast, which causes microseparation of different parts of the molecules

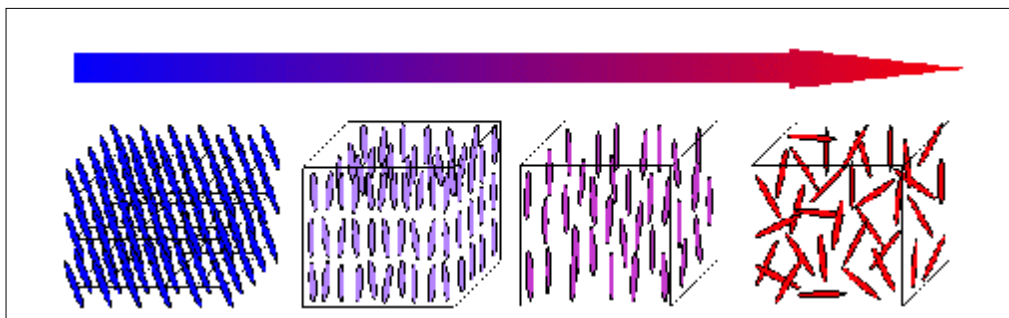


Figure 2.9: Arrangement of molecules in different states

In the crystalline solid state, as represented in Figure 2.9, the arrangement of molecules is regular, with a regularly repeating pattern in all directions. (Molecules of substances with a liquid crystal state are generally oblong and rigid, that is, rod-shaped.) The molecules are held in fixed positions by intermolecular forces. As the temperature of a substance increases, its molecules vibrate more vigorously. Eventually, these vibrations overcome the forces that hold the molecules in place, and the molecules start to move. In the liquid state, this motion overcomes the

intermolecular forces that maintain a crystalline state, and the molecules move into random positions, without pattern in location or orientation, as represented in Figure 2.9.

In materials that form liquid crystals, the intermolecular forces in the crystalline solid are not the same in all directions; in some directions the forces are weaker than in other directions. As such a material is heated, the increased molecular motion overcomes the weaker forces first, but its molecules remain bound by the stronger forces. This produces a molecular arrangement that is random in some directions and regular in others. The arrangement of molecules in one type of liquid crystal is represented in Figure 2.9. The molecules are still in layers, but within each layer, they are arranged in random positions, although they remain more or less parallel to each other. Within layers, the molecules can slide around each other, and the layers can slide over one another. This molecular mobility produces the fluidity characteristic of a liquid. [31]

Liquid crystals can be classified according to the physical parameters controlling the existence of the liquid crystalline phases. The corresponding classes of liquid crystals are referred to as lyotropics and thermotropics respectively [32].

2.4.1 Classification of Liquid Crystals

2.4.1.1 Lyotropic liquid crystals

Lyotropic liquid crystals are multi component systems formed in mixtures of amphiphilic molecules and a polar solvent. Amphiphilic molecules are consisted of a hydrophilic polar head attached to a hydrophobic hydrocarbon tail containing one or two alkyl chains [33]. The most common systems are those formed by water and amphiphilic molecules as illustrated in Figure 2.10 such as soaps, detergents and lipids. Here the most important variable that is controlling the existence of liquid crystalline phase is amount of solvent (or concentration). There are quite a number of phases observed in such water-amphiphilic systems, as the composition and the temperature varied; some appear as spherical micelles, and others posses ordered structures with one-, two-, or three-dimensional positional order. Lyotropic liquid crystals are mainly of interest in biological studies [34].

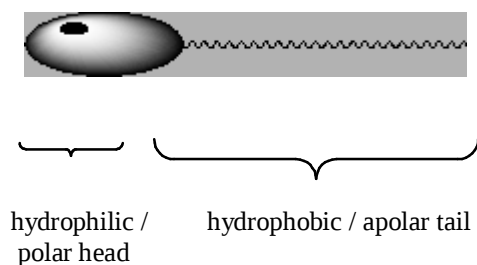


Figure 2.10: Lyotropic liquid crystals

2.4.1.2 Thermotropic Liquid Crystals

Thermotropic liquid crystals are obtained by partial melting of solid crystals of certain materials. These systems are consisted of single components and most known substances are organic compounds. These materials are isotropic liquid at higher temperatures and crystalline solids at lower temperatures. Liquid crystalline phase can be distinguished from isotropic liquid by its turbid appearance and from solid crystals from its flow properties [33].

2.4.2 Phases of Liquid Crystals

Liquid crystals are generally classified according to their basic molecular organization. Three main types are widely recognized: smectic, nematic, (Figure 2.11) and cholesteric. There are several methods used to identify liquid crystalline phases. Differential Scanning Calorimetry (DSC) can be used to determine transition temperatures, therefore to distinguish phases. But one can not identify the phases itself by this method. Polarizing microscope is the most widely used method in identifying different phases. One can look at a thin layer of liquid crystal substances placed in between two glass cover plates. Depending on the boundary condition and the type of phase, various textures which are characteristics of a phase are observed. Usually the textures change while going from one phase to the other. Polarizing microscopy is powerful too when used in combination with miscibility of binary mixtures. Most precise techniques in identifying phases and arrangements of molecules are X-ray and neutron scattering technique. These techniques provide direct information of the positional and orientation characteristics of liquid crystals [33].

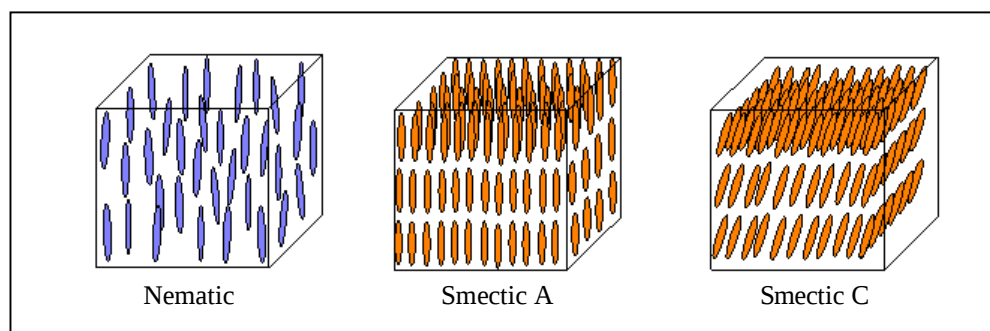


Figure 2.11: Thermotropic liquid crystal phases

2.4.2.1 Nematic phase

The nematic liquid crystal, N phase, is the only liquid crystal phase without any long range translational order. Nematics are the most important member in the family of the liquid crystals and are widely used in the display industry. In nematics, the molecules tend to be parallel to each other. The preferred direction of parallel orientation is characterized by the director. The nematic liquid crystal is shown in Figure 2.11 [35].

2.4.2.2 Smectic phase

As the temperature is further cooled, the molecules begin to segregate into planes giving rise to a smectic A or smectic C phase. In addition to the orientational order that the nematic phase shows, the smectic A and C phases exhibit a one-dimensional translational order, and can therefore form layered structures [35]. In smectic-A in each layer the molecules are positionally random, but directionally ordered with their long axis normal to the plane of the layer. If this director tilts away from the layer normal the smectic C phase is formed at lower temperatures.

2.4.2.3 Cholesteric phase

The cholesteric liquid crystal is the first discovered liquid crystal and is an important member of the liquid crystal family. In some of the literature, it is denoted as the N^* phase, the chiral nematic liquid phase. The molecules in that phase are arranged as thin layers. The molecules lie in the layers and are parallel to each other, but the director rotates along the helical axis continuously and uniformly. A schematic of cholesteric liquid crystals is illustrated in Figure 2.12 [35].

