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ZİNCİR TRANSFER REAKSİYONU VE "İNİFERTER" SİSTEMİ  
YARDIMIYLA BLOK KOPOLİMER SENTEZİ

YÜKSEK LİSANS TEZİ

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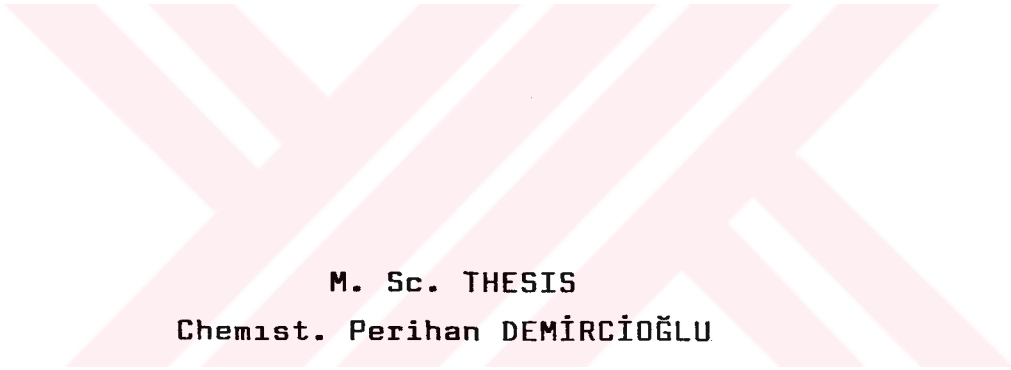
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SYNTHESIS OF BLOCKCOPOLYMERS BY THE COMBINATION OF CHAIN TRANSFER POLYMERIZATION  
AND INIFERTER TECHNIQUE



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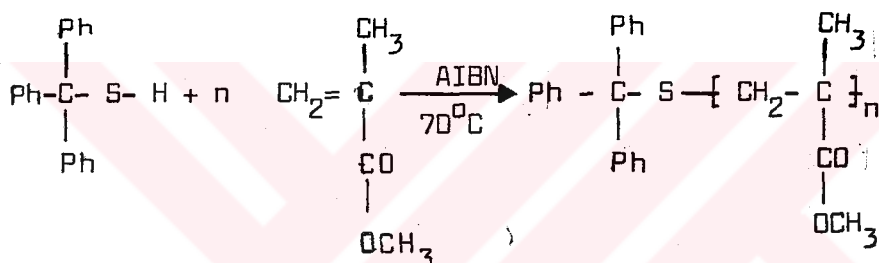
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## SUMMARY

In this study, we have tried to synthesize block copolymer by a two-step procedure. In the first step, terminally active prepolymers were prepared by using high chain transfer reactions of triphenylmethyl mercaptane (TPMM). For this purpose styrene (St) and methyl methacrylate (MMA) were polymerized with the aid of 2,2'-azobis(isocyanobutyronitrile) (AIBN) and TPMM to yield triphenylmethyl (trityl) terminated polymers according to the following reaction.



Transfer constants were found to be 17.8 and 0.71 for St and MMA respectively.

Presence of triphenylmethyl end groups was evidenced by spectral measurements. These prepolymers can polymerize the same or different monomers by free radical mechanism after cleavage of C-S bond attached to the trityl end group.

In the former case,  $\bar{M}_n$  of the polymers increased linearly with conversion which indicates that this polymerization proceeds via a quasi-living radical mechanism. This mechanism was substantiated by the GPC traces recorded with polymer isolated at various polymerization times.

Similarly, if these prepolymers were used as polymeric initiator in the second step, to polymerize another monomer, block copolymers were obtained, and characterized by  $^1\text{H-NMR}$  and GPC measurement.

