İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF ANTHRACENE LABELLED POLYMERS

M.Sc. Thesis by

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ANTRASEN SONLU POLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymers
M_w	: Weight average molecular weight of polymers
MWD	: Molecular weight distribution of polymers
PtBA	: Poly(tert-butyl acrylate)
PMMA	: Poly(methyl methacrylate)
PεCL	: Poly(ε-caprolactone)
PTHF	: Poly(tetrahydrofuran)
k_a, k_d	: Rate constants of activation and deactivation steps of the initiation in radical polymerization
Et_3N	: Triethylamine
€	: Molar absorbtion coefficient
I, M	: Initiator and monomer respectively

SUMMARY

SYNTHESIS AND CHARACTERIZATION OF ANTHRACENE-LABELLED POLYMERS

In the present work, anthracene-labelled polymers were synthesized by atom transfer radical polymerization (ATRP), cationic ring opening polymerization (CROP), and ring opening polymerization (ROP) techniques.

A required functional group can be introduced into a polymeric chain by initiation or termination stages of the particular polymerization involved.

In this work, introduction of anthracene moieties was carried out by initiation or termination stages.

Anthracene-labelled poly(methyl methacrylate) and poly(tert-butyl acrylate) were prepared via ATRP, where 9-anthryl methyl 2-bromo propanoate was used as the initiator.

Poly(ε-caprolactone), bearing the anthryl group at one chain end, which was initiated by 9-anthryl methanol, was synthesized by ROP.

Mono and bifunctional poly(tetrahydrofuran)s which were initiated by methyl triflate and triflic anhydride, respectively, bearing anthracene units, were synthesized by CROP. Anthracene units were attached to the polymer chains, at the termination stage of the polymerization, by sodium 9-anthryl methoxide.

GPC (Gel Permeation Chromatography), UV, ^{1}H-NMR and fluorescence spectral analysis showed that, the anthracene-labelled polymers were successfully synthesized.

ÖZET

ANTRASEN SONLU POLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

Bu çalışmada, antrasen sonlu polimerler, atom transfer radikal polimerizasyonu (ATRP), katyonik halka açılması polimerizasyonu (CROP) ve halka açılması polimerizasyonu (ROP) yöntemleriyle sentezlendi.

Bir fonksiyonel grup, bir polimer zincirine, polimerizasyonun başlama veya sonlanma aşamaları ile yerleştirilebilir. Bu çalışmada, antrasen polimer zincirine polimerizasyonun başlama veya sonlanma aşamalarında yerleştirildi.

Antrasen-sonlu metil metakrilat ve ter-butil akrilat polimerleri, başlatıcı olarak 9-antril metil 2-bromo propanoat'ın kullanıldığı, ATRP yöntemiyle hazırlandı.

9-antril metanol'le başlatılan, ε-kaprolakton polimerleri, ROP yöntemiyle sentezlendi.

Antrasen grubu taşıyan ve sırasıyla metil triflat ve triflik anhidrid ile başlatılan tetrahidrofuran polimerleri CROP metoduyla sentezlendi. Antrasen, polimer zincirine, polimerizasyonun sonlandırma aşamasında, sodyum 9-antril metoksit kullanılarak katıldı.

GPC (Jel Geçirgenlik Kromatografisi), UV, ^{1}H-NMR ve floresans spekroskopi cihazlarından alınan sonuçlar, antrasen-sonlu polimerlerin başarılı bir şekilde sentezlendiğini göstermiştir.

PART 1

INTRODUCTION

The field of photochemistry covers all processes which involve chemical change brought about by the action of visible or ultraviolet radiation, and these processes generally involve the direct participation of an electronically excited state of a molecule.

An electronically excited state contains two unpaired electrons in different orbitals, and these can be of the same (parallel) spin or of different (opposed) spin. Such states are triplet and singlet states respectively, and the two are distinct species, with different physicaland chemical properties. A triplet state has a lower energy than the corresponding singlet state because of the repulsive nature of the spin-spin interactionbetween electrons of the same spin. The magnitude of the difference in energy varies according to the degreeof spatial interaction (overlap) between the orbitals involved. For orbitals which occupy substantially different regions of space [as in (n,π^*) states of carbonyl compounds] orbital overlap is small and the singlet-triplet energy difference (splitting) is relatively small. For orbitals which occupy similar regions of space [as in (π,π^*) states of alkenes] the difference is much larger.
The excited states initially produced by absorption of a photon are almost always singlet states. This is because practically all molecules encountered in organic chemistry have a singlet ground state and the selection rules for absorption strongly favour conservation of spin during the absorption process. Different systems of describing excited states are employed depending on which properties of the state are to emphasized and on the amount of information available concerning the nature of the originating transition. Therefore, if symmetry considerations are dominant, group theoretical symbols will be adopted. For example, the ground state of benzene,

(anthracene consists of three benzene like rings joined side by side), ($^1A_{1g}$) is excited by the 253.7 nm mercury line into its first electronically excited state, designated $^1B_{2u}$, and the transition would be symbolized $^1A_{1g} \rightarrow {}^1B_{2u}$. Alternatively, the molecular orbitals involved in the transition may be specified. In the benzene example, an electron is promoted from a π to a π^* orbital; the transition is then ($\pi \rightarrow \pi^*$) and the state is symbolized (π,π^*). Since there are several π and π^* orbitals, clearly this nomenclature is less precise than that based upon group theory.

A state energy level diagram, can be used to represent diagrammatically the various electronic states of a molecule. The singlet and triplet states range in order of increasing energy and can be numbered in the same order S_o, S_1, S_2... and T_1, T_2... respectively. Each of the energy levels is the lowest energy point of a complete potential energy surface, and the horizontal axis in a simple state diagram has no significance.

It is possible to represent on such a diagram all the physical processes involved in the interconversion of the states (Figure1.1). These are absorption of a photon by the ground state to produce an excited singlet state, radiative decay processes, namely fluorescence (spin-allowed) and phosphorescence (spin-forbidden), and non-radiative decay processes, namely internal conversion (spin-allowed) and intersystem crossing (spin-forbidden). Such a diagram is known as a Jablonski diagram.

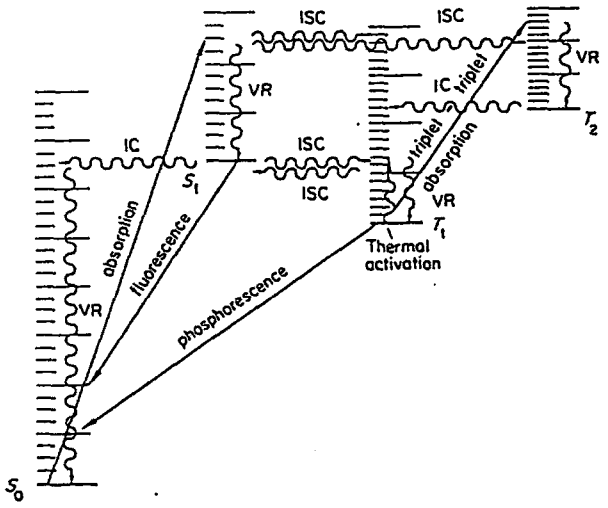
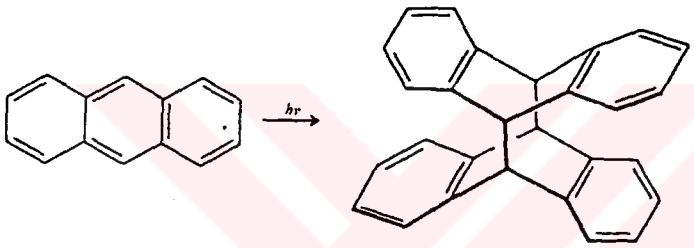


Figure 1.1 Jablonski diagram showing some of the radiative and non-radiative processes available to molecules (VR = vibrational, relaxation; IC = internal conversion; ISC = intersystem crossing)

Fluorescence is caused by a radiative transition between states of the same multiplicity, and it is a rapid process ($k_f \sim 10^6$-10^9 s^{-1}). For the polyatomic molecules encountered in organic chemistry, the transition is usually $S_1 \rightarrow S_o$, although $S_2 \rightarrow S_o$ fluorescence is occasionally observed and may often be hidden under the moreintense $S_1 \rightarrow S_o$ emission. A very weak $S_n \rightarrow S_m$ emission has recently been detected for a number of other molecules, as has $T_n \rightarrow T_m$ fluorescence. In sharp contrast, strong $S_n \rightarrow S_m$ fluorescence is observed in diatomics.

Photodimerization of anthracene is suggested as a method of coupling two polymer chains by an elegant and selective reaction. Photodimerization of anthracene can be seen in Scheme1.1.



Scheme 1.1 Photodimerization of anthracene

Fluorescence excitation spectroscopy can be used to identify and quantitatively to estimate fluorescent molecules. It supplements absorption spectroscopy, but with the difference that fluorimetric analysis is often orders of magnitude more sensitive. This increase in sensitivity is primarily due to the fact that the fluorescence signal can be observed, amplified and recorded directly, whereas with absorption spectroscopy what is measured is the signal due to the difference between the incident and transmitted light intensities.

As the fluorescence technique can sensibly detect the structural alterations at the immediate local environment around probes, it has become a popular tool in polymer sciences to study structural , conformational and dynamic properties of polymer molecules.

For this purpose a fluorescent probe must be introduced into a polymer chain without perturbing the mobility of the polymer chain. The probes can be incorporated by

initiation or termination stages of polymerization processes.

Anthracene or its derivatives are one of the most commonly used fluorescence probes because of the following peculiar characteristics: (i) they do not have any specific interactions with most polymers; (ii) many useful derivatives are available; (iii) the relatively small size and symmetric shape seldom hinder polymeric motions.

One way to introduce anthracene units in the polymeric backbone is "living" anionic polymerization. The labelled polymers prepared in this way have well-controlled molecular weights, however, anionic polymerization is experimentally demanding and not many kinds of polymers have been synthesized by this method for the present purpose.

Radical polymerization has also been employed for the preparation of anthracene-labelled polymers. Although the free radical polymerization is the most widely used technique, this method lacks the control of molecular weight and molecular architecture due to the chain transfer and the termination processes.

Introduction of anthracene moieties into polymer chains, can also be achieved by atom transfer radical polymerization (ATRP), living cationic ring opening polymerization (CROP) and living ring opening polymerization (ROP), which provide a good control over molecular weight and structure.

In the present work, anthracene-labelled poly(methyl methacrylate) and poly(tert-butyl acrylate) were synthesized by ATRP, mono and bifunctional poly(tetrahydrofuran)s were prepared by CROP, and poly(ε-caprolactone) was formed by ROP. In ATRP and ROP methods, anthracene was attached to the polymer chains by initiation, and in CROP method by termination steps.

PART 2

THEORETICAL PART

2.1 ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

ATRP is the most versatile polymerization method being able to polymerize a variety of monomers like methyl methacrylate, acrylate and styrene monomers with well-controlled molecular weights and well-defined structures [1-4].

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 (2.1), involves the abstraction of a halogen from the dormant chain by a metal center, such as complexes of Cu^1, in a redox process [5]. 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 ($DP=\Delta[M]/[I_o]$) and M_w/M_n is quite low (1,05-1,5), and good controi of functionalities is achieved [6].

Initiation

$$R\text{-}X + Cu(I)/Ligand \underset{k^o_d}{\overset{k^o_a}{\rightleftharpoons}} R\cdot + XCu(II)/Ligand \quad (2.1)$$

$$R\cdot \xrightarrow{k_i, +M} R\text{-}M\cdot$$

$$R\text{-}M\text{-}X + Cu(I)/Ligand \rightleftharpoons R\text{-}M\cdot + XCu(II)/Ligand$$

$$R\text{-}M\cdot \xrightarrow{k_p, +M_n} R\text{-}M_n\cdot$$

Propagation

$$R\text{-}M_n\text{-}X + Cu(I)/Ligand \rightleftharpoons R\text{-}M_n\cdot + XCu(II)/Ligand$$

Termination

$$R\text{-}M_n\cdot + R\text{-}M_m\cdot \xrightarrow{k_t} R\text{-}M_{n+m}\text{-}R + R\text{-}M_nH / R\text{-}M_m^{=}$$

ATRP is a multy-component system, so concentrations and the structures of all these compounds affect the polymerization rate and the properties of the resulting polymer.

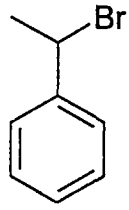
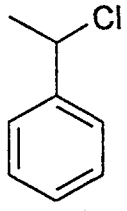
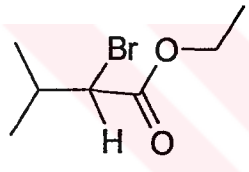
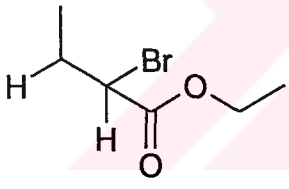
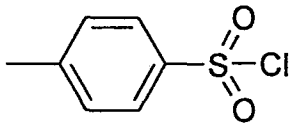
2.1.1 Initiators

There is a large class of halogenated compounds that can be used as initiators in ATRP. The only requirement is that the initiator must have labile halogen attached to an atom containing radical stabilizing substituents [7].