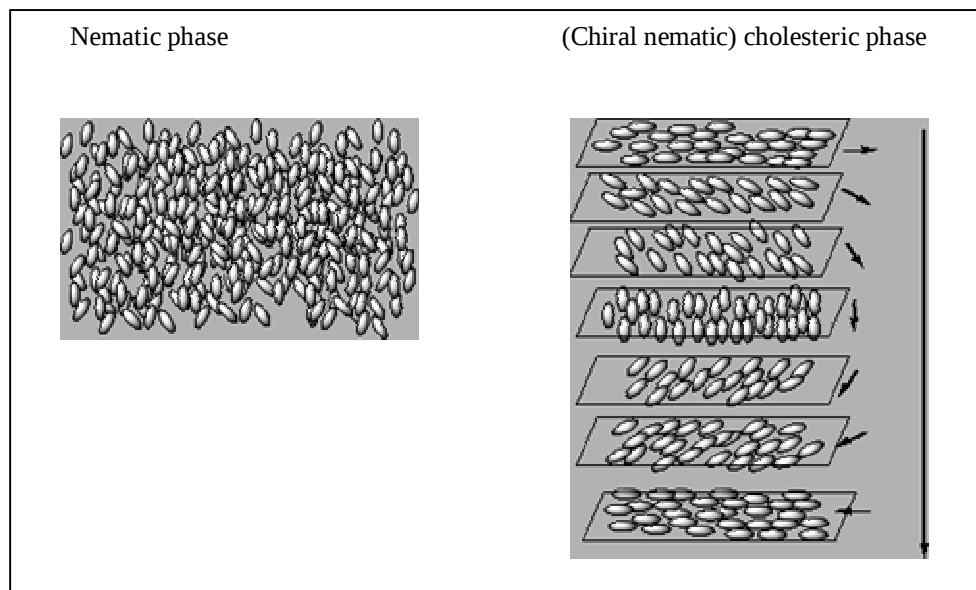


Figure 2.12: Nematic and Cholesteric phases

2.5 Liquid Crystalline Polymers

Liquid crystalline polymers (LCPs) are a class of materials that combine the properties of polymers with those of liquid crystals. These "hybrids" show the same mesophases characteristic of ordinary liquid crystals, yet retain many of the useful and versatile properties of polymers. 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 LCP that is formed. Main-chain polymer liquid crystals or MC-LCPs are formed when the mesogens are themselves part of the main chain of a polymer. Conversely, side chain polymer liquid crystals or SC-LCPs are formed when the mesogens are connected as side chains to the polymer by a flexible "bridge" (called the spacer) (Figure 2.13). [36]

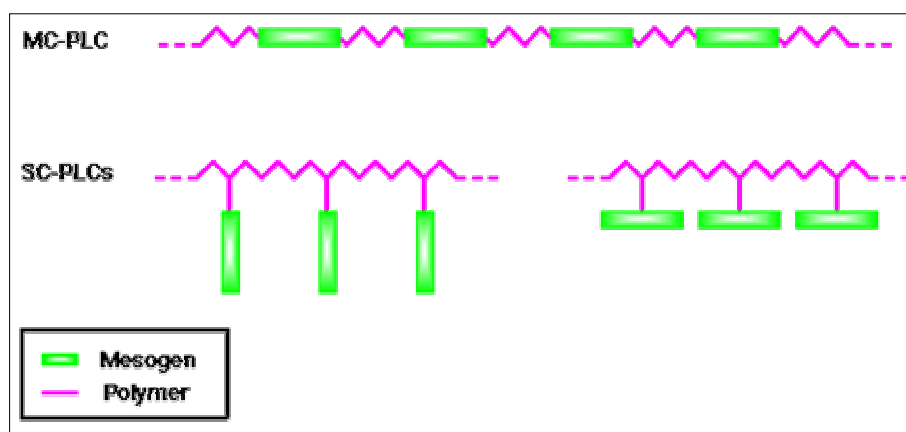


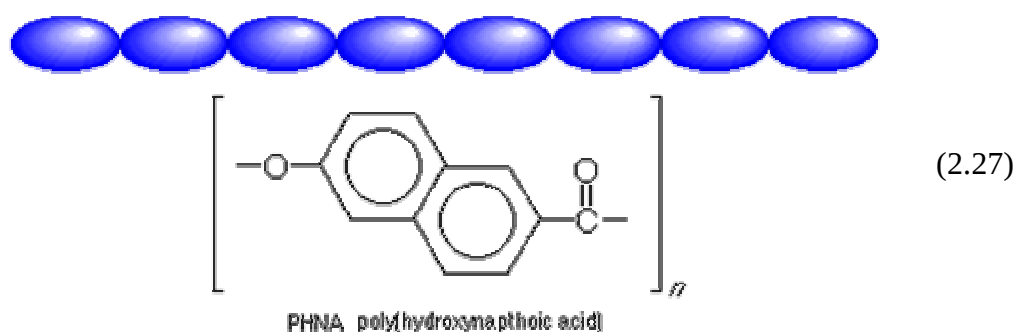
Figure 2.13: General templates for MC-LCP and SC-LCPs

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.

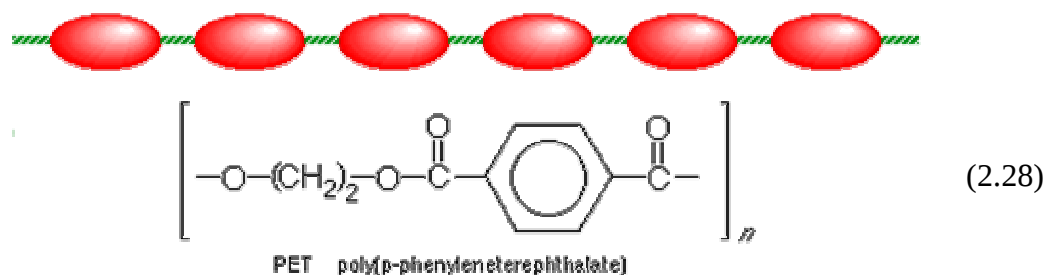
2.5.1 Main-chain liquid crystalline polymers (MC-LCPs)

Main chain liquid crystalline polymers 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. There are two distinct groups of MC-LCPs, differentiated by the manner in which the stiff regions are formed.

The first group of main chain polymer liquid crystals is characterized by stiff, rod-like monomers. These monomers are typically made up of several aromatic rings which provide the necessary size. The following diagram (2.27) shows an example of this kind of MC-LCP.

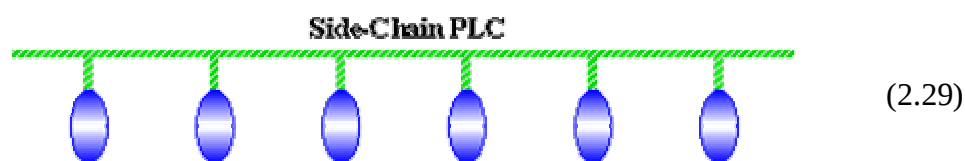


In a semi-flexible MC-LCP, the mesogenic groups are separated by flexible spacers such as alkyl chains (2.28); this enhanced molecular flexibility reduces the melting points of these polymers and renders the liquid crystallinity accessible [36].