## ZİNCİR TRANSFER REAKSİYONU VE "İNİFERTER" SİSTEMİ YARDIMIYLA BLOK KOPOLİMER SENTEZİ

### ÖZET

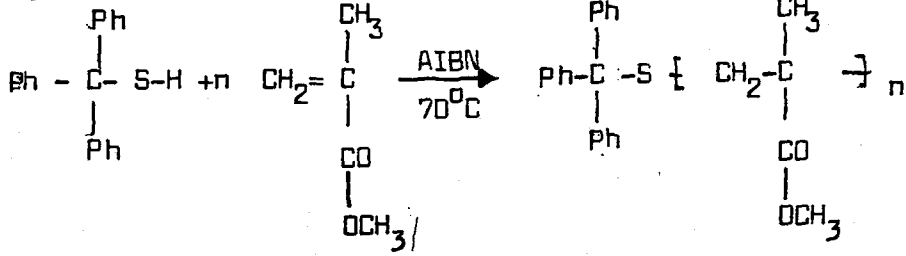
Aynı mekanizma ile polimerleşebilen monomerlerin blok kopolimerizasyonu için uygulanan klasik yöntemler mevcuttur. Bu yöntemlerin belirli sayıda monomer türüne uygulanması ve karşılaşılan sentez güçlükleri, bu yöntemlerin kullanılabilirliğini sınırlamaktadır. Bu yüzden çok daha fazla monomer kombinasyonuyla değişik özellikte blok kopolimer sentezine olanak sağlayan dönüşüm (transformasyon) reaksiyonları geliştirilmiştir. Bu reaksiyonlarda önce bir monomer bir mekanizma ile polimerleştirilip ucunda veya ortasında aktif grup olacak şekilde sonlandırılır. Daha sonra başka bir yöntemle polimerleşebilen ikinci bir monomer, prepolimer üzerindeki aktif gruplar yardımıyla polimerleştirilir ve blok kopolimer ele geçer. Bu dönüşümlerin, katyonik-radikal, anyonik-radikal, kondenzasyon-radikal, redoks-ısısal radikal ve ısısal radikal-fotokimyasal radikal olanları literatürde gösterilmiştir.

Birkaç organik disülfidler ve fenilazotrifenil metan fotokimyasal ve ısısal iniferterler olarak kullanılmıştır. İniferter kullanımı ile elde edilen polimerler diğer bir monomerin polimerizasyonu başlatabilecek iniferter fonksiyonuna sahiptir.

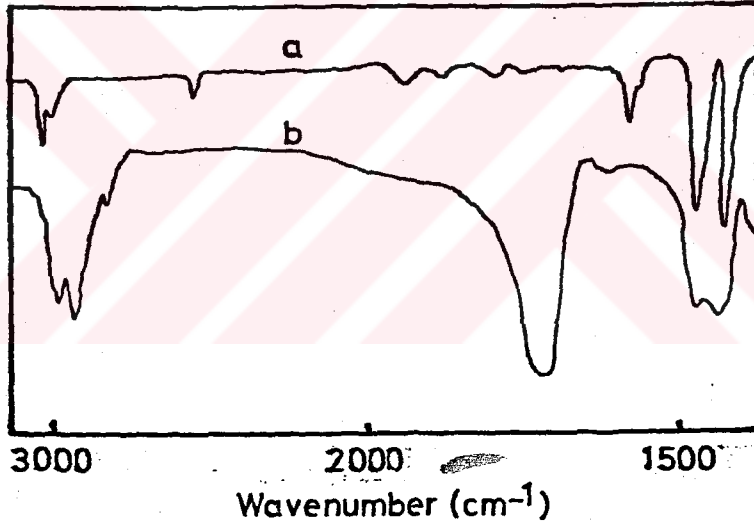
Zincir transfer reaksiyonlarından yararlanarak polimer uçlarına istenilen fonksiyonel gruplar sokulabilir. Son zamanlarda uygun merkaptö bileşiği kullanarak karboksi ve Taç-eter (crown-ether) ile sonlandırılmış poli (metilmetakrilat) hazırlanmıştır.

Bu bilgiler ışığında, çalışmamızda zincir transfer reaksiyonları yardımıyla polimerlerin uçlarına trifenil metil(tritil) grupları sokulmaya çalışılmıştır.

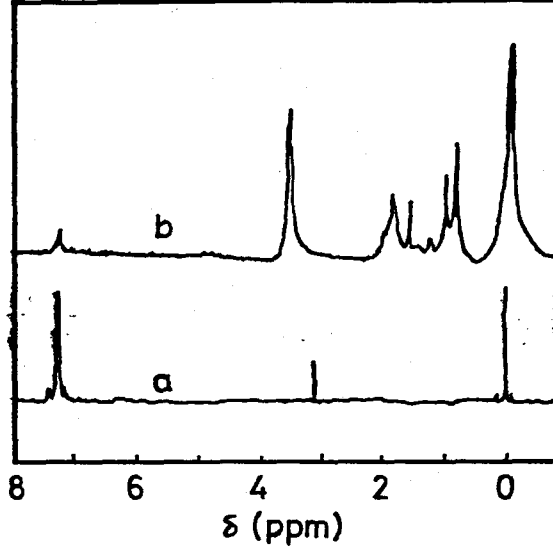
Bu amaçla Stiren (St) ve metilmetakrilat (MMA), başlatıcı olarak azoisobutironitril (AIBN), transfer bileşiği olarak trifenilmetilmerkaptan (TPMM) kullanılarak aşağıdaki reaksiyon uyarınca polimerleştirilmiştir.



Aşağıdaki şekilde TPMM'a ve tritil sonlandırılmış PMMA'a (TPM-PMMA) ait IR spektralleri verilmiştir. TPMM'nin IR spektrumunda  $2570 \text{ cm}^{-1}$  deki S-H grubuna ait band polimerin IR spektrumunda yoktur. Buda S-H bağının bulunmadığını göstermektedir.