In ATRP both effective initiation and good control of the polymerization rely heavily on the position of the equilibrium in both the initiation and the propagation steps, and also on reactivities of the radicals generated in the initiation step. Thus, choosing a suitable organic halide and $Cu^{(I)}$ halide is necessary for the controlled polymerization.

The most frequently used initiator types in ATRP systems are given in Table 2.1.

Table 2.1 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

2.1.2 Transition Metals Used in ATRP

Basic requirements for the good catalyst are high selectivity towards atom transfer process and high lability of the resulting $X\text{-}M_t^{n+1}$ 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 ligand → X-Cu(II) / 2 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) / $3PR_3$.

2.1.3 Ligand

Ligands play a very important role by solubilizing the catalyst and electronically affecting its redox potential in the M_t^n / M_t^{n+1} cycle. Steric effects are equally important, because atom transfer proceeds with the expansion of the coordination sphere of the metal. 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), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimethylamino) ethyl]amine (Me_6-TREN) and Alkylpyridylmethaneimines are also used.

Since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bipy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates, enables better control, and thus simple amines are very attractive alternatives to bipy and its derivatives as the ligands [8,9]. It is stated that when PMDETA and HMTETA are used, the ratio of 1:1, when bipy or TMEDA is used, the ratio of 1:2 is sufficient to achieve maximum rates and control of polymerization.

2.1.4 Monomers

Styrenes, acrylates, methacrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and dienes can be polymerized by ATRP, and well defined polymers are achieved.

As a result, atom transfer radical polymerization (ATRP) is a powerful technique allowing the polymerization of a variety of monomers with a high degree of control over the molecular weights and the molecular weight distributions of the resulting polymers. Additionally,since the polymerization conditions are relatively simple, various types of macromolecular structures can be achieved with a simple polymerization system via this method.

2.2 Living Cationic Ring Opening Polymerization (CROP) of Tetrahydrofuran (THF) Initiated by Methyl Triflate and Triflic Anhydride

THF is an unsubstituted five-membered cyclic ether, containing four methylene groups connected by an oxygen bridge. Since the ring contains an oxygen atom with two unshared pairs of electrons, THF is a nucleophilic monomer [10].

2.2.1 Initiation

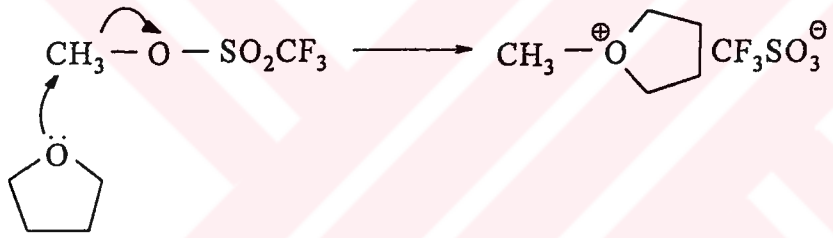
The species which initiates THF polymerization is comprised of a cation and an anion. The polymerization is initiated by a nucleophilic attack of the free electrons of the THF oxygen on the carbon adjacent to the oxygen .

The nature of the counter ion, X^-, is very important . It is useful to consider these anions in terms of the position of the elements of which they are composed in the periodic table . The elements that comprise stable counter ions for THF polymerizations are found almost exclusively among nonmetals in groups VA, VIA, and VIIA. These elements include the most highly electronegative element, F. More firmly bonded elements in a complex ion lead to more stable and more suitable counterions for THF polymerization and fewer side reactions. Whereas maximum stability of the counterion itself is desirable, intermediate stability of the complex is

preferable. The complex should not be so stable that polymerization or desired termination reactions are inhibited.

Methyl triflate (methyl trifluoromethane sulfonate, $CH_3SO_3CF_3$) and triflic anhydride (trifluoromethane sulfonic anhydride, $CF_3SO_2OSO_2CF_3$), which are derivatives of trifluoromethane sulfonicacid ($HOSO_2CF_3$), are excellent initiators for the living polymerization of THF. The growing sites are long-living, provided that reaction medium does not contain any transfer agents such as alcohols, ethers, amines or acids.

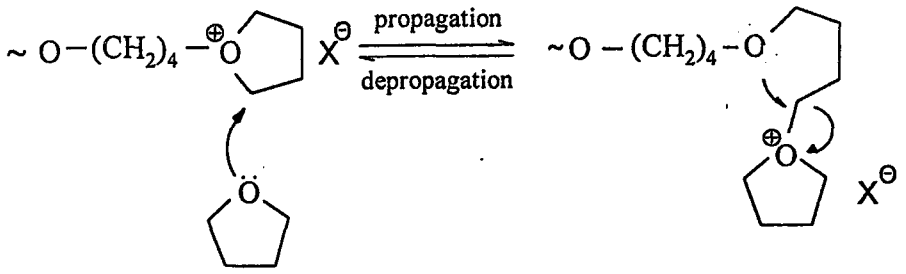
Triflic anhydride as a bifunctional initiator leads to PTHF capable of growing on both ends, whereas methyl triflate produces PTHF, growing at one end only. The mechanism by which the required oxonium ion is formed, is direct alkylation of the oxygen of THF, which is shown in (2.2) for initiation by methyl triflate.



(2.2)

2.2.2 Propagation

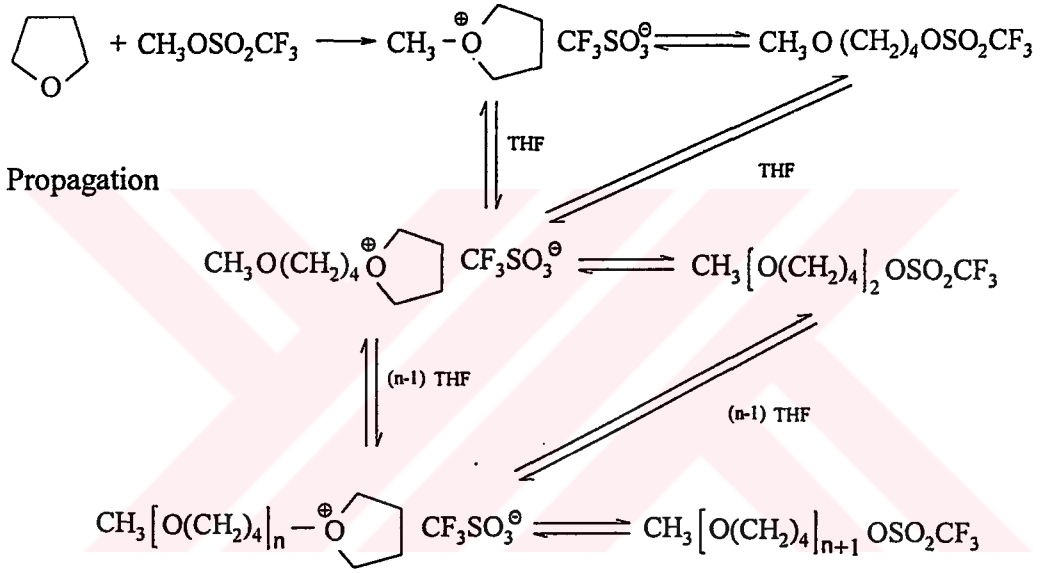
The propagating species in THF polymerization is an oxonium ion, and it associates with a negatively charged species. Ring strain of THF is lower than that of three- and four-membered rings. Thus polymerization is highly reversible, and propagation-depropagation reactions take place [11-14].



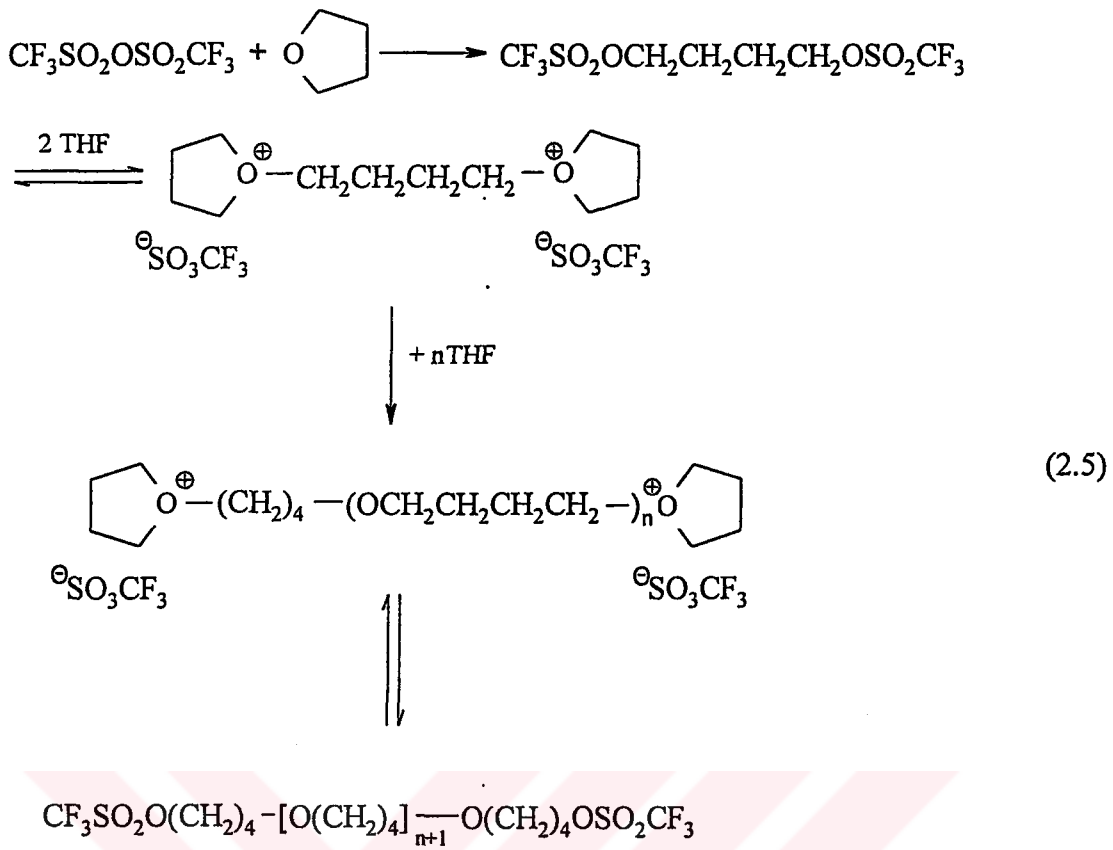
(2.3)

With methyl triflate and triflic anhydride as initiators, in addition to the propagation-depropagation reactions involving oxonium ions, the equilibrium between oxonium ion and an ester, formed with the counterion, occurs. At each stage of the polymerization, the oxonium ion-counterion complex is in equilibrium with its corresponding ester. The propagation-depropagation reactions and the oxonium ion-counterion equilibria is shown in (2.4) for the polymerization initiated by methyl triflate , and the general mechanism of polymerization initiated by triflic anhydride is represented by (2.5) .

Initiation



(2.4)



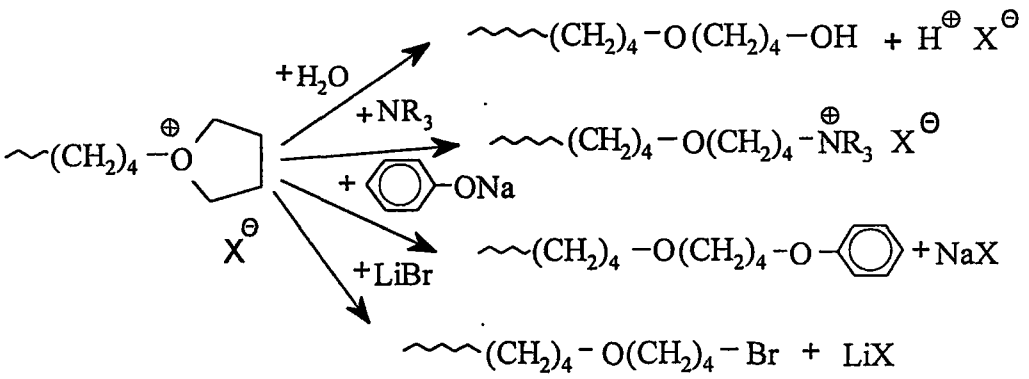
(2.5)

$$CF_3SO_2O(CH_2)_4\text{-}[O(CH_2)_4]_{n+1}\text{—}O(CH_2)_4OSO_2CF_3$$

In this type of polymerization, the concentration of growing centers is equal or close to the initial initiator concentration. Polymers with low polydispersity can be prepared, only at low conversions and short times, or if the propagation proceeds at low temperatures. As conversion increases, transfer to polymer oxygen occurs and tends to broaden the molecular weight distribution at longer times and higher temperatures. In addition some cyclization reactions also occur.

2.2.3 Termination

The polymerization can be terminated by a variety of nucleophilic reagents such as excess water, tertiary amines, phenolates or lithium bromide, which are shown in (2.6). Under the above mentioned conditions, almost any desired end groups can be introduced.