2.5.2 Side-chain liquid crystalline polymers (SC-LCPs)

Side-chain liquid crystal polymers have attracted considerable research interest since their discovery in the late seventies, because of their considerable application potential in a range of advanced electro-optic technologies, including optical information storage and non-linear optics, and they challenge our understanding of the molecular factors that promote self-organization in polymeric systems. [37]



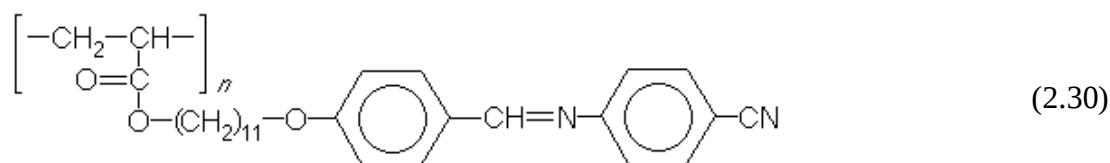
Side-chain liquid crystal polymers comprise three essential structural components: a polymer backbone, a mesogenic unit, and a flexible spacer (2.29). The flexible spacer plays a critical role because it decouples, to some extent, the ordering tendencies of the mesogenic units from those of the backbones to adopt random coil conformations. Its presence endows upon the polymer a unique duality of properties. Thus, side-chain liquid crystal polymers exhibit macromolecular characteristics, such as ease of processability and mechanical integrity, coupled with the electro-optic properties of low molar mass mesogens, albeit on a much slower time-scale. It is this unique combination of properties that forms the basis of the proposed applications. [38]

2.5.2.1 The Backbone

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. In order to lower this temperature, the polymer backbone can be made more flexible [36].

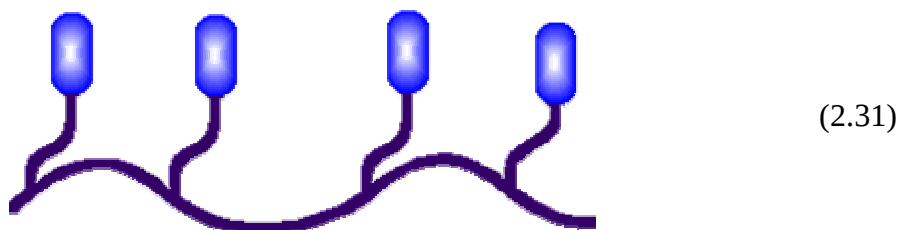
2.5.2.2 The Mesogen

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. The following diagram (2.30) is a typical repeating unit in a side chain polymer liquid crystal. Notice the spacer of methylene units and the mesogen of aromatic rings. [36]



2.5.2.3 The Spacer

Like their main chain counterparts, 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. Notice in the following diagram (2.31) that even though the polymer may be in a tangled conformation, orientation of the mesogens is still possible because of the decoupling action of the spacer.



The structure of the spacer is an important determining factor in side chain polymer liquid crystals. Generally, the spacer consists of two to four methylene (CH_2) groups attached together in a line. Accordingly, the spacer length has a profound effect on the temperature and type of phase transitions. Usually, the glass transition temperature decreases with increasing spacer length. Short spacers tend to lead to nematic phases, while longer spacers lead to smectic phases.

3. EXPERIMENTAL WORK

3.1 Materials

3.1.1 Purification of Materials

3.1.1.1 Monomer

N-Cyclohexylmaleimide (NCMI) (Aldrich)

Recrystallized twice from dry acetone, it was dried under vacuum before use.

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 sulphoxide (DMSO) (Lab Scan)

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

Ethanol (J.T.Baker)

Predried over magnesium sulfate and then distilled from calcium hydride before use.

Methanol (Lab Scan)

It was used without further purification.

Benzene (Merck)

It was used without further purification.

Toluene (Merck)

Refluxed over CaH_2 for 24 hours, then distilled over sodium prior to use.

Anisole (Acros)

It was used without further purification.

3.1.1.3 Other Chemicals and Reagents

4'-Hydroxy-4-biphenylcarbonitrile (Aldrich)

It was used without further purification.

6-Chloro-1-hexanol (Aldrich)

It was used without further purification.

Potassium carbonate (J.T.Baker)

It was used without further purification.

Acryloyl chloride (Aldrich)

It was used without further purification.

Triethylamine (TEA) (Acros)

It was used without further purification.

Sodium hydroxide (Acros)

It was used without further purification.

2-Bromopropionyl bromide (Aldrich)

It was used without further purification.

Copper (I) bromide (Aldrich)

It was used without further purification.

Pentamethyldiethylenetriamine (PMDETA) (Aldrich)

It was used without further purification.

Azobisisobutyronitrile (AIBN) (Aldrich)

It was used without further purification.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H-NMR analyses were recorded on a Bruker 250 MHz Spectrometer.

3.2.2 Gel Permeation Chromatography (GPC)

Molecular weights were analyzed using GPC. GPC analyses were carried out with a set up consisting of the Agilent pump and refractive index detector and three Agilent Zorbax Columns (1000S, 300S, and 60S). THF was used as the eluent at a flow rate of 0.5 ml/min at 30°C. The molecular weights of the polymers were calculated with the aid of polystyrene.

3.2.3 Differential Scanning Calorimeter (DSC)

The glass transition temperatures of the copolymers were measured by differential scanning calorimetry (TA DSC Q10) in a flowing nitrogen atmosphere at heating rate 10⁰C / min.

3.2.4 Thermogravimetric Analysis (TGA)

Thermal gravimetric analysis was performed on a TA TGA Q50 instrument.

3.3 Synthesis of Chemical Compounds

3.3.1 Synthesis of 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate (LC6)

3.3.1.1 Synthesis of 6-(4-Cyanobiphenyl-4'-oxy)hexane-1-ol

Under nitrogen 6-chloro-1-hexanol (20 mmol, 2.25 ml) was added dropwise to a stirring mixture of 4'-hydroxy-4-biphenylcarbonitrile (15.1 mmol, 3 g) and anhydrous K₂CO₃ (14.5 mmol, 2 g) 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 of 10% NaOH solution at room temperature and filtered. The resultant was dried at 40°C in vacuum. It was recrystallized from benzene. White crystalline product was obtained and dried under vacuum (yield 75%).

3.3.1.2 Synthesis of LC6

Under nitrogen atmosphere acryloyl chloride (16.69 mmol, 1.36 ml) in 20 ml of dry THF was added dropwise to a stirring mixture of triethylamine (21.03 mmol, 2.93 ml) and 6-(4-cyanobiphenyl-4'-oxy)hexane-1-ol (10.12 mmol, 2.99 g) 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 of 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 (yield 75-80%) [39,40].

3.3.2 General Copolymerization Procedure for FRP of NCMI with LC6

A schlenk flask with a stirring bar was cycled between vacuum and nitrogen three times to remove the oxygen. While the nitrogen was passing through the reaction system, required amounts of monomers (NCMI, LC6) and initiator (AIBN) were introduced into the flask and dissolved in solvent (toluene). The flask sealed and then was immersed in an oil bath held by a thermostat at required temperature. After reacting for determined time periods, the polymer was precipitated by addition of excess of methanol with rapid stirring to precipitate the product. The precipitated polymer was filtered and washed thoroughly with methanol, purified by reprecipitation from the THF solution into excess methanol. The polymer was then dried in vacuum for several hours. The amounts of monomers NCMI and LC6, initiator AIBN, reaction time and conversions are collected in Table 4.1.