Bu bulgular  $^1\text{H-NMR}$  spektrumuyla da desteklenmiştir. TPMM (a) ve TPM-PMMA'in (b)  $^1\text{H-NMR}$  spektralleri aşağıdaki şekilde gösterilmiştir. Buna göre 7.2 ppm bölgesindeki aromatik protonlar, 3.6 ppm 'de  $\text{OCH}_3$ 'e ait ve 1.4 - 2.0 ppm'de vinil protonlara ait pikler görülmektedir.



Polimerin UV spektrumu alındığında 330nm bölgesi civarında bir absorpsiyon bandı görülmektedir ki bu da tritil son grupların polimere bağlı olduğunu göstermektedir.

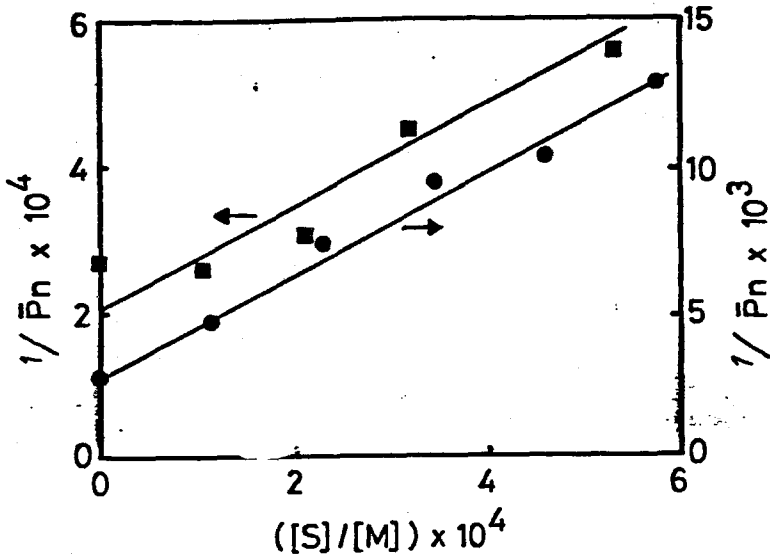
Bu bulgulardan anlaşıldığına göre TPMM (trifenilmetil merkaptan), Stiren (St) ve metil metakrilat (MMA) polimerizasyonunda etkin bir transfer bileşiği olarak davranmıştır.

Stiren için transfer sabiti 17.8, metilmetakrilat için 0.71 bulunmuştur. Bu değerler  $1/\bar{P}_n$ 'e karşı  $[S]/[M]$  arasında grafik çizilip bu grafiğin eğiminden yararlanarak hesaplanmıştır.

Stiren'in zincir transfer sabiti metilmetakrilatından önemli derecede yüksektir. Genelde bilinen zincir transfer bileşikleri ile aynı davranışlar gözlenir.

$\bar{P}_n$  = Polimerizasyon derecesi  
 $[M]$  = Monomerin konsantrasyonu  
 $[S]$  = TPMM'in konsantrasyonu

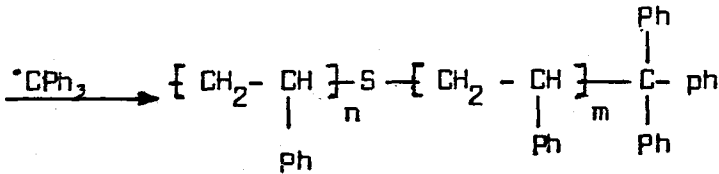
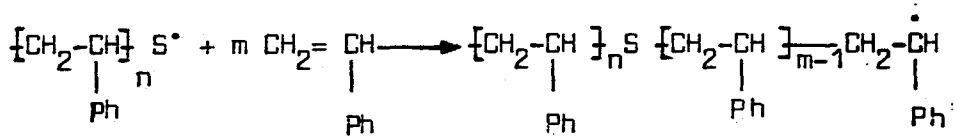




(●) Stiren ve

(■) Metilmetakrilat'ın polimerizasyonu.

Bu sentetik yöntemle ele geçen, tritil ile sonlanmış polistiren, stirenin polimerizasyonunda ısısız iniferter olarak kullanılabilir.



Burada S-C bağının kopabileceği iki olasılık mevcuttur, polimer yönündeki C-S bağı (a) veya uç gruptaki tritil'e bağlı C-S bağı (b). Tritil'e bağlı C-S bağının kopma olasılığı karbon atomunun bir tersiyer karbon

atomu olması ve bağı zayıflatması dolayısıyla daha fazladır. Buna göre tilit radikali ( $\sim S^*$ ) monomer ile reaksiyona girerken tritil radikali sadece çoğalan radikallerle birleşerek sonlanma aşamasında görev alır. Eğer ikinci aşamada polimerik iniferter diğer bir monomerin polimerizasyonunda kullanılırsa aynı mekanizma uyarınca blok kopolimer ele geçer.