2.3 Living Ring Opening Polymerization (ROP) of ε-Caprolactone (ε-CL)

Polyesters can be synthesized by a step-growth process, i.e., a polycondensation, from a mixture of a diol and a diacid, or from a hydroxy-acid [17]. Molecular weight of the polycondensates is usually limited to a few tens of thousands ($M_n \leq 30000$), and the only way to control it in this limited range of chain length is the use of terminating (monofunctional) agents. Even though conversion of the hydroxyl and acid groups is close to completion, any departure from the reaction stoichiometry has a very detrimental effect on the chain length.

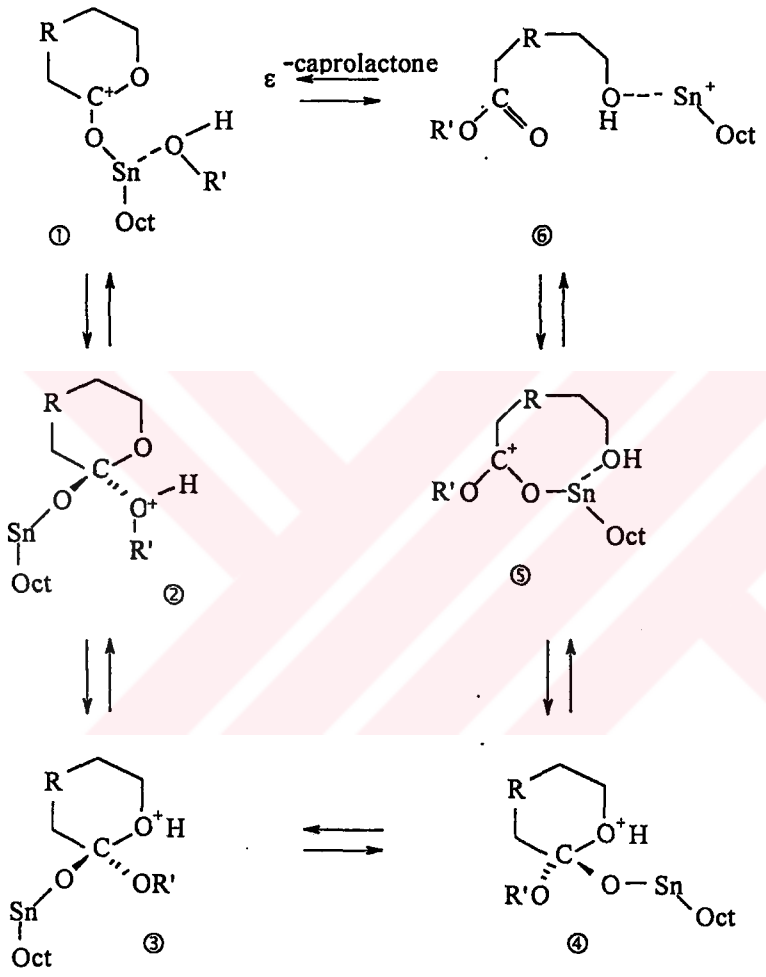
Ring opening polymerization (ROP) of cyclic esters and related compounds is an alternative method for the synthesis of aliphatic polyesters. The first attemts at ROP have been mainly based on anionic and cationic processes [18]. In most cases, polyesters of low molecular weight were recovered and there was no control on the polymerization process due to the occurence of side intra- and intermolecular transesterification reactions responsible for a mixture of linear and cyclic molecules.

Under mild conditions, ROP is usually free of limitations and high molecular weight aliphatic polyesters can be prepared.

The discovery that some organometallic compounds are affective in the synthesis of high molecular weight PCL [19] promoted a renewed interest in the ROP of ε-CL, particularly with alkyl metals, metal alkoxides etc.

Depending on the structure of the organometallic derivatives, they can act as catalyst or as initiators.

- Metal halides, oxides, and carboxylates act as Lewis acid catalysts in an ROP actually initiated with a hydroxyl-containing compound, such as water, alcohol etc. Polymerization is assumed to proceed through an insertion mechanism. The most frequently incountered Lewis acid catalyst is stannous 2-ethyl hexanoate, referred to as stannous octoate.



(2.7)

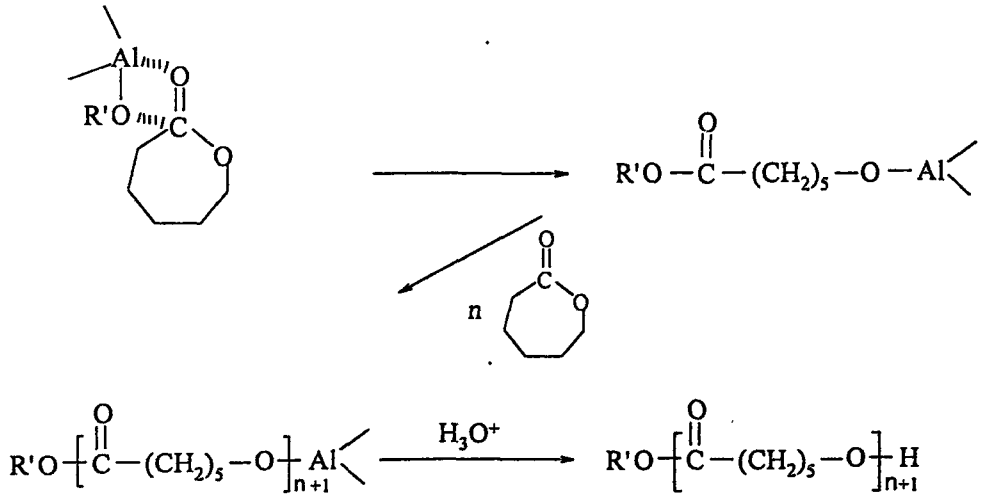
The mechanism of the ROP of ε-CL is seen in (2.7).

The polymerization starts when the hydroxyl-containing compound R'OH reacts with the lactone/Sn^+(Oct) complex through a nucleophilic attack at the carbon (structurs 1 and 2 in (2.7)). After coordination complex 6 is formed, the coordination with new ε-CL generates species 1 again, where in this case R' is the growing polymer chain. The catalyst is not bonded to the growing chain end (structure 6 in

(2.7)), so that they can activate more than one chain. As a result, the average degree of polymerization is not directly controlled by the monomer-to-catalyst molar ratio [20]. Molecular weight can be predicted by the monomer-to-initiator molar ratio and the molecular weight distributions are narrow. Good solubility of the catalyst in the monomer melt is important and ($Sn(Oct)_2$) yields high molecular weight PεCLs when a low concentration is used.

- Metal alkoxides containing free p-, d-, or f- orbitals of a favorable energy (Mg-, Sn-, Ti-, Fe-, Al-, Zn-alkoxides) are used as initiators, a two-step "coordination-insertion" mechanism prevails, which consists of the lactone complexation onto the propagating species, i.e., leading to the cleavage of the metal-oxygen bond of the propagating species and acyl-oxygen bond of the cyclic monomer.

Among these, aluminum alkoxides have proved to promote a ROP with a restricted occurence of termination, transfer, and transesterification side-reactions, showing a high degree of livingness. Kricheldorf has studied different metal alkoxides and he has reported that "active covalent" bonds of the investigated metal alkoxides were reactive enough to generate intramolecular transesterification reactions-also known as "back-biting" reactions-yealding cyclic oligomers as by-products. Within the limits of the studied initiators, aluminum triisopropoxide ($Al(O^iPr)_3$ showed the least reactivity.

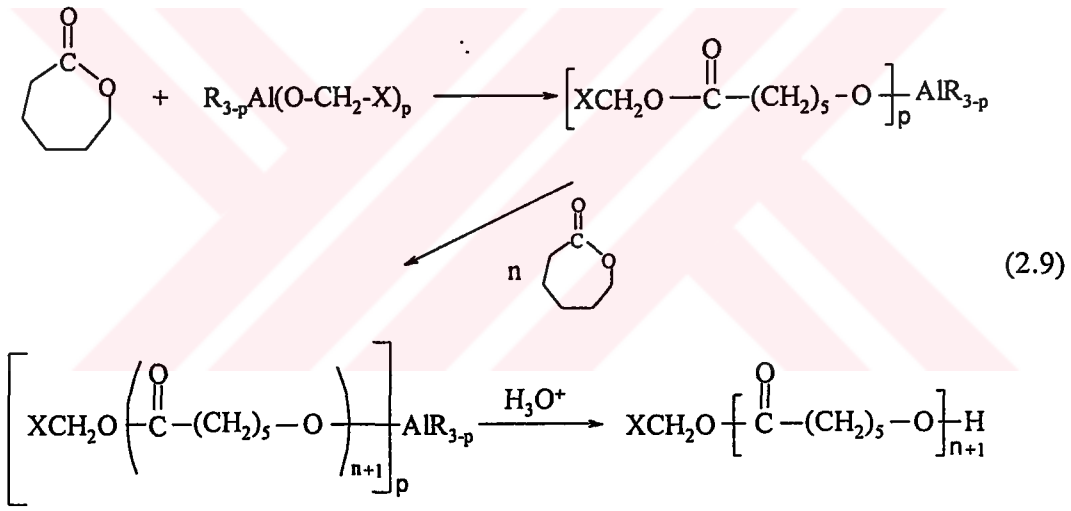


(2.8)

R' = ^{i}Pr

In (2.8) the ROP of ε-CL initiated by ($Al(O^iPr)_3$ is presented. In this two-step "coordination-insertion" mechanism which involves the insertion of the monomer into the "Al-O" bond of the initiator, the acyl-oxygen bond of ε-CL is cleaved in a way which maintains the growing chain attached to aluminum through an alkoxide bond. Polymerization is stopped by hydrolysis of the active aluminum alkoxide bond which leads to the formation of a hydroxyl end-group.

Al derivatives containing p (p = 1,3) functional alkoxide groups associated with 3-p inactive alkyl groups have also proved to be highly effective. In agreement with the "coordination-insertion" mechanism, the funcional group (OCH_2X) of the aluminum alkoxides is selectively attached to the α-chain end via an ester linkage, whereas a hydroxyl end group is present in the ω-position, as the result of the hydrolytic deactivation of the propagating aluminum alkoxide species.



(2.9)

PART 3

EXPERIMENTAL PART

3.1 Chemicals Used

a) Monomers

Methyl methacrylate (MMA, 99% Fluka) was passed through basic alumina column to remove inhibitors and then was vacuum-distilled over CaH_2 before use.

Tetrahydrofuran (THF, 99.8%, J.T. Baker HPLC grade) was dried and distilled over CaH_2, then it was let mixing over sodium/benzophenon ketyl, and was distilled prior to use.

ε-Caprolactone (ε-CL, 99% Fluka) was distilled over CaH_2 under high vacuum before use.

b) Solvents

Tetrahydrofuran (THF, 99.8%, J.T. Baker) technical grade was used. Dichloromethane was purchased from Aldrich and used after distillation over P_2O_5.

Unless otherwise specified, other reagents were purchased from commercial sources and used as received.

3.2 Synthesis of 9-anthryl methyl 2-bromo propanoate

To a round bottom flask were added 9-anthryl methanol (2 g, 9.6 mmol), triethylamine (1.4 ml, 10 mmol), and 20 ml of dry THF. To the reaction mixture, stirred at 0°C under nitrogen was added dropwise 2-bromopropanoyl bromide (1.1ml, 10.4 mmol) in 10 ml of dry THF over a period of one hour. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, crude product was dissolved in dichloromethane and washed successfully with water and dried over anhydrous sodium sulfate (Na_2SO_4). CH_2Cl_2 was removed and the yellow residue was crystallized over 2:1 ratio of hexane / trichloromethane ($CHCl_3$) [21].

3.3 Preparation of sodium 9-anthryl methoxide

Method 1

A graded tube equipped with a nitrogen inlet, and a rubber septum was connected to a vacuum line. The tube was dried by heating under vacuum. After cooling to room temperature, 15ml of THF was distilled into the tube. The tube was disconnected under nitrogen. NaH (80%) (0.03 g, 0.95mmol) was reacted with 9-anthryl methanol (0.2 g, 0.95 mmol) in 15 ml of distilled THF in an erlenmeyer flask.

Method 2

NaH (80 %) (0.072 g, 2.4 mmol) was reacted with 9-anthryl methanol (0.5 g, 2.4 mmol) in 15 mL of THF, distilled as mentioned in Method 1, in an erlenmeyer flask.

The mixture was stirred at room temperature. During mixing hydrogen evolved and a homogeneous solution formed.