3.3.3 General Copolymerization Procedure for ATRP of NCMI with LC6

A schlenk tube with a stirring bar was cycled between vacuum and nitrogen for three times. While the nitrogen flow was passing through the schlenk tube, required amounts of LC6 (2.86 mmol, 1.0 g) and NCMI (0.5 g, 2.86 mmol) was dissolved in anisole (3 ml). Then PMDETA (0.114 mmol, 24 μ l), Cu(I)Br (0.057 mmol, 8.2 mg) and 2-bromopropionyl bromide (0.057 mmol, 6 μ l) were introduced into tube respectively. The schlenk tube was then heated to 110°C and left for a determined time. After the reaction was complete, the product mixture was dissolved in THF after it was cooled to room temperature; the mixture was passed through a short alumina column and then concentrated with evaporation. Afterwards, it was precipitated into methanol. A white precipitate was isolate and dried in vacuum oven for 24 h. The conversion was determined gravimetrically. Copolymerization conditions are given in the Table 4.3.

4. RESULTS AND DISCUSSION

4.1 Synthesis of 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate (LC6)

Liquid crystalline acrylate monomer (LC6) was synthesized according to the procedure [39,40] by reacting 4'-hydroxy-4-biphenyl carbonitrile with 6-chloro-1-hexanol to yield 6-(4-Cyanobiphenyl-4'-oxy)hexane-1-ol in the first stage (Figure 4.1) .

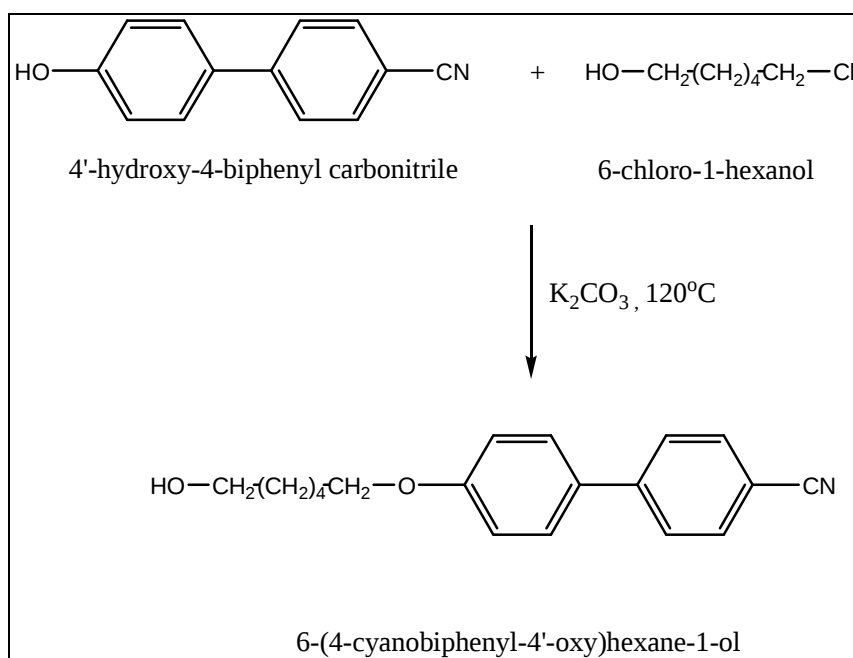


Figure 4.1: Synthesis of 6-(4-Cyanobiphenyl-4'-oxy)hexane-1-ol

In the second stage, LC6 was obtained by reacting acryloyl chloride with 6-(4-Cyanobiphenyl-4' oxy)hexane-1-ol as shown in Figure 4.2.

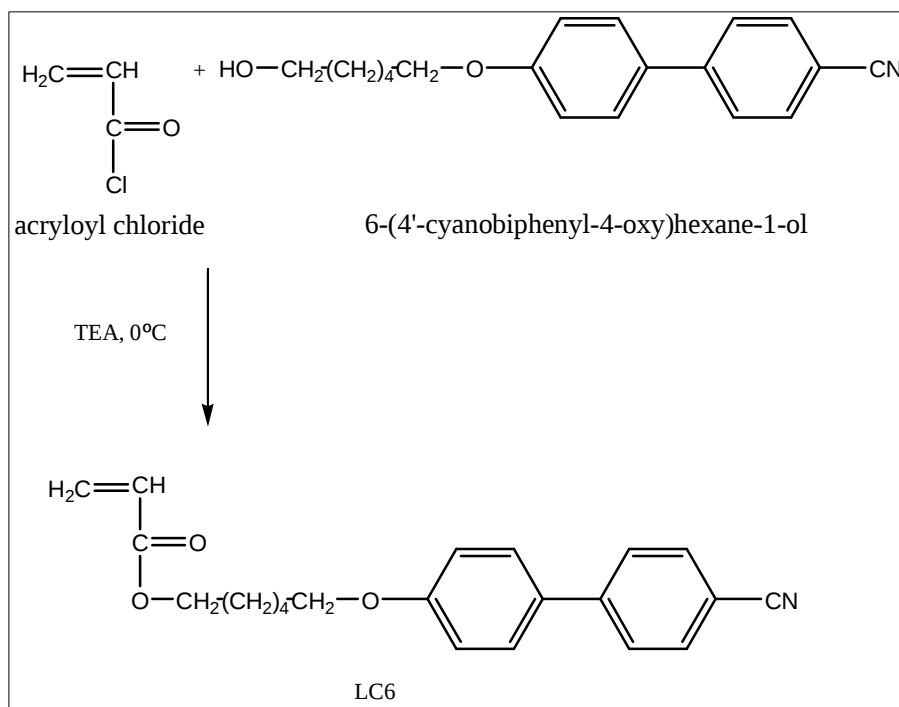


Figure 4.2: Synthesis of 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate (LC6)

The structure of resulting product was confirmed by ^1H -NMR spectrum. ^1H -NMR; (in CDCl_3): $\delta = 6.9\text{--}7.6$ ppm; aromatic protons of LC6 (d), $6.4\text{--}5.8$ ppm; vinyl protons of LC6 (a), $3.9\text{--}4.2$ ppm; $-\text{OCH}_2$ protons of LC6 (b), $2.1\text{--}1.2$ ppm; aliphatic protons of LC6 (c) (Figure 4.3).