Stiren ve metil metakrilatın blok kopolimerizasyonu zincir transfer ve iniferter prosesleriyle deneysel olarak gerçekleştirilmiş.

## CHAPTER 1. INTRODUCTION

There has been several classical methods for the preparation of block copolymers which generally involve the successive polymerization of two or more monomers by the same mechanism. Transformation reactions extend the range of possible monomer combinations in block copolymer [1,2]. This approach allows polymers produced by one type of polymerization to be terminally functionalised by groups capable of initiating a different mode of polymerization. It has reported the synthesis of block copolymers may be accomplished by the combination of cationic and radical [3,4], anionic and radical [5], condensation and radical [6-7], redox and thermal radical [8,9] and thermal radical and photochemical radical polymerization [10-11] routes.

Iniferter method for the preparation of block copolymers was extensively explored during last decade mainly by Otsu and coworkers [12]. Several organic disulfides and phenylazotriphenylmethane were found to serve as photo and thermal iniferters, respectively. Polymers obtained by using iniferters still have iniferter function capable of initiating the polymerization of another monomer yielding block copolymers.

It has been shown that radical transfer polymerization can be used successfully for the preparation of polymers with functional end groups. Chujo et al recently prepared carboxy [13] and crown-ether terminated [14] poly (methyl methacrylate) (PMMA) using appropriate mercapto compound.

On the basis of these approaches, this work deals with the synthesis of polymers with terminal trityl (triphenylmethyl) group, using the corresponding chain transfer compound, capable of acting as thermal iniferter and its further use for the preparation of block copolymers.



## CHAPTER 2. THEORETICAL PART

### 2.1. General Concepts

A polymer is a large molecule constructed of many smaller structural units called monomer. The essential requirement for a small molecule to qualify as a monomer is the possession of two or more bonding sites through which each can be linked to other monomers to form the polymer chain and the number of the bonding sites is referred to as the functionality.

When only one species of monomer is used to build a macromolecule the product is called a homopolymer, normally referred to simply as polymer. If the chains are composed of two types of monomer unit, the material is known as a copolymer and if three different monomers are incorporated in one chain a terpolymer results.

-A-A-A-A-

Homopolymer

-A-A-A-B-A-B-B-A-B-A-A-

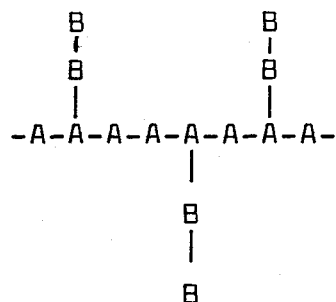
Random copolymer

-A-B-A-B-A-B-A-

Alternating copolymer

-A-A-A-A-A-B-B-B-A-A-A-

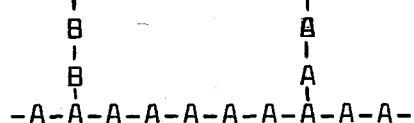
Block copolymer



Graft copolymer

-A-A-A-A-A-A-A-A-A-

Cross-link copolymer



## 2.2. Classification Of Polymerization Reactions

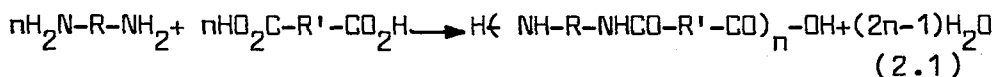
A process used to convert monomer molecules into a polymer is called polymerization and the two most important groups are step-growth and addition.

### 2.2.1. Step Growth Polymerization

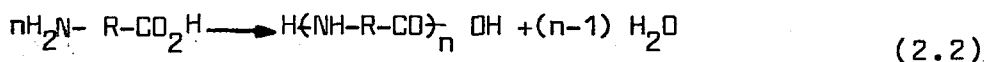
Condensation or step-reaction polymerization is entirely analogous to condensation in low molecular weight compounds, in polymer formation the condensation takes place between two polyfunctional molecules to produce one larger polyfunctional molecule, with the elimination of small molecule like water. The reaction continues until almost all of one of the reagents is used up.

All step polymerizations fall into two groups depending on the type of monomers used.

The first involves two different bifunctional or polyfunctional monomers (in which each monomer contains two functional groups per molecule). The second involves a single monomer containing both types of functional groups. The synthesis of polyamids illustrates both groups of polymerization reactions. Thus polyamids can be obtained from the reaction of diamines with diacids.



or from the reaction of amino acids with themselves.