3.4 Synthesis of Poly(methyl methacrylate), (PMMA), and Poly(tert-butyl acrylate), (PtBA), by ATRP

General procedure for the atom transfer radical polymerization was as follows: Into a schlenk tube eqipped with a magnetic stirring bar, monomer, solvent, ligand, catalyst

and initiator were added in the order mentioned. The tube was degassed by three freeze-thaw cycles, left under vacuum and placed in a thermostated oil bath at 90°C for PMMA and at 80°C for PtBA. After a given time polymerization was terminated by cooling the tube to room temperature. The reaction mixture was diluted with THF and passed through a column of neutral alumina to remove metal salt. THF was passed through the column of neutral alumina right before the reaction mixture was passed, in order to prevent the polymer to be kept inside the column. The excess of THF and unreacted monomer was evaporated under reduced pressure. PMMA was dissolved in THF and precipitated in methanol, filtered and dried under vacuum. Conversions were determined gravimetrically. PMMA was prepared in 50 vol % diphenylether (DPE) solution at 90°C using CuCl / N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) as the catalyst and 9-anthryl methyl 2-bromo propanoate as the initiator.

PtBA, was prepared in bulk at 80°C using CuBr as the catalyst, PMDETA as the ligand and 9-anthryl methyl 2-bromo propanoate as the initiator.

3.5 Synthesis of poly(tetrahydrofuran), (PTHF), by living cationic ring opening polymerization, (CROP)

A graded tube equipped with a nitrogen inlet, and a rubber septum was connected to a vacuum line. The tube was dried by heating under vacuum. After cooling to room temperature, a certain amount of THF was distilled into the tube. The flask was disconnected under nitrogen and was placed into a thermostatically controlled bath at 25°C. Then, the polymerization of the THF was initiated by the addition of methyl triflate for monofunctional PTHF or addition of triflic anhydride for bifunctional PTHF. After a given time a certain amount of sample was removed from the reaction mixture and injected into methanol, and a solution of sodium 9-anthryl methoxide was introduced into the reaction tube in order to terminate the polymerization, simultaneously. The reaction mixture was then stirred for 15 min, then it was poured into methanol. Polymer was dissolved in methanol at room temperature, precipitation was performed by cooling the solution down to -30°C. The precipitated polymer was filtered and dried under vacuum. Conversions were determined gravimetrically.

3.6 Synthesis of poly(ε-caprolactone), (PεCL), by living ring opening polymerization, (ROP)

Into a tube eqipped with a magnetic stirring bar, and a rubber septum, monomer (ε-caprolactone), initiator (9-anthryl methanol) and catalyst (stannous 2-ethylhexanoate, $Sn(Oct)_2$) were introduced. The tube was degassed by two freeze-thaw cycles, left under vacuum and placed in a thermostated oil bath at 110°C. After a given time the polymerization was terminated by cooling the tube to room temperature. The reaction mixture was dissolved in THF, precipitated into methanol, filtered and dried under vacuum. Conversions were determined gravimetrically. Then the obtained polymer was dissolved in dichloromethane and precipitated in methanol again, in order to remove, if there were any, unreacted 9-anthryl methanol. It was filtered and dried under vacuum.

3.7 Characterization

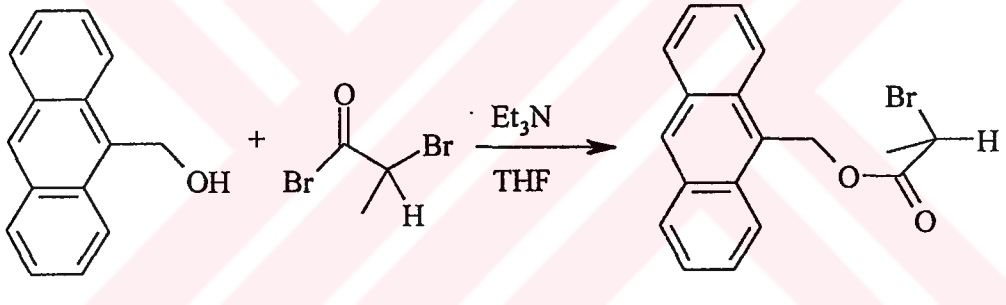
Gel permeation chromaographic (GPC) analysis were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and three Waters Styragel columns (HR 4, HR 3, and HR 2). THF was used as the eluent at a flow rate of 0,3 mL/min. Molecular weight of the polymers was calculated with the aid of polystyrene standarts. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC 250 (250 MHz for proton and 62.90 MHz for carbon) in $CDCL_3$. UV-visible spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in dichloromethane. Fluorescence emission spectra were obtained on a Perkin Elmer Luminescence Spectrophotometer, LS50 in chloroform.

PART 4

RESULTS AND DISCUSSIONS

4.1 Synthesis of 9-anthryl methyl 2-bromo propanoate

The synthesis of 9-anthryl methyl 2-bromo propanoate is represented in Scheme 4.1.



Scheme 4.1 Synthesis of 9-anthryl methyl 2-bromo propanoate

The ^{1}H-NMR spectra of the initiator showed no signal corresponding to OH bond and this is an evidence for a good esterification reaction (Fig. 4.1).

According to the integration of ^{1}H-NMR ($CDCl_3$) spectrum of 9-anthryl methyl 2-bromo propanoate; δ 7.47-8.53 ppm (m, 9 ArH of anthracene), 6.23 ppm (q, $C\underline{H}_2$-O), 4.36 ppm (q, J=6.9Hz, 1H, CH_3-C<u>H</u>-Br), 1.79 ppm (d, J=6.9Hz, 3H, $C\underline{H}_3$-CH-Br).

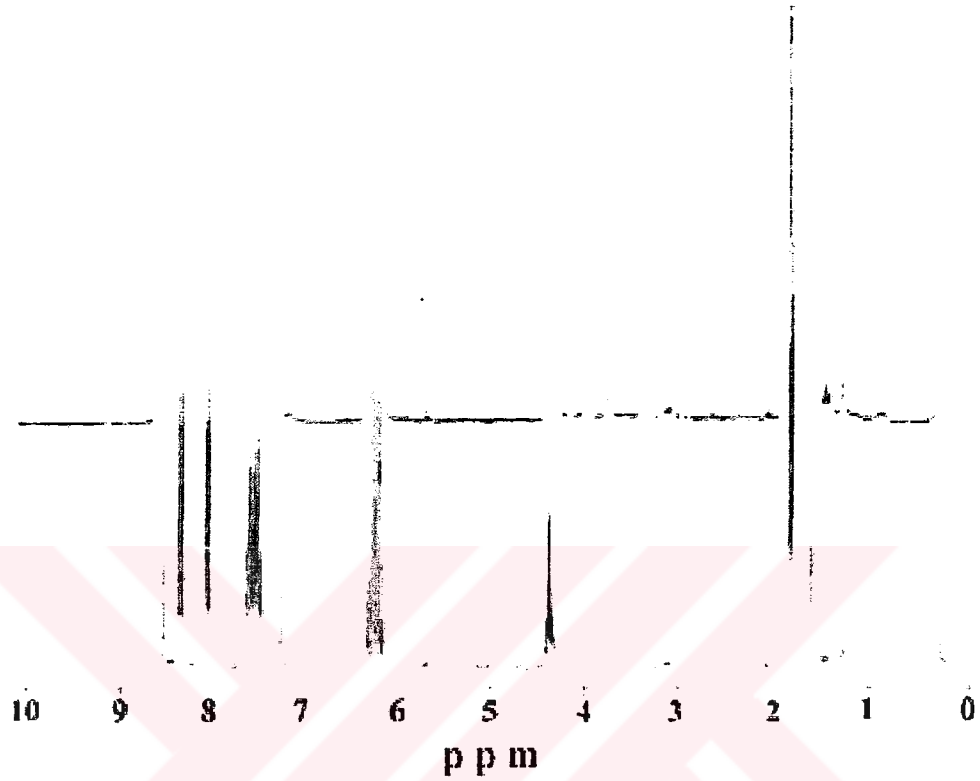


Figure 4.1 The ^{1}H-NMR spectra of 9-anthryl methyl 2-bromo propanoate

The ^{13}C-NMR ($CDCl_3$) spectra (Fig.4.2) showed that 9-anthryl methyl 2-bromo propanoate was formed. According to the spectra; δ 170.49 ppm (C=O); 122.93,123.90, 125.20, 125.48, 126.85, 129.20, 129.55, 131.30 and 131.54 ppm (ArC of anthracene); 60.61 ppm (CH_2-O); 40.10 ppm (CH_3-CH-Br); 21.72 ppm (CH_3-CH-Br).

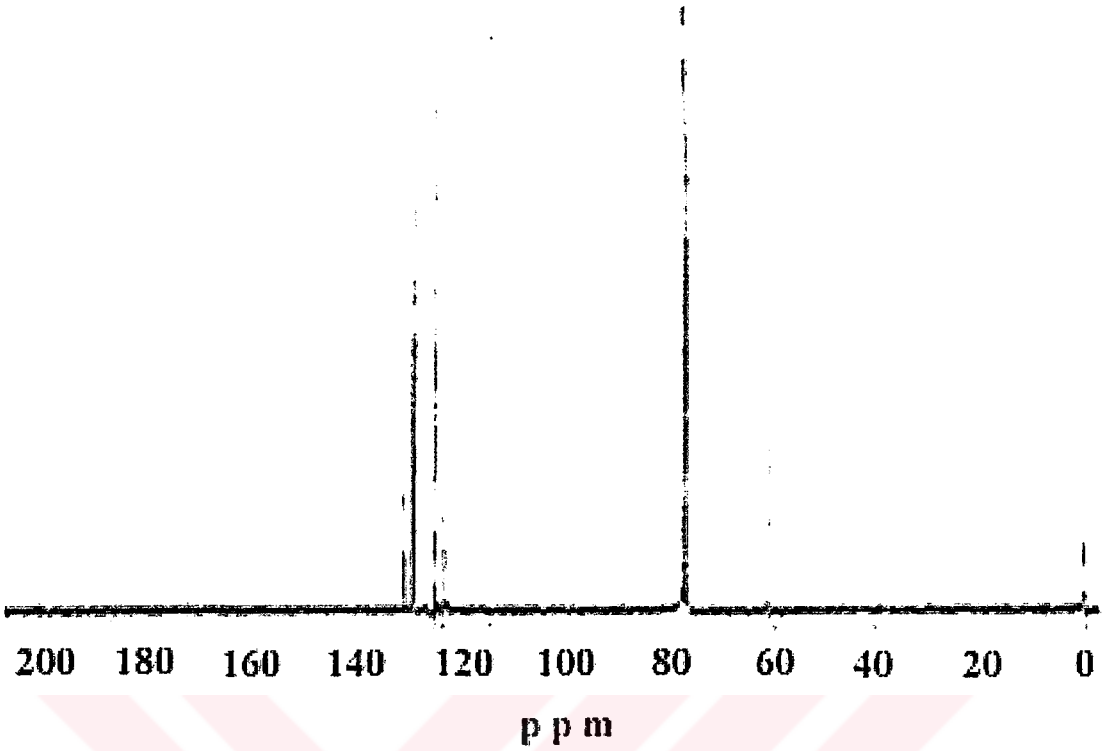


Figure 4.2 The ^{13}C-NMR spectra of 9-anthryl methyl 2-bromo propanoate

The initiator has the same UV spectra as the anthracene itself. The relationship between the absorbance and the wavelength of the anthracene-labelled initiator, given in Figure 4.3, provides an evidence that the anthracene molecule was surely incorporated into the initiator[21].

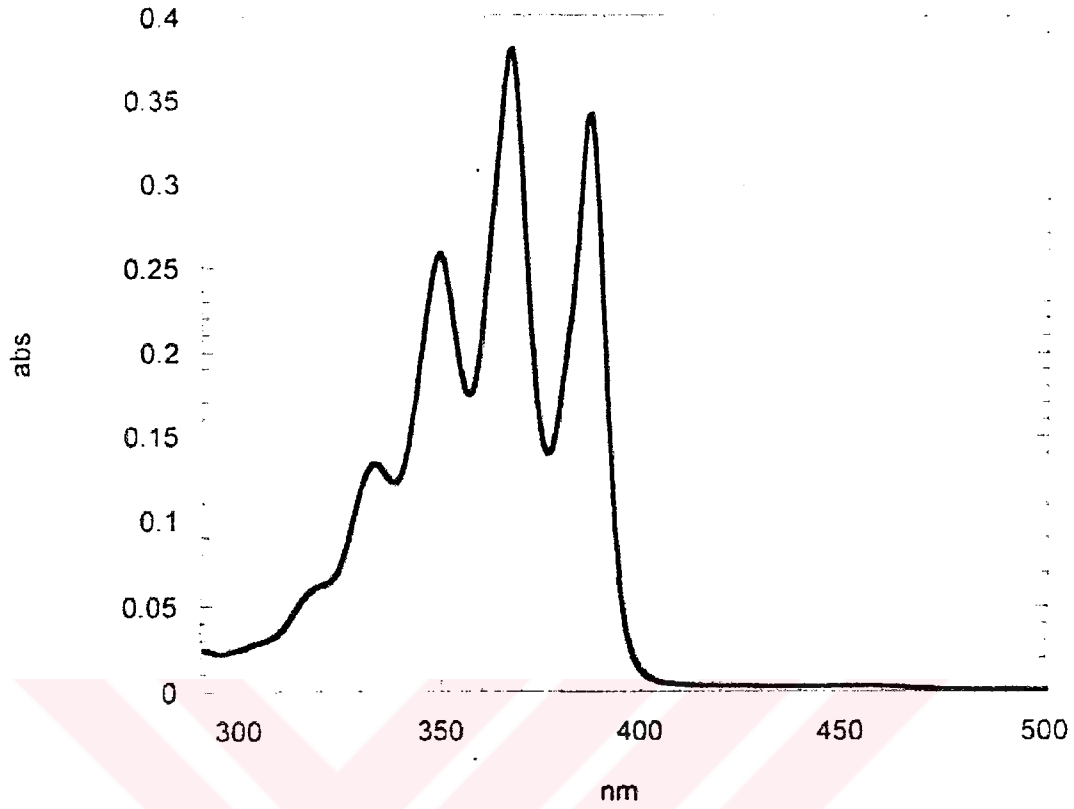


Figure 4.3 UV spectra of 9-anthryl methyl 2-bromo propanoate

Absorbance value of 9-anthryl methyl 2-bromo propanoate changed linearly with respect to its concentration. This is of importance in the calculation of its molar absorbtion coefficient, Є. The absorbance of the anthracene-labelled polymers, at a certain concentration, are measured at a certain wavelength, and with the aid of Є value, the M_n of the polymers are calculated from their UV spectra.. The UV-based number average molecular weights of polymers can be calculated by using the Lambert Beer Law that dictates the equation given below.