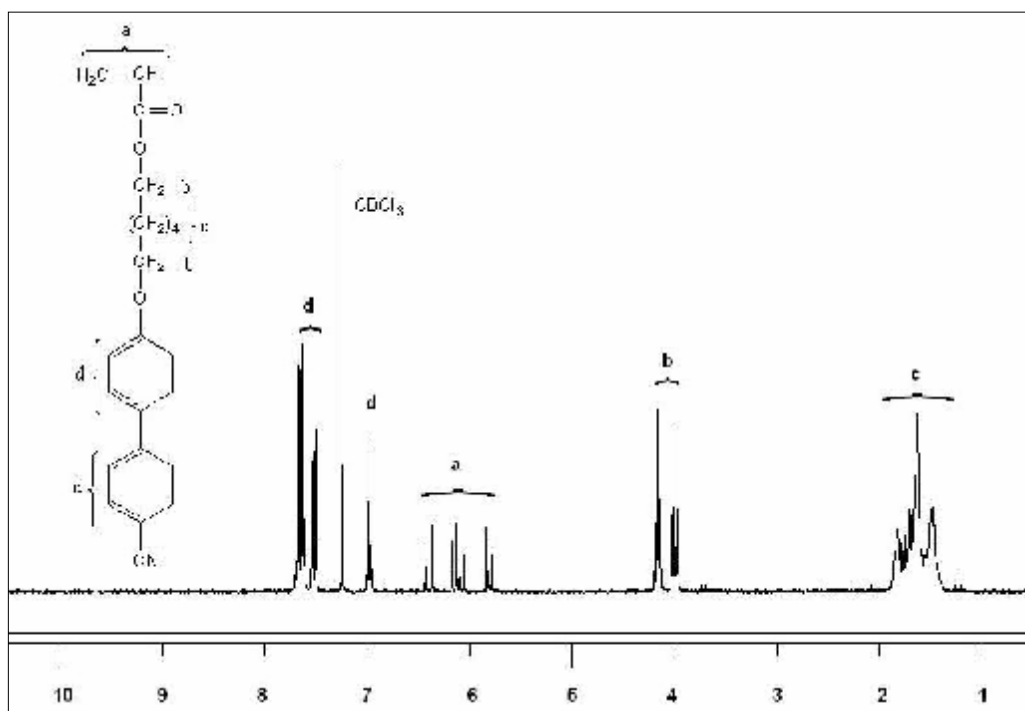


Figure 4.3: ^1H -NMR Spectrum of LC6 monomer

4.2 Synthesis of Alternating Copolymers of N-Cyclohexylmaleimide with LC6 by FRP

The synthesis of alternating copolymers of 6-(4-Cyanobiphenyl-4'-oxy)hexyl acrylate (LC6) and N-Cyclohexylmaleimide (NCMI) were achieved by conventional free radical copolymerization in toluene using AIBN as initiator (Figure 4.4). The polymerization conditions and results are summarized in Table 4.1.

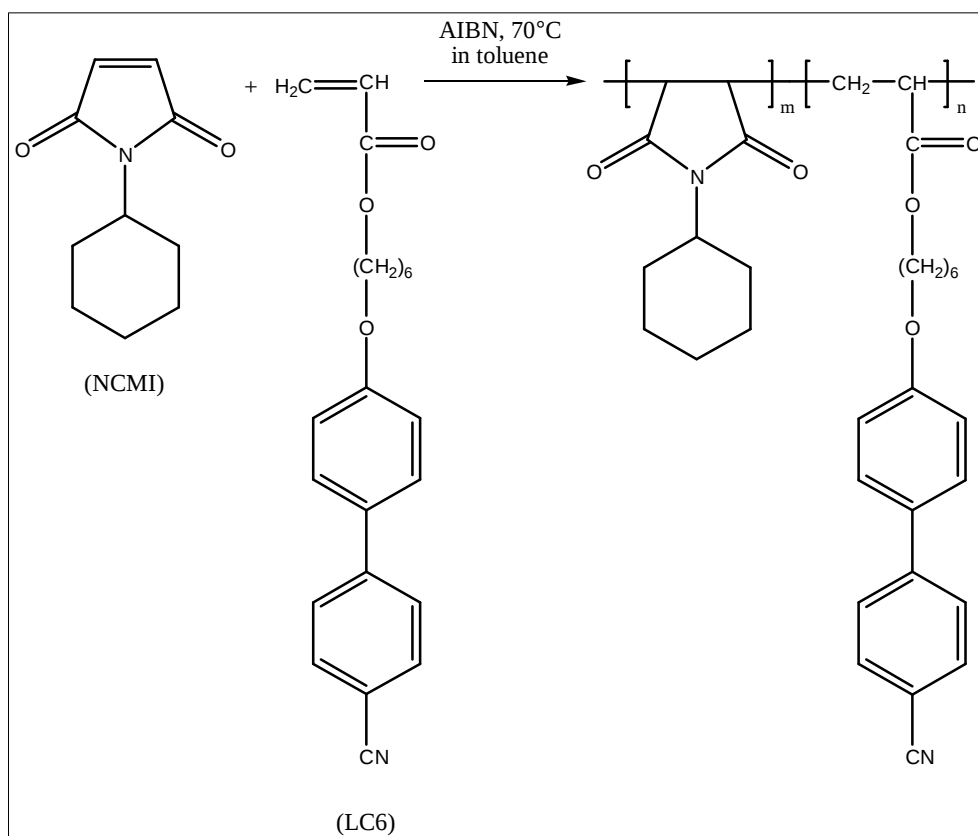


Figure 4.4: Synthesis of poly(LC6)-alt-poly(NCMI) by FRP

The obtained copolymers were characterized by $^1\text{H-NMR}$; (in CDCl_3): $\delta = 6.9\text{--}7.6$ ppm; aromatic protons of LC6, 3.9–4.1 ppm; $-\text{OCH}_2$ protons of LC6, 3.7–3.9 ppm; methine proton of NCMI, 2.1–1.2 ppm; aliphatic protons of LC6 and methylene protons of the alicyclic ring of NCMI (Figure 4.5). Ratio of the monomer units in alternating copolymer was determined by the integral areas in the $^1\text{H-NMR}$ spectrum.