The characteristics of these two polymerization reactions are very similar. The polymerization proceeds in this stepwise manner with the molecular weight of the polymer continuously increasing with time. Step polymerizations are characterised by the disappearance of monomer very early in the reaction for before the production mixture at any distance consists of various-sized diol, diacid and hydroxy acid molecules. Any HO containing molecule can react with any COOH containing molecule. Rate of polymerization is maximum at the start and decreases continuously during the reaction as the concentration of functional groups decreases.

### 2.2.2. Addition Polymerization

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 bifunctional units where the special reactivity or  $\pi$  bonds in the carbon to carbon double bond makes them susceptible to rearrangement if activated by reaction must be capable of rupturing one of the bonds in the monomer and may be either a radical, electrophile or nucleophile. The choice of the most convenient one depends on the groups  $\text{R}_1$  and  $\text{R}_2$  in the monomer and their effect on the double bond.

Generally electron withdrawing substituents;  $-\text{CN}$ ,  $\text{COOR}$ ,  $-\text{CONH}_2$  reduce the electron density at the double bond and favour propagation by an anionic species. Groups which tend to increase the double bond nucleophilicity by donating electrons such as alkenyl, alkoxyl, and phenyl encourage attack by cationic initiators and in addition the active centers formed are resonance stabilized.

As resonance stabilization of the active center is an important factor, monomers like styrene and 1,3-

butadiene can undergo polymerization by both ionic methods.

Because of its electrical neutrality, free radical is a less selective and more generally useful initiator because most substituents can provide some resonance stabilization for this propagating species. 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 characterised by a long sequence of identical events, namely the repeated addition of a monomer to the growing chain.

iii)- Termination, where by the kinetic chain is brought to a halt by the neutralization or transfer of the active center.

At this type of polymerization production of polymer involves the rapid addition of monomer to a few active centers, the monomer concentration decreases slowly throughout the reaction. High molecular weight polymer is present even at low conversions. The reaction mixture always consists of high polymer and unreacted monomer. Typically the polymer formed has the same chemical composition as the monomer, i.e. each unit in the chain is complete monomer and not a residue as in step-growth reactions.

Successful addition polymerization requires highly purified materials to avoid adventitious termination by impurities.



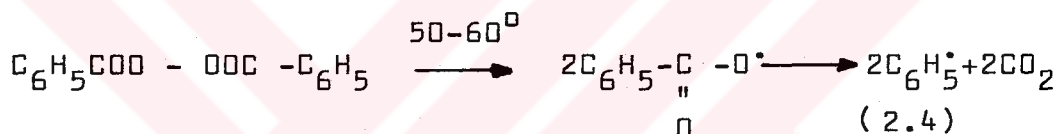
### 2.2.2.1. Free Radical Polymerization

A free radical is an atomic or molecular species having an odd number of electrons and an unpaired electron. The radical is capable of reacting with an olefinic monomer to generate a chain carrier which can retain its activity long enough to propagate a macromolecular chain under the appropriate conditions.

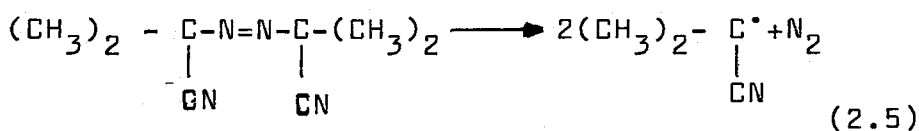


Radicals can be produced with many ways:

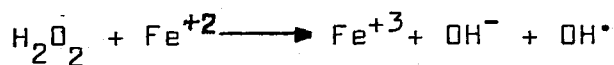
a)- Thermal decomposition: This is applied to organic peroxides or azocompounds.



b)- Photochemical decomposition: This one is applicable to metal iodides, metal alkyls and azo compounds, e.g.  $\alpha$ - $\alpha'$ -azobis isobutyronitrile is decomposed by radiation with a wavelength of 360nm.



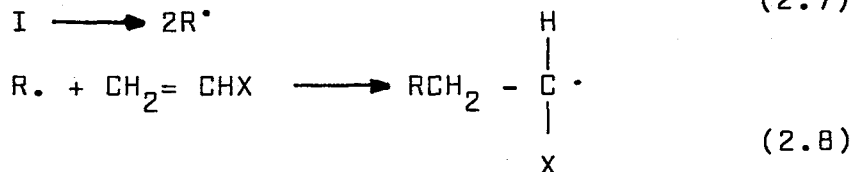
c)- Redox reactions: For example the reaction between the ferrous ion and hydrogen peroxide in solution produces hydroxyl radicals,



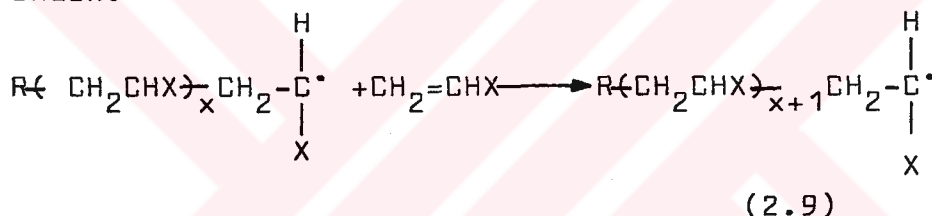
(2.6)

Alkyl hydroperoxides may be used in place of  $H_2O_2$ . Free radical polymerization can be regarded as a chain reaction and it proceeds in initiation, propagation and termination stages.