$A = Є * C * L$

A = Absorbance

C = Concentration (mol / L)

L = Distance (cm), through which the light passes, in our experiments L = 1 cm

The concentration, (mol/ L), corresponding to that absorbance value is determined by the Lambert Beer Law given in Scheme 4.2. Since the concentration of the polymer

in terms of (mass / volume) is already known, M_n value of the polymer can be calculated by dividing these two concentrations to each other;

M_n = Concentration taken (mass / volume) / Concentration calculated (mol / L)

The relationship between the absorbance and the concentration values of the initiator, is seen in Figure 4.4. Molar absorbtion coefficient, Є, was found from the slope of the above equation in Scheme 4.2, as 8291 for 9-anthryl methyl 2-bromo propanoate. [21] Solvent was dichloromethane. The M_n of PMMA and PtBA, which were initiated by this initiator, were calculated by the above mentioned procedure.

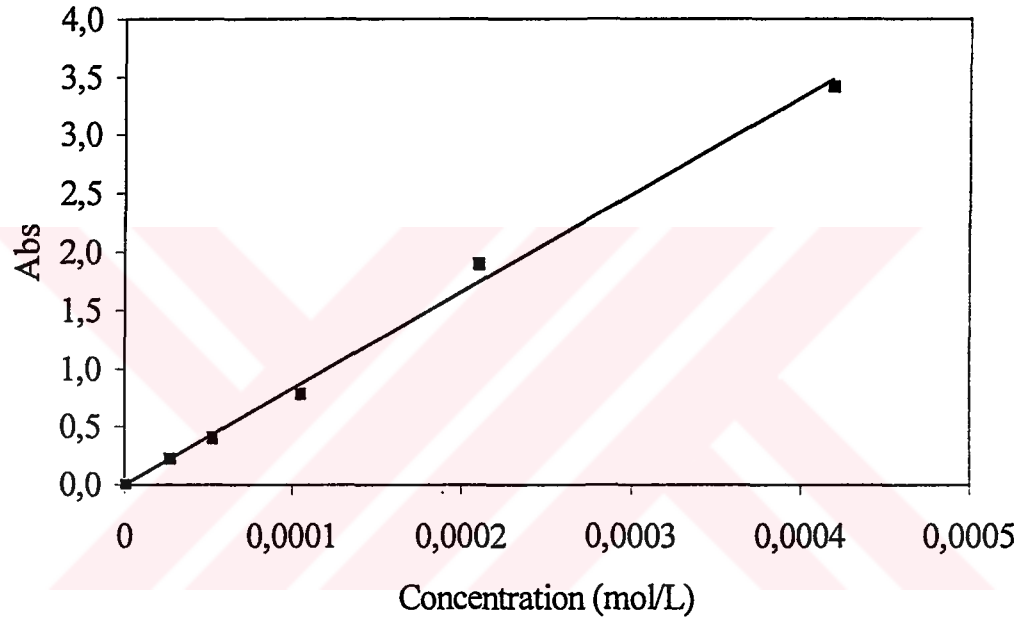
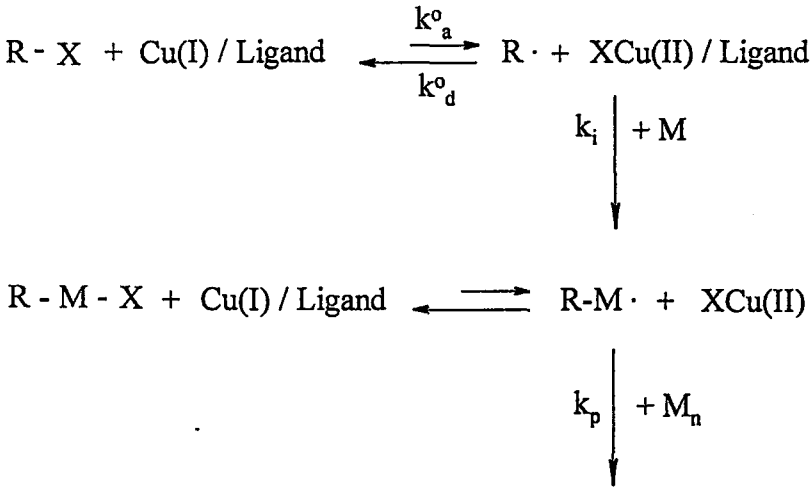


Figure 4.4 The relationship between absorbance and the concentration of 9-anthryl methyl 2-bromo propanoate

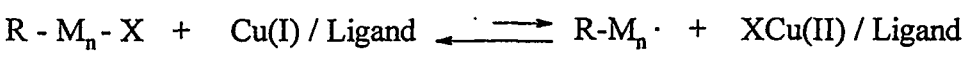
4.2 Synthesis of PMMA and PtBA by ATRP

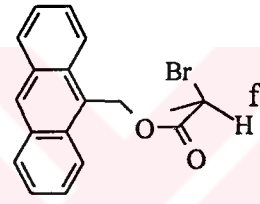
9-anthryl methyl 2-bromo propanoate was used to initiate the controlled polymerization of both PMMA, and PtBA. The representation of the synthesis is seen in Scheme 4.3.

Initiation



Propagation



Where R—X is  for methyl methacrylate and t-butyl acrylate

Ligand = PMDETA; M represents the monomer

Scheme 4.3 Atom transfer radical polymerization (ATRP) of PMMA and PtBA as a schematic representation

For the polymerization of MMA; CuCl, complexed by PMDETA, was used as the catalyst at 90°C in 50 vol. % diphenylether. For the polymerization of tBA; CuBr, complexed by PMDETA, was used as the catalyst. Consequently PMMA and PtBA with anthracene moieties at their chain ends, were formed.

UV and GPC analysis were done for both PMMAs and PtBA. Theoretical molecular weights were calculated. The results are presented in Table 4.1 for PMMA, and in Table 4.2 for PtBA. In addition to these analysis, molecular weight of PMMA1, which is in Table 4.1, was also determined by ^{1}H-NMR spectra, which is seen in Figure 4.7. GPC trace of PMMA1 can be seen in Figure 4.5.

Table 4.1 ATRP of methyl methacrylate initiated by 9-anthryl methyl 2-bromo propanoate

Polymer	Time Min	Conversion %	$M_{n,\ theo}$	$M_{n,\ UV}$	$M_{n,\ NMR}$	$M_{n,\ GPC}$	MWD	*f*
PMMA1	13	10	1000	8300	8000	8500	1,098	1
PMMA2	120	98	9800	11500	Nd	17500	1,148	1,5

M = MMA, I = 9-anthryl methyl 2-bromo propanoate, CuX = CuCl, Ligand=PMDETA, $[M_o]$=4.67M, $[M_o]/[I_o]/[CuX]/[L]$ = 100/1/1/1, temperature=90°C
Solvent = diphenylether
$M_{n,UV}$ was determined at λ = 366 nm
$M_{n,\ NMR}$ was determined by comparing the integrals of the $-OCH_3$ group of the end group CH_3-C-Br-CO-OCH_3 to the -OCH_3 group of methyl methacrylates.
$M_{n,\ GPC}$ was calculated on the basis of the polystyrene standarts
Nd = not determined
f = functionality

Table 4.2 ATRP of tert-butyl acrylate initiated by 9-anthryl methyl 2-bromo propanoate

Polymer	Time Min	Conversion (%)	$M_{n,\ theo}$	$M_{n,\ uv}$	$M_{n,\ gpc}$	MWD	*f*
PtBA	395	50	32000	42800	20000	1,301	0,5

M = tBA, I = 9-anthryl methyl 2-bromo propanoate, CuX =CuBr, Ligand=PMDETA, $[M_o]$ = 6.83M (bulk), $[M_o]/[I_o]/[CuX]/[L]$ = 500/1/1/1,
temperature = 80°C
$M_{n,UV}$ was determined at λ = 366 nm
$M_{n,\ GPC}$ was calculated on the basis of the poly styrene standarts
f = functionality

% conversion was calculated by the formula; % Conversion = (W / M) * 100, where W is the weight of the formed polymer and M represents the mass of the monomer initially taken.

Theoretical molecular weights were calculated by; $M_{n\ (theoretical)} = ([M_o]/[I_o]) * (\%\ Conversion/100) * MW_{monomer}$ where $MW_{monomer}$ is the molecular weight of the monomer.

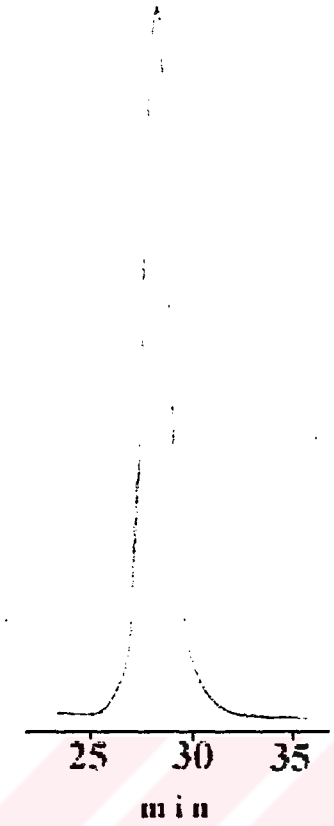


Figure 4.5 GPC (Gel Permeation Chromatography) trace of PMMA1

UV spectra of PMMA1 is seen in Figure 4.6.