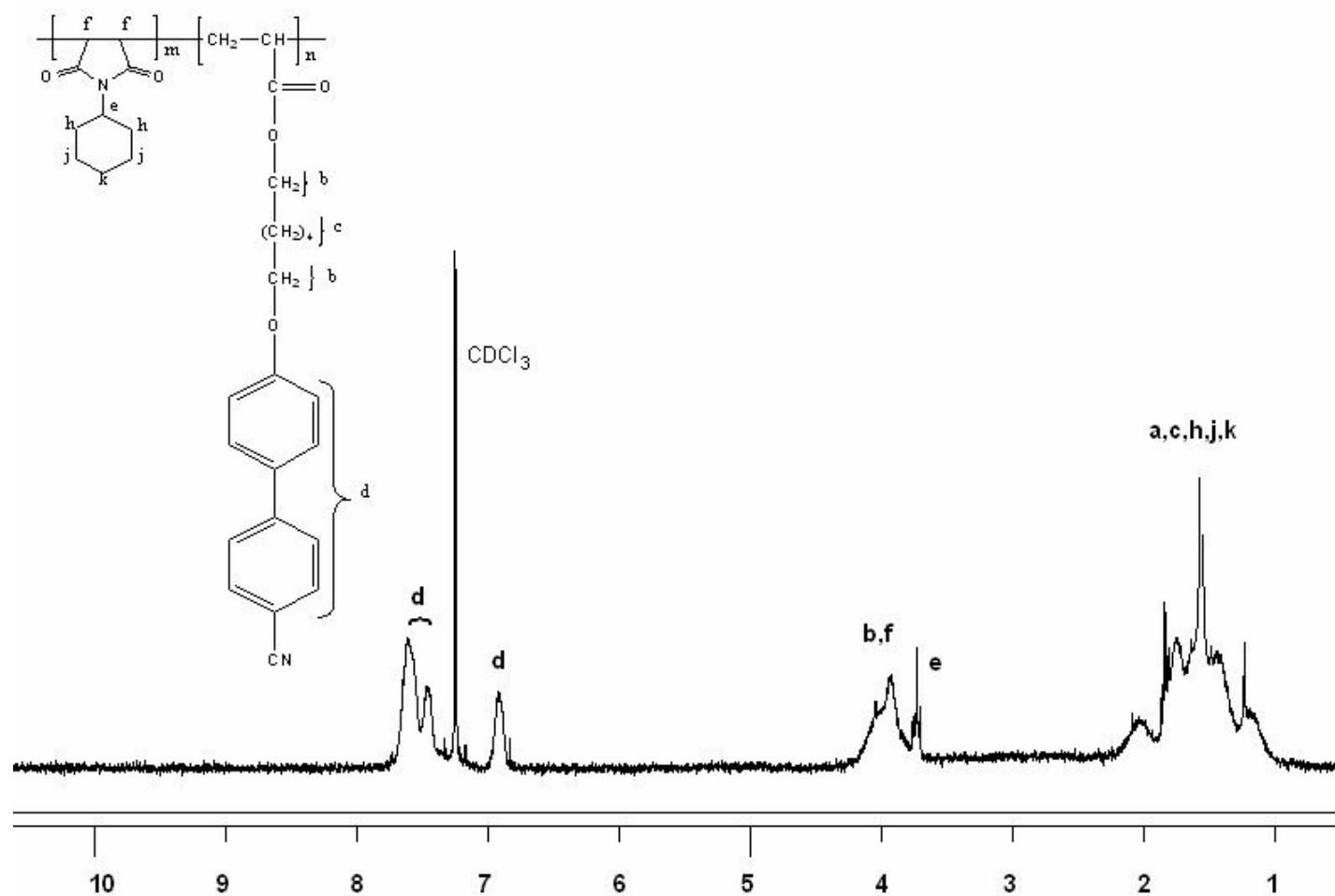


Figure 4.5: ^1H -NMR Spectrum of poly(LC6)-alt-poly(NCMI)

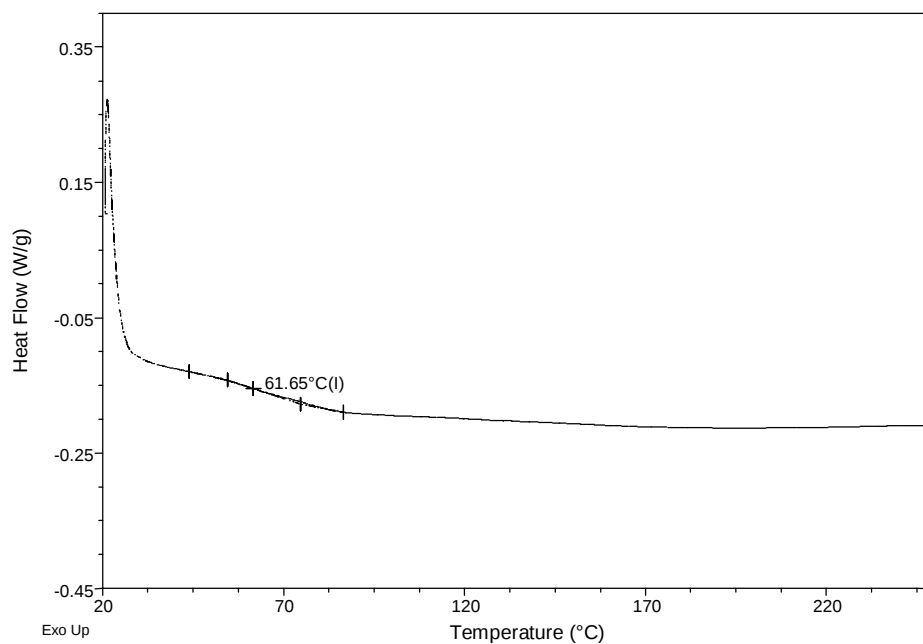
Table 4.1: Synthesis of poly(LC6)-alt-poly(NCMI) by FRP

	[LC6]/[NCMI] (mol/l)	[I ₀] (mol/l) x10 ⁻²	Time (h)	Conv. (%)	Composition ^c (%) [LC6]/[NCMI]	M _n ^d	M _w /M _n ^d
M1 ^a	0,33 / 0,33	0,33	24	70	43 / 57	10500	2,1
M2 ^b	0,66 / 0,33	0,33	24	95	52 / 48	10100	2,5

^a [LC6]:[NCMI]:[AIBN]:100:100:1 at 70°C in toluene^b [LC6]:[NCMI]:[AIBN]: 200:100:1 at 70°C in toluene^c Calculated from ¹H-NMR spectrum of resultant copolymers^d Determined by GPC based on PSt standards

Under the identical polymerization condition and after the same reaction time, high reaction conversion occurring near the equimolar feed composition indicates the formation of charge transfer complexes (CTC) between LC6 (electron-donor) and NCMI (electron-acceptor).

The thermal properties of resultant copolymers were evaluated by means of Differential Scanning Calorimeter (DSC) and Thermogravimetric Analysis (TGA) measurements. DSC measurements were conducted with a heating rate of 10 °C/min under nitrogen. The DSC curve of M1 is shown in Figure 4.6.

**Figure 4.6:** DSC thermogram of M1

The thermal stability of resultant copolymers was investigated by TGA. The sample was heated from 30°C to 500°C at a scan rate of 20°C/min under nitrogen atmosphere. Figure 4.7 shows the thermal stability and the weight loss.

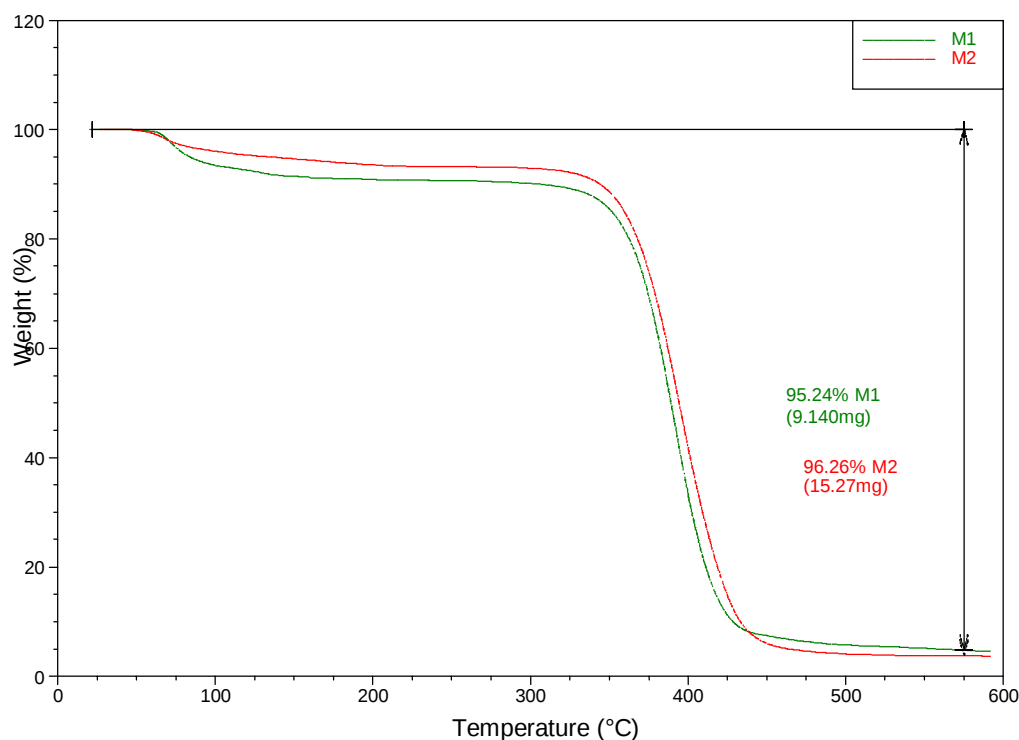


Figure 4.7: TGA curves of M1 and M2

The glass transition temperature (T_g), the initial decomposition temperature (T_i), the half-weight loss temperature (T_{50}) and the residual weights obtained are summarized in Table 4.2. All of these values increased with increasing content of NCMI. It is concluded that the thermal stability of the polymeric materials could be improved through copolymerization with NCMI.