Initiation: When free radicals are generated in the presence of a vinyl monomer the radical adds to the double bond with the regeneration of another radical.



Propagation: The chain radical formed in the initiation step is capable of adding monomers to propagate the chain.



Termination: Propagation will continue until all monomer in the system is consumed. But free radicals are particularly reactive species and interact as quickly as possible to form inactive covalent bonds, that's why short chains are produced if the radical concentration is high.

Termination of chains can take place in several ways:

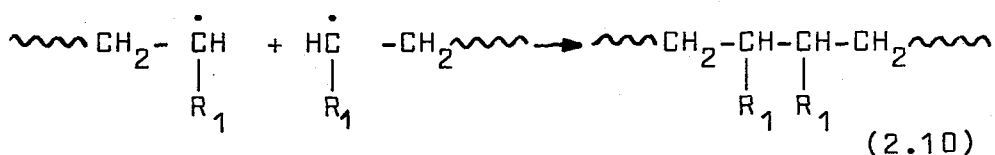
- i)- The interaction of two active chain ends.
- ii)- The reaction of an active chain end with an initiator radical.
- iii)- Termination, by transfer of the active center to another molecule which may be solvent, initiator or monomer.

iiii)- Intereaction with impurities (e.g. oxygen) or inhibitors.

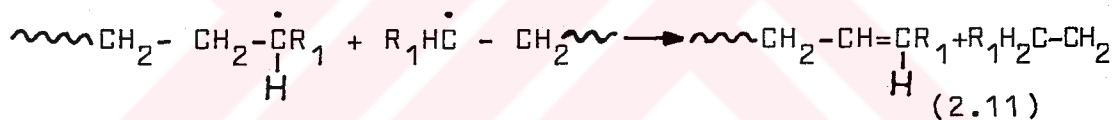
The most important termination reaction is a bimolecular intereaction between two chain ends.

Two routes are possible:

i)- Combination where two chain ends couple together to form one long chain



ii)- Disproportionation with hydrogen abstraction from one end to give unsaturated group and two dead polymer chains.

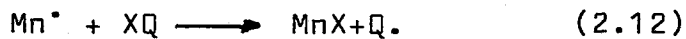


One or both processes may be active in any system depending on the monomer and polymerization conditions [15].

### 2.3. Chain Transfer Reaction

A growing polymer often reacts with a neighboring molecule to form a "dead" polymer with the concurrent creation of a new center of growth—a death procreating a new seed of life, as it were. This is the basic picture of chain transfer. All free radicals, big or small, are involved in radical displacement reactions, in which a radical extracts an atom (or a group of atoms) from the nearest available source to saturate

its free valency, with the production of a new free radical, as shown in equation (2.12) for a radical  $Mn^{\bullet}$ . If the radical  $Mn^{\bullet}$  is a growing polyradical, this reaction is called a chain-transfer reaction and the molecule  $XQ$ , a chain-transfer agent



The basic points in chain transfer are, first, that it is an ubiquitous though inessential side reaction in polymerization which adversely affects molecular weight and often, also the rate of reaction; second, that the chain can be transferred to any species present, whether it is a solvent, a monomer, a catalyst, or a preformed polymer molecule; and third, that not only radical polymerization but also ionic polymerization involves chain transfer. The study of chain transfer helps to throw light on the quantitative aspect of radical displacement reactions, to give an insight into telomerization processes which are now rapidly gaining in industrial importance, to show how to prepare branched-chain polymers and graft copolymers, and to understand the behavior of the so-called modifiers and regulators which are extensively used for controlling molecular weight in industrial polymerization.