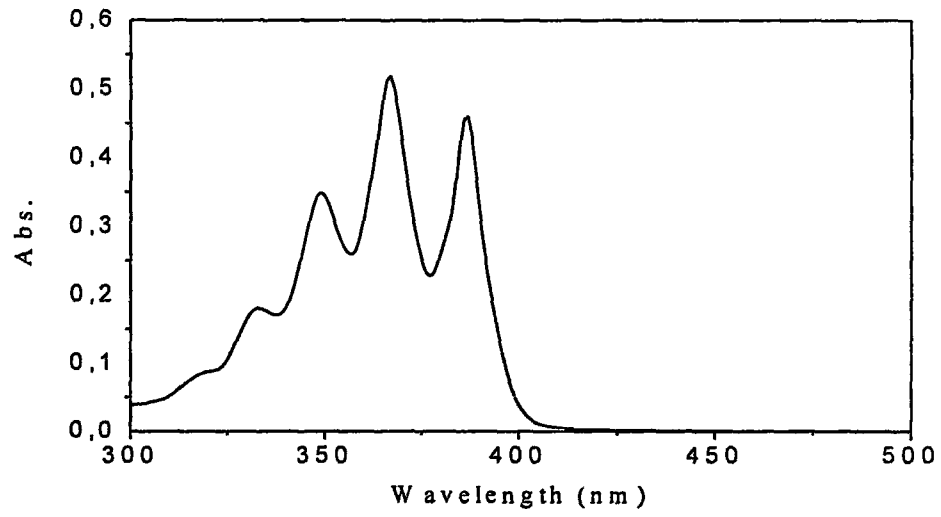


Figure 4.6 UV spectra of PMMA1

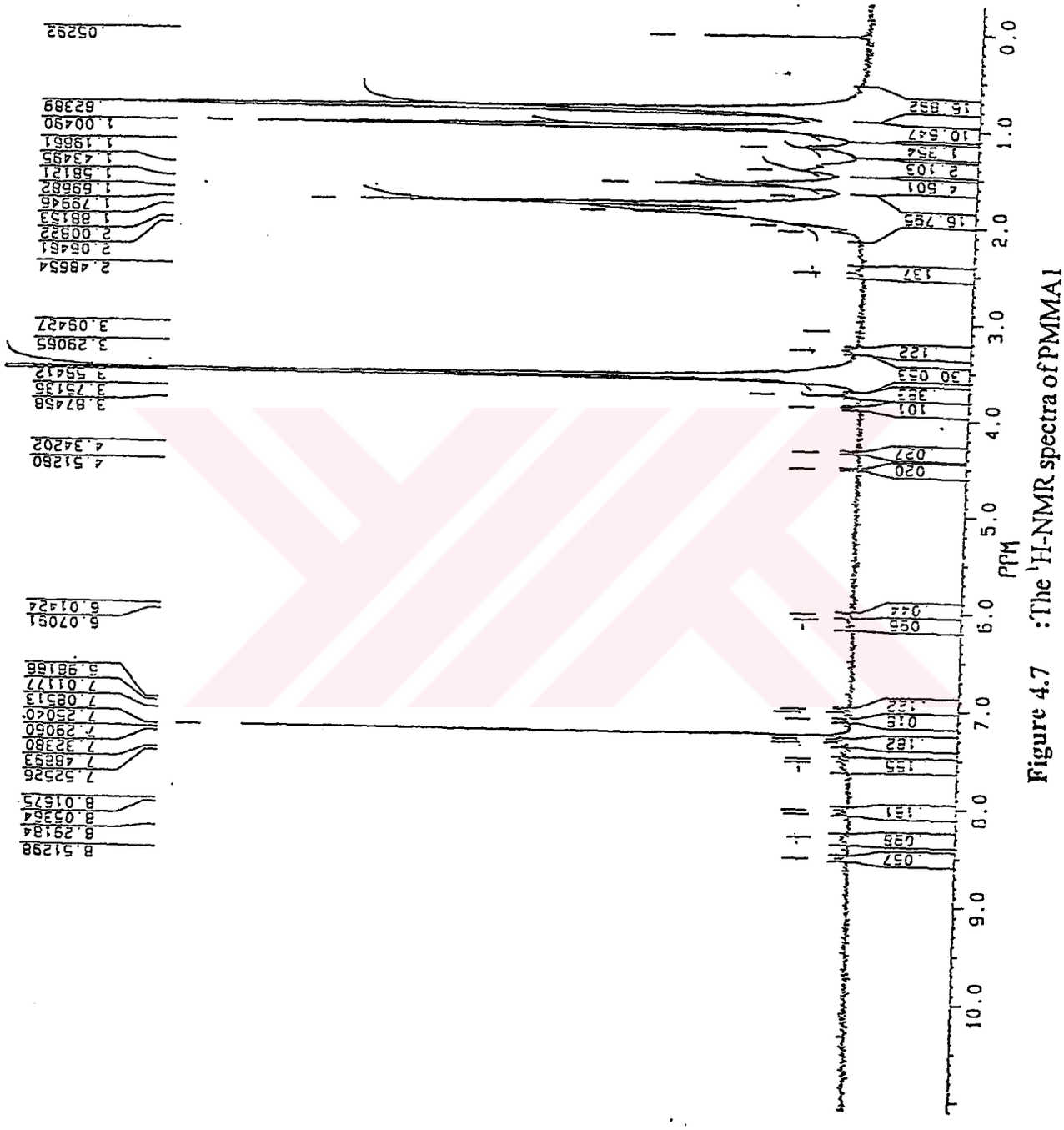


Figure 4.7 : The ^{1}H-NMR spectra of PMMA1

Fluorescence emission spectra of a poly(methyl methacrylate) sample bearing an anthryl group at its chain end, is seen in Figure 4.8.

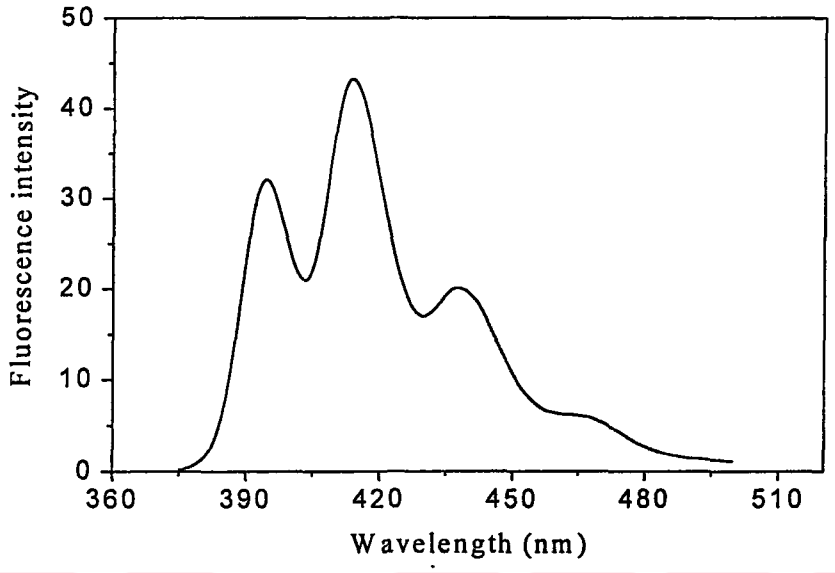
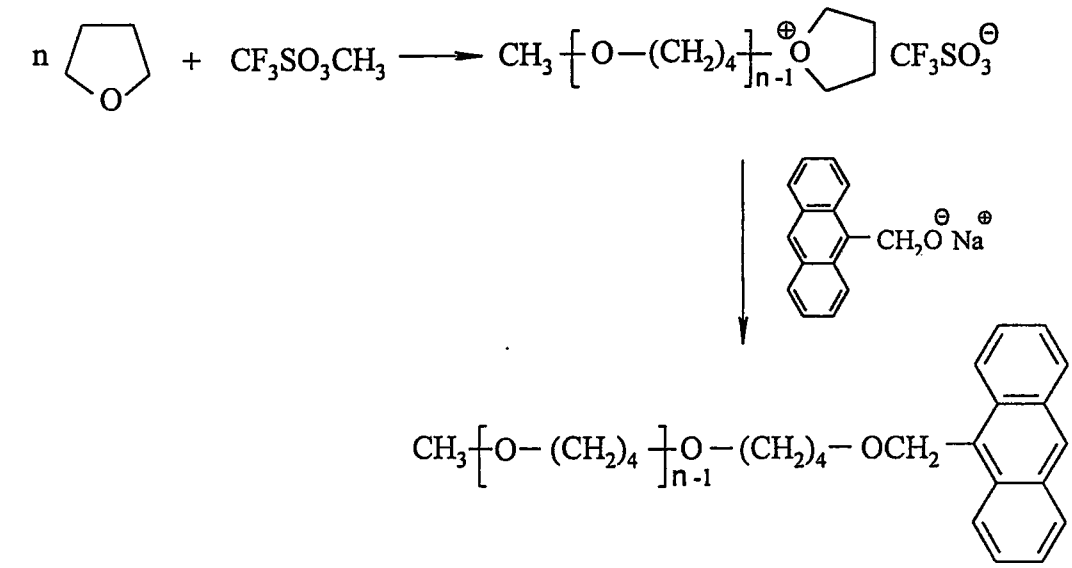


Figure 4.8 Fluorescence emission spectra of an anthracene-labelled poly(methyl methacrylate in chloroform. The excitation wavelength was 366 nm

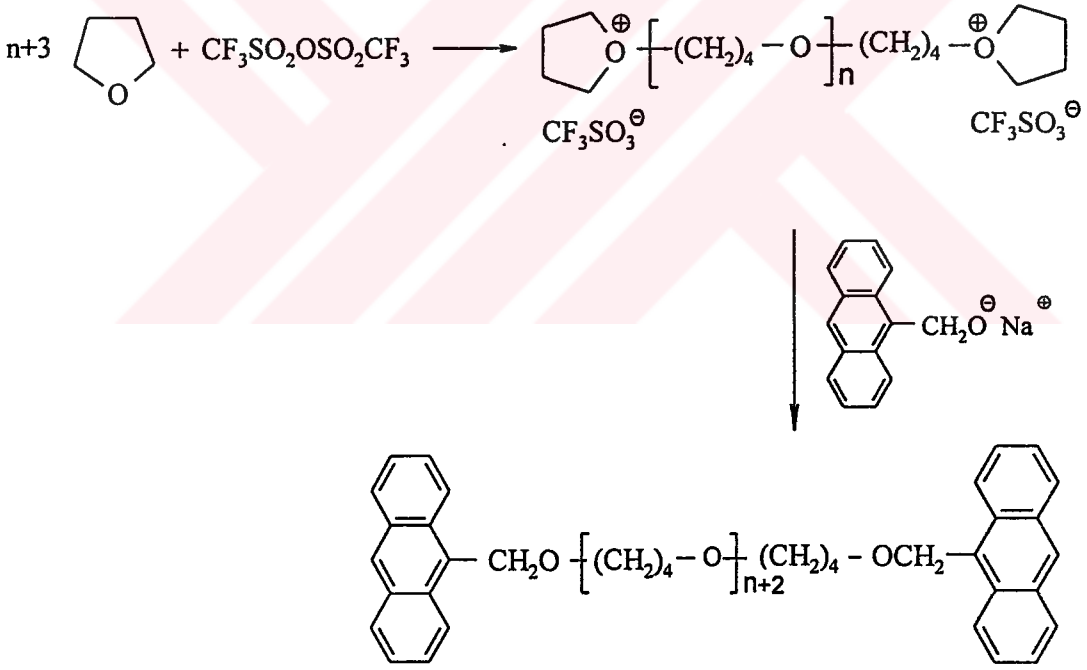
4.2 Synthesis of PTHF by living CROP

Methyl triflate (methyl trifluoromethane sulfonate, $CH_3SO_3CF_3$) and triflic anhydride (trifluoromethane sulfonic anhydride, $CF_3SO_2OSO_2CF_3$) at given concentrations were used to initiate the living, bulk polymerization of tetrahydrofuran at 25°C. These initiators led to formation of mono and bifunctional PTHFs, respectively. Polymerizations were terminated by sodium 9-anthryl methoxide, the preparation of which is given in Section 3.3, in Method 1 for methyl triflate and Method 2 for triflic anhydride. Methyl triflate initiated polymers bearing anthracene, at one chain end, and triflic anhydride initiated polymers, bearing anthracene at both chain ends were formed.

Synthesis of poly(tetrahydrofuran)s bearing anthryl groups are presented in Scheme 4.4 and 4.5.



Scheme 4.4 Synthesis of poly(tetrahydrofuran), bearing an anthryl group at one chain end



Scheme 4.5 Synthesis of poly(tetrahydrofuran) bearing anthryl groups at both chain ends

At the end of the polymerization time certain amounts of reaction mixtures were taken from the medium and terminated by precipitating in methanol with ammonium hydroxide after a given time. These polymers, did not have anthracene moieties at

their chain ends, and were used as reference to estimate the termination efficiency. GPC of both anthracene-labelled polymers and of the ones terminated in methanol were taken.

GPC trace of monofunctional poly(tetrahydrofuran), MPTHF, bearing an anthryl group at one chain end, is seen in Figure 4.9.

Figure 4.9 GPC (Gel Permeation Chromatography) trace of MPTHF

GPC trace of MPTHF and of methanol terminated poly(tetrahydrofuran), MRPTHF, which are presented in Figure 4.10, are in agreement.

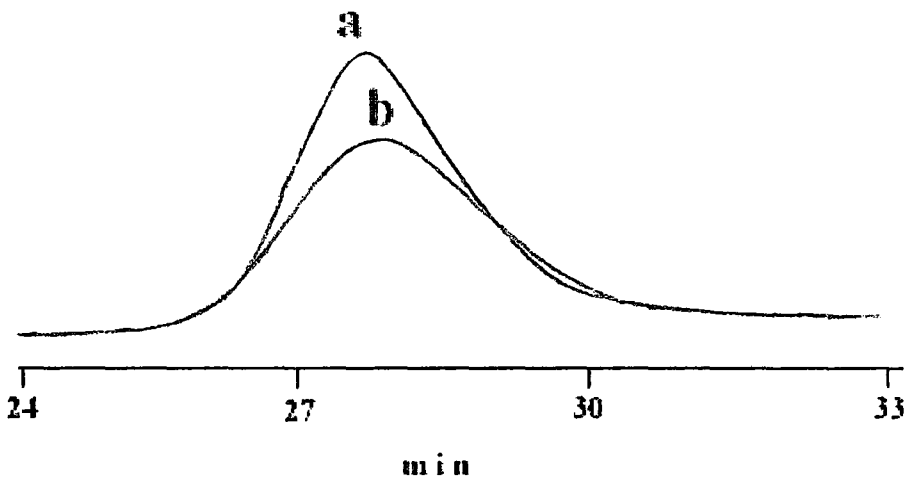


Figure 4.10 GPC traces of MRPTHF (a) and MPTHF (b)

In Table 4.3, molecular weights obtained from GPC and UV spectrum, theoretical molecular weights (calculated by the formula given in section 4.2) of polymers and molecular weight of MPTHF obtained from ^{1}H-NMR spectrum are presented.