Table 4.2: Thermal properties of copolymers obtained by FRP

	f_{NCMI}^a	F_{NCMI}^b	T_g (°C)	T_i (°C)	T_{50} (°C)	Residue at 500°C (%)
M1	0,50	0,57	61,6	306	389	4,8
M2	0,33	0,48	58,5	310	394	3,7

^a The initial molar composition of the comonomer feed.

^b The molar fraction of NCMI in the copolymer.

4.3 Synthesis of Alternating Copolymers of N-Cyclohexylmaleimide with LC6 by ATRP

Atom Transfer Radical Polymerization (ATRP) was applied to copolymerize liquid crystalline acrylate (6-(4-cyanobiphenyl-4'-oxy)hexyl acrylate) (LC6) monomer and N-Cyclohexylmaleimide (NCMI) monomer (Figure 4.8). Copolymerization of LC6 and NCMI in the presence of Cu(I)Br / PMDETA catalyst system using anisole as a solvent at 110°C initiated by 2-bromopropionyl bromide afforded well-defined copolymers. The conditions and results of the polymerization reactions are summarized in Table 4.3.

The structure of the alternating copolymers was assigned by means of ^1H -NMR spectral measurements recorded in CDCl_3 . Spectrums represents characteristic signals of both segments as also represented for the copolymers obtained by FRP (Figure 4.5). Similarly ratio of the monomer units in alternating copolymer was determined by the integral areas in the ^1H -NMR spectrum.

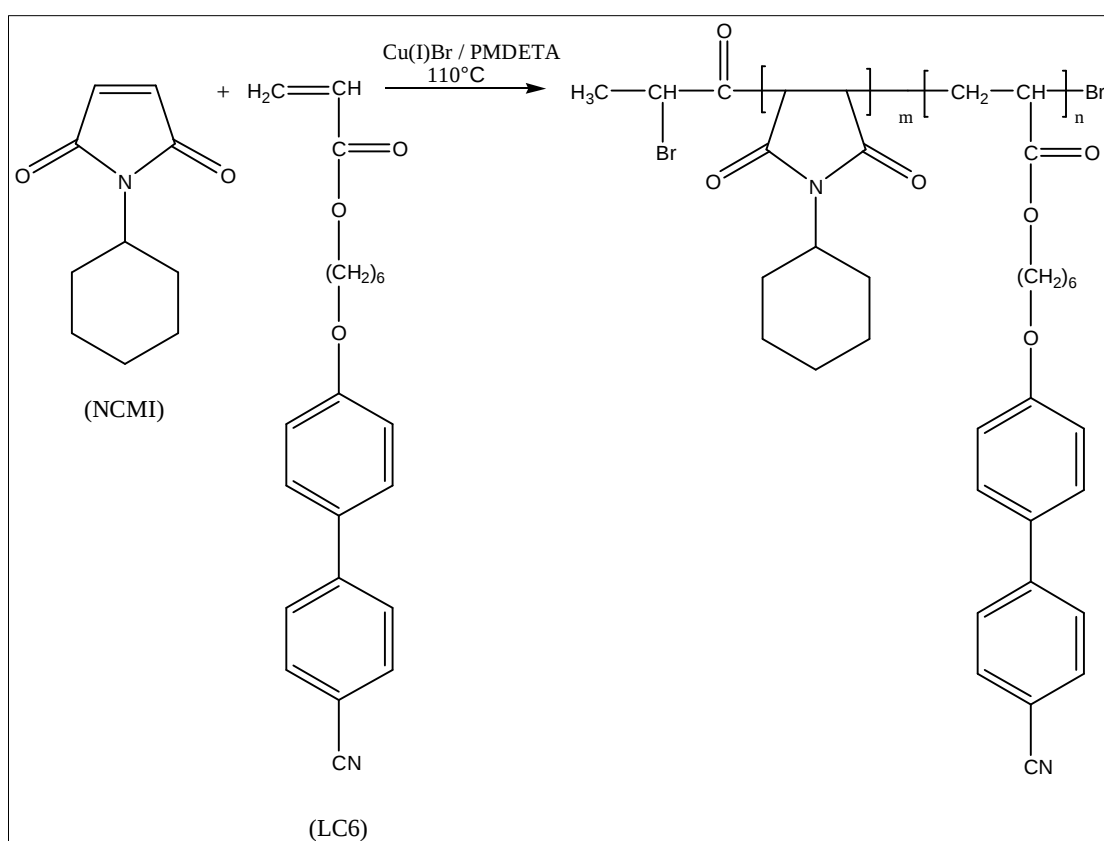


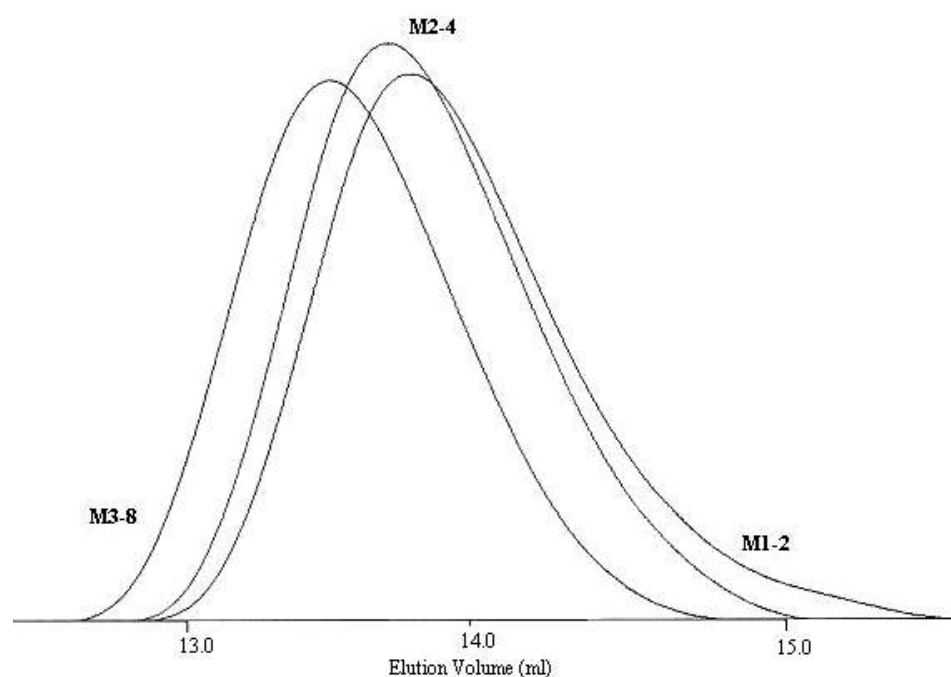
Figure 4.8: Synthesis of poly(LC6)-alt-poly(NCMI) by ATRP

Table 4.3: Synthesis of poly(LC6)-alt-poly(NCMI) by ATRP^a

	[LC6]/[NCMI] (mol/l)	[I ₀] ^b (mol/l)	Time (day)	Conv. (%)	Composition ^c (%)	M _n ^d	M _w /M _n ^d
					[LC6]/[NCMI]		
M1-2	0,95 / 0,95	0,019	2	3	58 / 42	4400	1,17
M2-4	0,95 / 0,95	0,019	4	5	43 / 57	5100	1,20
M3-8	0,95 / 0,95	0,019	8	8	39 / 61	6900	1,17

^a [LC6]:[NCMI]:[I]:[CuBr]:[PMDETA]:50:50:1:1:2 at 110°C in anisole^b Initiator: 2-bromopropionyl bromide^c Calculated from H-NMR spectrum of resultant copolymers^d Determined by GPC based on PSt standards

Resulting copolymers were analyzed by GPC (Figure 4.9). The monomodal shape of the GPC trace of the obtained polymers suggested the formation of copolymers without homopolymerization. An increase in the molecular weight by time without a significant increase in polydispersity was observed.