#### The Mayo Equation:

In solvent polymerization the second term of the general equation (2.13) usually makes the major contribution. By keeping the initiator concentration low or, preferably, through the choice of an initiator such as an aliphatic azonitrile which is not susceptible to chain transfer the third term is rendered negligible. The last term of the general equation may be kept constant by so adjusting the initiator concentration as

to keep  $R_p/[M]^2$  constant while concentration of the solvent is varied. In the case of thermal polymerization, which follows second-order kinetics.  $R_p/[M]^2$  is constant with dilution and no adjustment is needed. As a consequence the last term of the general equation is a constant and equation (2.13) reduces to equation (2.14), in which  $\overline{DP}_0$  is the degree of polymerization in the absence of a solvent. This is the well-known Mayo equation (2.13) extensively used for determining  $C_s$ , the solvent chain-transfer coefficient [16].

$$\frac{1}{\overline{DP}} = C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} + \frac{\delta^2}{[M]^2} R_p \quad (2.13)$$

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + C_S \frac{[S]}{[M]} \quad (2.14)$$

## 2.4. Block Copolymers

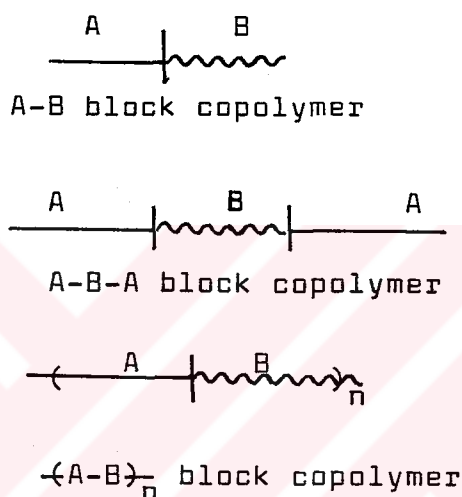
Block copolymers are becoming increasingly important in technological applications, and are currently used as thermoplastics, elastomers, adhesives etc. Their synthesis and properties have recently been comprehensively reviewed. The preparation of block copolymers was greatly stimulated by the development of living (i.e. terminationless) anionic polymerization techniques by Szwarc. Preparing AB block copolymers using an anionic mechanism is certainly the best way of obtaining monodisperse copolymers, homogeneous in composition. Free of homopolymers, with well defined and predetermined structure and molecular weight and which can be easily functionalised (alcohol, acid, acyl chloride, alkyl, etc)

Since Szwarc [17] first demonstrated the living character of anionic polymerization involving a "living

chain" mechanism, a tremendous amount of research has been performed to synthesize block polymers. This peculiar type of chemical structure displays unusual physical properties which are dependent on the aggregation state as well in solution as in bulk. Block polymers consist of generally immiscible sequence resulting in a phase separation process which ultimately controls the colloidal and mechanical properties of the material.

The ability of block polymers to improve properties like surface activity, adhesion, elasticity and impact strength deserves great interest. Several important types of these polymers have reached commercial development as raw materials for surfactants, adhesives, fibers, elastomers, thermoplastics and thermoplastic elastomers. Another recent technological development focuses on polymer blends as heterophase polymeric materials, in which the useful properties of each polymeric partner can be combined at a very low cost to compete with block polymers in their field of application. However, immiscible polymer blends generally display disappointing mechanical performances due to lack of interfacial adhesion and to uncontrolled phase-separation process. In that fastly growing area of industrial research and development, block polymers find their way as surfactants. Indeed it has been reported that limited amounts of block polymers of suitable composition and structure are able to control the morphology of polymer blend and to alleviate their ultimate properties. The synthesis of block polymers of known composition and molecular weight combining a large number of chemically different chains is therefore a renewed challenge for polymer researchers [18].

Block copolymers are macromolecules comprised of chemically dissimilar, terminally connected segments. Their sequential arrangement can vary from A-B structures, containing two segments only, to A-B-A block copolymers with three segments, to multiblock  $\{A-B\}_n$  systems possessing many segments. These are shown in Scheme 2-2. It is obvious that to prepare the above well-defined structures it is necessary to resort to sophisticated synthetic techniques,



Scheme-2-2

The requirements include (a) accurate knowledge and control of initiating and propagating species (b) low impurity levels, (c) the use of low concentration solution polymerization methods, and/or (d) the need for separately producing reactive polymeric intermediates of known functionality. These requirements can result in an economic penalty with respect to production of the other polymeric hybrids. Step-growth, anionic, cationic and, to some extent. Free radical methods have been used with varying degrees of success to prepare block copolymers. A number of useful reviews on synthesis and characterization have been published.

The best block copolymer syntheses are based on sequential anionic addition or ring opening polymerization techniques or on step-growth polymerization. These methods allow the control of block integrity and Sequential architecture that is so important for achieving the ultimate attainable properties. Although block copolymers are more difficult to prepare than random copolymers, they are not hampered by the comonomer reactivity ratio restrictions of the latter. Furthermore, combinations of techniques can be used for synthesizing the various block copolymer segments.