Table 4.3 Living cationic ring opening polymerization (CROP) of tetrahydrofuran, (THF), initiated by methyl triflate and triflic anhydride

Polymer	Conversion (%)	$M_{n,\,theo}$	$M_{n,\,UV}$	$M_{n,\,NMR}$	$M_{n,\,GPC}$	MWD	*f*
MPTHF[a]	10	7500	5100	4900	5100	1,150	1
MRPTHF[b]	10	7500	Nd	Nd	5400	1,124	-
BPTHF[c]	13	9600	11000	Nd	12300	1,272	1,1
BRPTHF[d]	13	9600	Nd	Nd	13600	1,155	-

M = THF, I = methyl triflate and triflic anhydride, $[M_o]$=12.3 M (bulk), $[I_o]$ = 0.012 M, temperature = 25°C, reaction time=25 min

$M_{n,UV}$ was determined at λ = 366 nm, by the aid of ϵ of 9-anthryl methanol, which is 5385. Solvent: dichloromethane [16]

$M_{n,\,NMR}$ was determined by comparing the integrals of the $-CH_2-CH_2-$ protons of PTHF to the $-OCH_2-$ protons of 9-anthryl methoxide.

[a] Monofunctional PTHF, bearing an anthryl group at one chain end

[b] Monofunctional PTHF, terminated by methanol

[c] Bifunctional PTHF, bearing anthryl groups at both chain ends

[d] Bifunctional PTHF, terminated by methanol

Nd = not determined

f = functionality

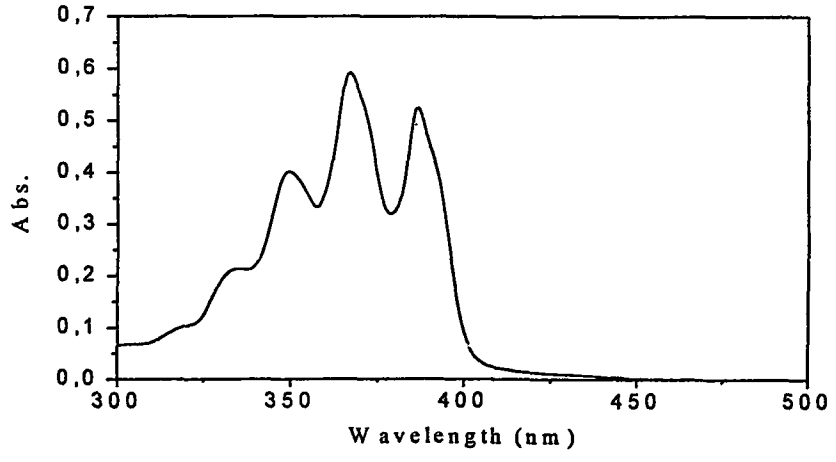


Figure 4.11 UV spectra of MPTHF

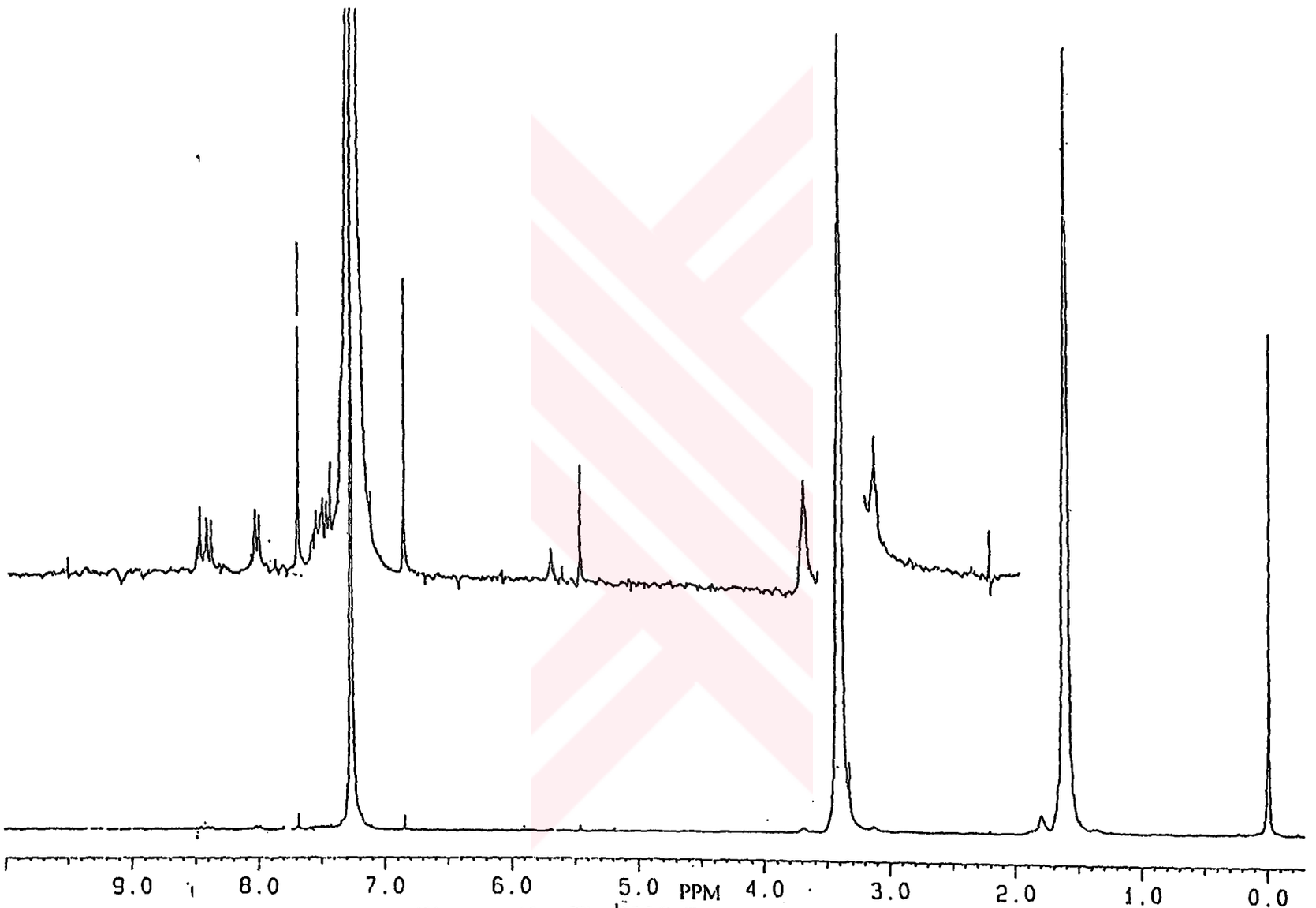


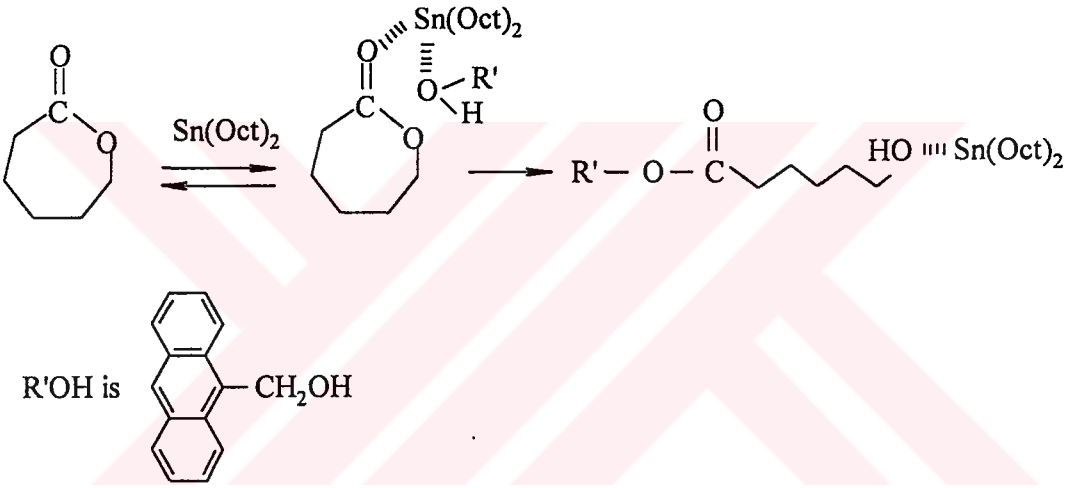
Figure 4.12 :The ^{1}H-NMR spectra of MPTHF

In Figure 4.11 and 4.12, UV and ^{1}H-NMR spectra of MPTHF are presented respectively.

According to the ^{1}H-NMR ($CDCl_3$) spectrum of MPTHF; δ 3.32-3.41 ppm (O-C<u>H</u>$_2$ of PTHF); 1.48-1.61 ppm (C<u>H</u>$_2$- C<u>H</u>$_2$ of PTHF); 3.68 ppm (Ant C<u>H</u>$_2$-O); 7.26-8.45 ppm (9 ArH of anthracene).

4.4 Synthesis of PεCL by living ROP

Mechanism of synthesis of poly(ε-caprolactone) is shown in Scheme 4.4.



Scheme 4.4 Mechanism of sythesis of poly(ε-caprolactone), bearing anthryl group at one chain end

As indicated in Scheme 4.4, 9-anthryl methanol was used as the initiator, $Sn(Oct)_2$ was used as the catalyst at given concentrations, and at different $[M_o]/[I_o]$ ratio. The reaction temperature was 110°C.

In Table 4.4 molecular weights obtained from UV spectra and GPC analysis, and from calculations are presented for polymerizations conducted at different $[M_o]/[I_o]$ ratios.

Table 4.4 Synthesis of poly(ε-caprolactone), PεCL, initiated by 9-anthryl methanol-$Sn(Oct)_2$

Polymer	$[M_o]/[I_o]$	$[I_o]$ mol/L	$[catalyst_o]$ mol/L	Conv. (%)	$M_{n,theo}$	$M_{n,UV}$	$M_{n,GPC}$	MWD	*f*
PεCL1	20	0,438	$1,07x10^{-3}$	90	2000	2300	2800	1,216	1,2
PεCL2	30	0,292	$7,13x10^{-4}$	96	3300	3700	3600	1,193	1
PεCL3	40	0,219	$5,35x10^{-4}$	99	4500	4500	5600	1,350	1,2
PεCL4	50	0,175	$2,34x10^{-3}$	99	5650	5200	5000	1,192	1
PεCL5	60	0,146	$1,96x10^{-3}$	99	6800	5300	5800	1,260	1

M = εCL, I =9-anthryl methanol, $[catalyst_o] = Sn(Oct)_2$ $[M_o]$ = 9,02 M (bulk), temperature =110°C, reaction time=24h

$M_{n,\ UV}$ was determined at λ = 366 nm, Є of 9-anthryl methanol = 5385 in dichloromethane

f = functionality

The relationship between the initial 9-anthryl methanol concentration,$[I_o]$, and $M_{n,\ UV}$ as well as $M_{n,\ GPC}$ are shown in Figure 4.13 and 4.14.

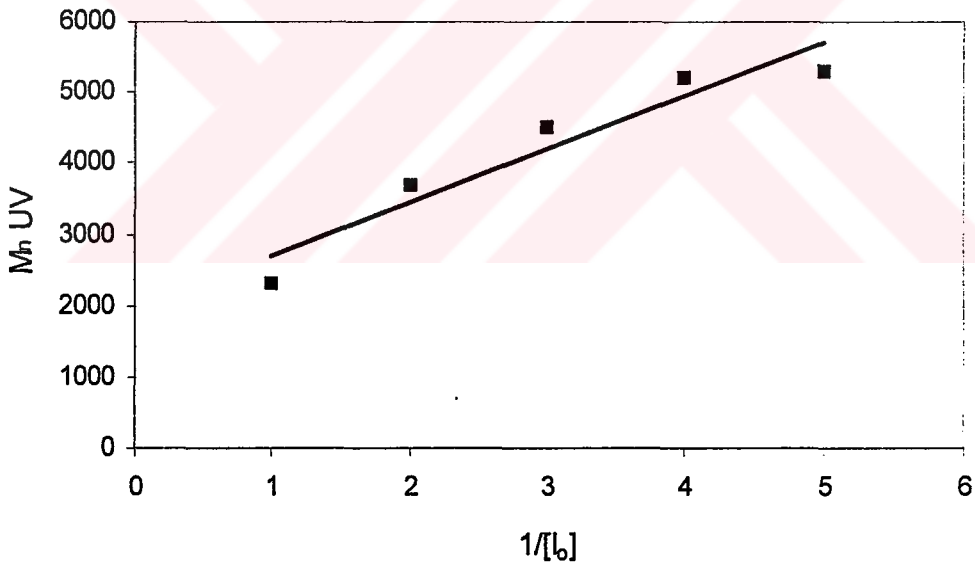


Figure 4.13 The relationship between the initial 9-anthryl methanol concentration and M_n UV of PεCL

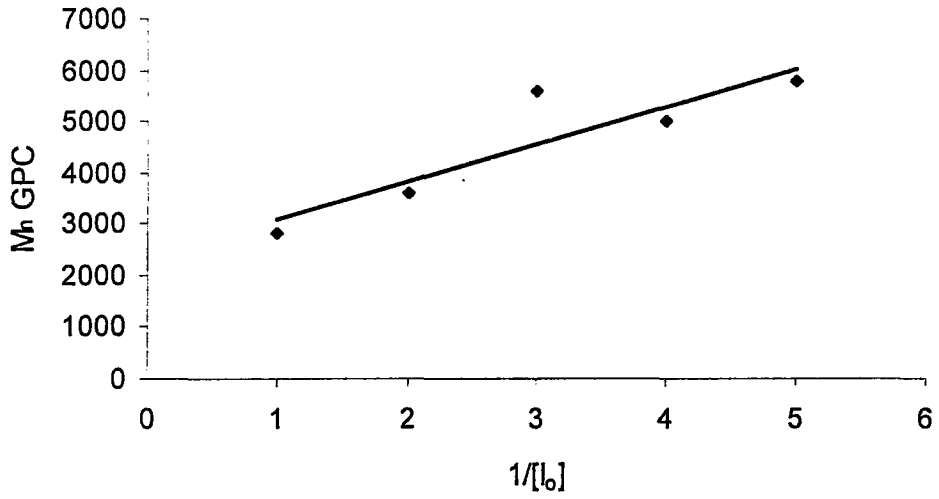


Figure 4.14 The relationship between the initial 9-anthryl methanol concentration and M_n GPC of PεCL

Typical UV spectra, GPC trace, fluorescence and ^{1}H-NMR spectra of a PεCL is seen in Figure 4.15, 4.16,4.17 and 4.18, respectively.