**Figure 4.9:** GPC traces of resulting copolymers obtained by ATRP

The glass transition temperature (T_g) of the copolymers were measured by DSC in a flowing nitrogen atmosphere (the heating rate was $10^\circ\text{C}/\text{min}$). The DSC curves of copolymers obtained by ATRP are shown in Figure 4.10.

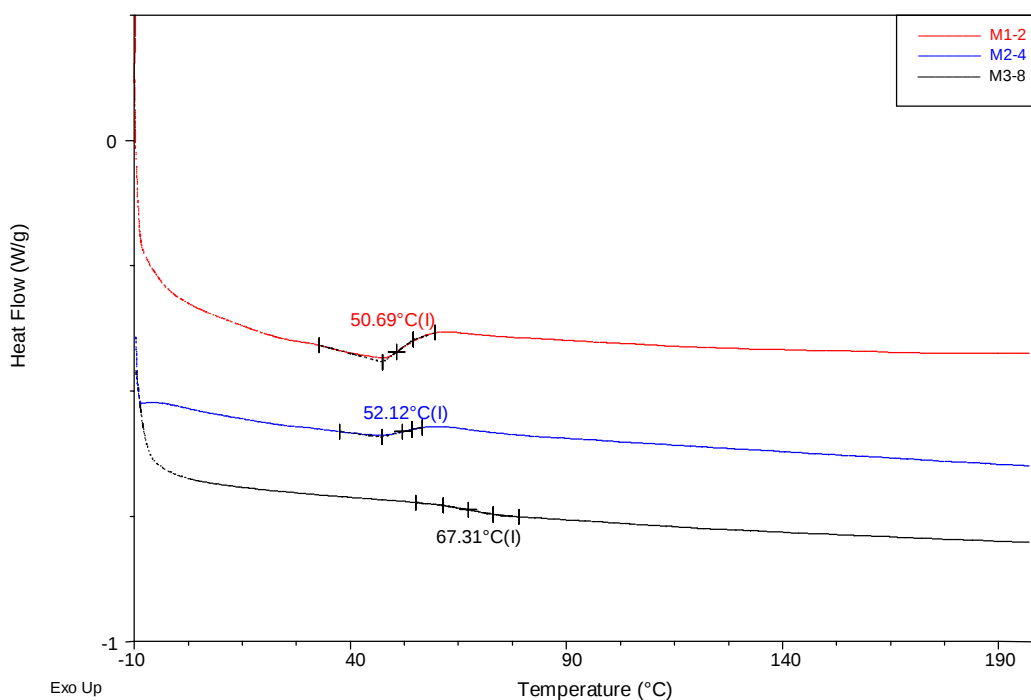


Figure 4.10: DSC thermograms of copolymers obtained by ATRP

In the case of ATRP, T_g of the copolymers increases by increase in molecular weight.

TGA was carried out in a nitrogen stream at a heating rate of $20^\circ\text{C}/\text{min}$ for analysing thermal stabilities of the copolymers. Figure 4.11 shows TGA curves for copolymers obtained by ATRP with various reaction times.

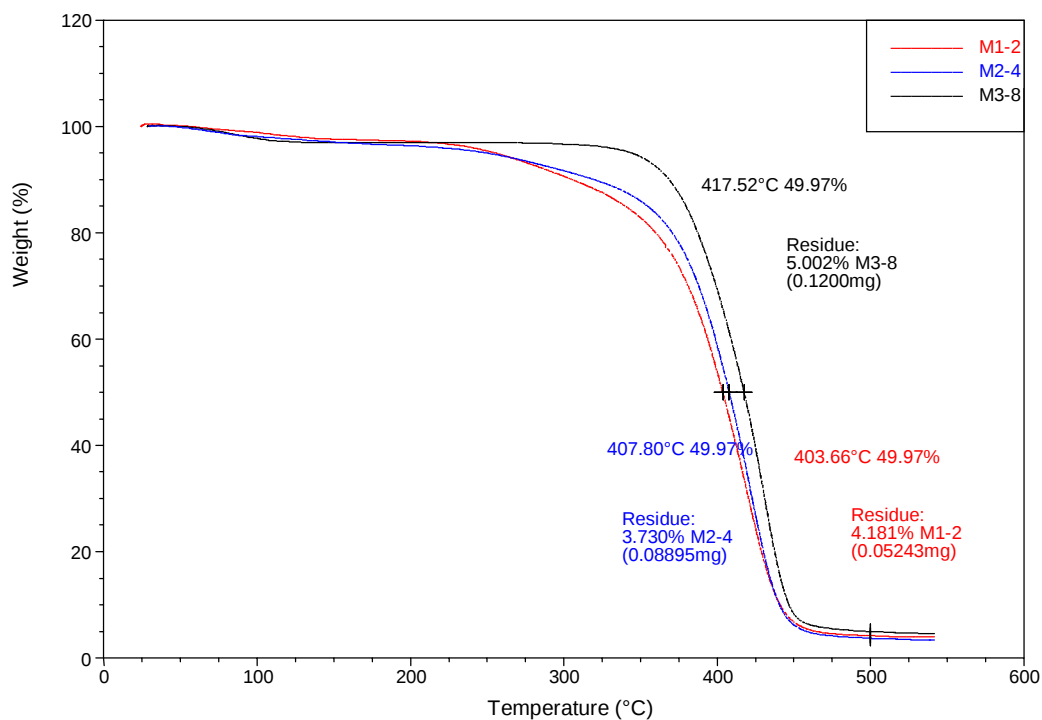


Figure 4.11: TGA curves of copolymers obtained by ATRP

The thermal data of the copolymers are shown in Table 4.4. As the molar fraction of NCMI in the copolymer increases, the T_g increases and decomposition temperatures shifts to the higher temperature range.

Table 4.4: Thermal properties of copolymers obtained by ATRP

	f_{NCMI}^a	F_{NCMI}^a	T_g (°C)	T_i (°C)	T_{50} (°C)	Residue at 500°C (%)
M1-2	0,50	0,42	50,7	215	403,6	4,2
M2-4	0,50	0,57	52,1	261	407,8	3,7
M3-8	0,50	0,61	67,3	307	417,5	5,0

^a The initial molar composition of the comonomer feed.

^b The molar fraction of NCMI in the copolymer.

The T_g of the homopolymer of LC6 (PLC6, $M_n = 10000$ g/mol) is about 40°C. So the results show us that thermal stabilities of the copolymers improved due to the incorporation of NCMI segments into the copolymer.

5. CONCLUSIONS

The liquid crystalline containing maleimide copolymers were synthesized by using two polymerization methods namely FRP and ATRP.

The molar fractions of monomers in the copolymers determined by the ^1H -NMR spectrum confirmed the alternating structure. Copolymers with controlled molecular weight and narrow molecular weight distribution were obtained by ATRP.

The thermal properties of the resulting copolymers were investigated by DSC and TGA measurements. The glass transition temperature and thermal stabilities of the copolymers increased by increasing the N-substituted maleimide (NCMI) content.

As a result thermally stable liquid crystalline polymers were synthesized by introducing maleimide segments into the polymer.

Additionally, further investigations about LC properties of resulting copolymers can be developed by using Polarized Optical Microscope (POM) and DSC measurements.

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RESUME

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