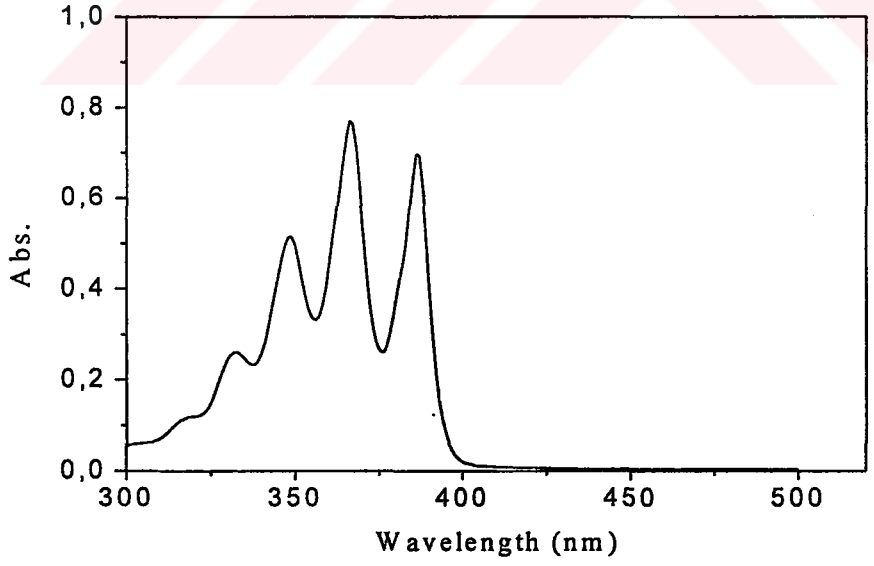


Figure 4.15 UV spectra of an anthracene-labelled PεCL

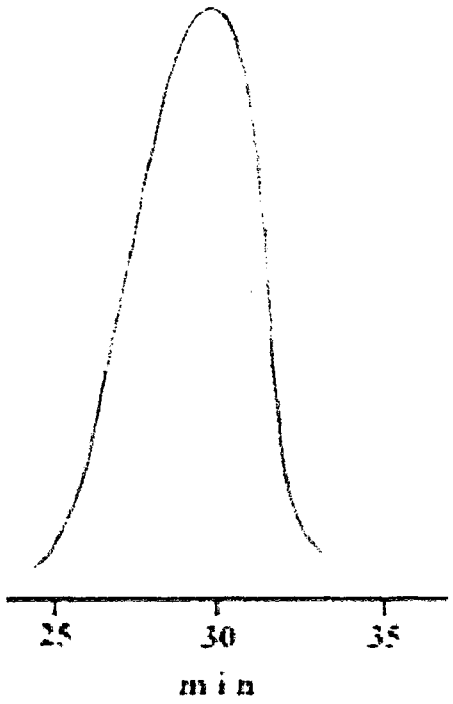


Figure 4.16 GPC trace of an anthracene-labelled PεCL

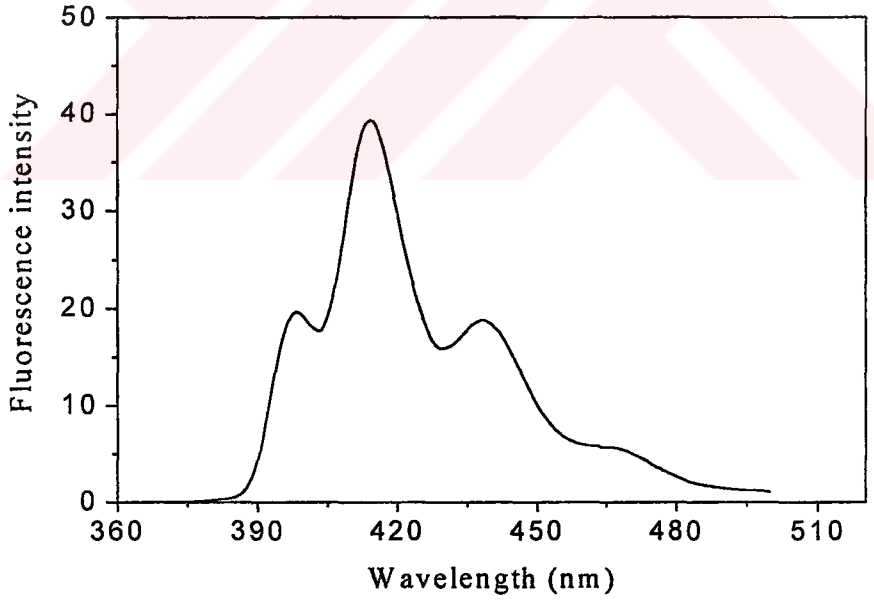


Figure 4.17 Fluorescence emission spectra of an anthracene-labelled PεCL

According to the ^{1}H-NMR spectra of PεCL in Figure 4.18; δ 7.25, 7.47, 7.50, 7.55, 8.00, 8.03, 8.29, 8.32 and 8.50 ppm (9 ArH of anthracene), 4.01-4.06 ppm (-COOC$\underline{H}_2$-), 2.25-2.31 ppm (-COC$\underline{H}_2$-) and 1.35-1.65 ppm (-C$\underline{H}_2$-C$\underline{H}_2$-C$\underline{H}_2$-).

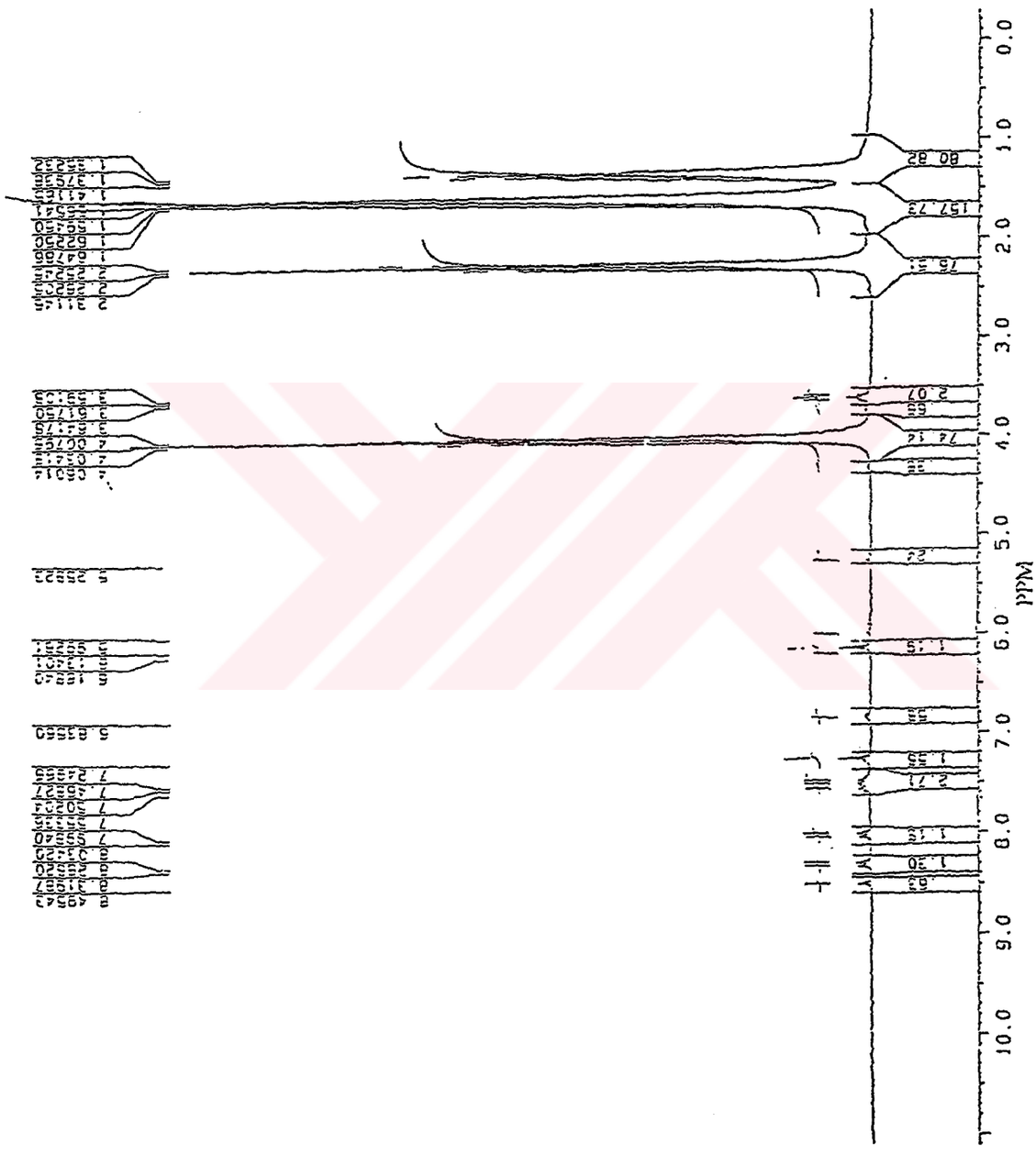


Figure 4.18 :The ^{1}H-NMR spectra of an anthracene-labelled poly(ε-caprolactone)

CONCLUSIONS

Different polymers bearing anthracene moieties were synthesized by atom transfer radical polymeriation (ATRP), cationic ring opening polymerization (CROP) and ring opening polymerization (ROP) techniques.

In the synthesis of PMMA by ATRP, 9-anthryl methyl 2-bromo propanoate was used as the initiator, which is a secondary initiator with respect to the C atom to which Br atom is bonded. For PMMA2 coded polymer, it can be concluded that, the difference between $M_{n,theo,}$ and $M_{n,GPC}$ is due to the low initiator efficiency (f = 0,56). The high $M_{n,GPC}$ value could be result of the differences between the hydrodynamic volumes of poly(methyl methacrylate) and poly styrene standarts.

PtBA was synthesized by ATRP, and 9-anthryl methyl 2-bromo propanoate was used as the initiator. The difference between $M_{n,theo}$ and $M_{n,UV}$ may be attributed to the uncomplete drying of PtBA, which could cause unreacted monomer to remain in the medium. $M_{n,theo}$ and $M_{n,UV}$ calculated from UV spectra could deviate also due to unreliable weighing of the polymer.

PTHFs were synthesized by CROP. Monofunctional PTHF and bifunctional PTHF were initiated by methyl triflate and triflic anhydride, respectively. Anthracene-labelled PTHFs were formed by terminating the polymers by sodium 9-anthryl methoxide. Polymers without anthracene moieties at their chain ends were formed by terminating the polymers in methanol, which were used as references. It can be concluded that the difference between $M_{n,GPC}$ values of the bifunctional PTHFs terminated by sodium 9-anthryl methoxide and terminated in methanol could be the result of the low nucleophylicity of sodium 9-anthryl methoxide. In case of monofunctional poly(tetrahydrofuran) $M_{n,GPC}$ of the anthracene-labelled polmer is in reasonable agreement with the one obtained for poly(tetrahydrofuran) terminated in

methanol. It can be concluded that sodium 9-anthryl methoxide could not exhibit its effect of low nucleophylicity for monofunctional poly(tetrahydrofuran). $M_{n,NMR}$ is very close to those obtained from UV and GPC measurements.

PεCL was synthesized by ROP, where 9-anthryl methanol was used as the initiator and anthryl groups at their chain ends were synthesized, whose $M_{n,theo}$ is in agreement with $M_{n,UV}$ and $M_{n,GPC}$.

In conclusion, anthracene-labelled polymers with narrow molecular weight distributions were successfully synthesized by controlled polymerization techniques; ATRP, CROP, and ROP.

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