A basic difference between, block and graft copolymers is the number of intersegment linkage sites one or two versus many. It is this difference that makes free radical techniques more applicable to graft copolymerization than to block systems. Because of the many potential grafting sites present in backbone polymers, the probability is high for forming at least some grafted segments along with significant quantities of homopolymer. However, in block systems, prepared by free radical techniques, the probability of forming copolymer structures is lower due to the non selective nature of the polymerization process. Ionic synthetic methods are suitable for graft as well as block copolymers, but step-growth techniques do not give thermoplastic graft copolymers, since these multifunctional reactions would produce cross-linked systems. In contrast, the applicability of step-growth techniques to block copolymers permits the synthesis of a wide spectrum of high performance compositions.

The degree to which structural control is achieved can only be ascertained through the use of effective characterization tools. The characterization techniques traditionally used to analyze homopolymers can also be



employed in elucidating hybrids. Simple physical blends, in principle, are the easiest hybrids to characterize. Separation of the blend components via solution fractionation or extraction techniques should lead to the easily characterized homopolymer components. Both random and block copolymers are more difficult to characterize than homopolymers or polymer blends. Since most block copolymers are, in reality, contaminated to at least a minor degree with homopolymer, they are frequently more difficult to define than uniform statistical copolymers. In addition, the question of the determination of block copolymer architecture (e.g., A-B versus A-B-A) is indeed a difficult feature to elucidate.

Graft copolymers clearly present additional obstacles to accurate structural characterization. These macromolecules are even more complex than block copolymers for several reasons while the number of segments in a block copolymer can be deduced with some certainty from the synthetic technique employed, this is rarely possible with graft copolymers due to the multifunctional nature of the backbone and to the questionable efficiency with which these functionalities participate in the grafting reaction.

The length of the graft segments and their polydispersity are also more imponderable for the same reasons. An important further complication is the unanswered question of the spacing of graft junction points along the backbone. In block copolymers, this parameter is more accessible. In A-B and in A-B-A block copolymers there are, by definition one and two junction points, respectively. In  $\langle A-B \rangle_n$  block copolymers, the distance between intersegment linkages can be deduced from a knowledge of the block molecular weight.

### 2.4.1. Properties Of Block Copolymers

Many basic characteristics of block copolymers and graft copolymers are similar. This is due to an important feature that they have in common, namely, the presence of intersegment chemical linkages. From a simplistic point of view block and graft copolymers resemble incompatible physical blends in some respects and homogeneous random copolymers in others. Such systems usually exhibit two-phase morphology but this occurs on a micro-scale rather than the macroscale dimension of incompatible physical blends. This is due to the influence of the intersegment linkage, which restricts the extent to which the phases can separate. The small domain size and excellent interphase adhesion resulting from this microphase morphology can produce a high degree of transparency and a good balance of mechanical properties. This behavior is reminiscent of homogeneous copolymers and is not typical of polymer blends many other properties, such as permeability and chemical resistance, are dependent upon which segment exists in the continuous phase.

The thermal properties of block and graft copolymers resemble those of physical blends. They display multiple thermal transitions such as glass transitions and/or crystalline melting points, characteristic of each of the components.

In contrast, homogeneous random copolymers display a single, compositionally dependent glass transition temperature. Furthermore, while crystallinity is possible in block or graft copolymers, due to long sequences. It is diminished or eliminated in the random systems due to a disruption of chain regularity.

The presence of long segments in block and graft copolymers presents the possibility of using these materials as emulsifiers or surfactants. The incompatibility of homopolymer blends, both in solution and in the solid state, is reduced by the addition of small quantities of the respective block or graft copolymers. In addition, blending a block or graft copolymer with one of the respective homopolymers provides a means of achieving a fine dispersion of the "foreign" segment in the homopolymer matrix. The latter feature is made use of in important commercial products such as impact-modified thermoplastics. The above discussion points out of similarities of two-phase block and graft copolymers and the features that distinguish them from physical blends and random copolymers. It is important to recognize that a high degree of structural control and integrity is necessary in order to achieve the ultimate properties inherent in such two-phase systems. It is in this respect that block copolymers offer a clear advantage over graft copolymers. Because of the greater reliability and predictability of block copolymer synthetic techniques. It is possible to achieve desired structures more precisely.

This results in much better control of important parameters such as sequence architecture, segment length and spacing polydispersity, and contamination by homopolymer or undesired copolymer architectures. These factors lead to a higher degree of morphological perfection in block copolymers than in graft copolymers, which, in turn, is reflected in superior physical properties.

A unique development resulting from block copolymer technology is the concept of thermoplastic elastomeric behavior. Block copolymer systems of this type are

characterized by rubbery behavior in the absence of chemical cross-linking. This feature permits the fabrication of these materials by means of conventional thermoplastic processing techniques. The key to this unique behavior is the ability to achieve a network structure by physical rather than chemical means. This in turn, results from finely controlled morphology in A-B-A or (A-B) systems containing both flexible and rigid segments. In principle, this type of behavior is also attainable with graft copolymer structures. However, in actual practice, only limited success has been achieved to date. This is undoubtedly due to the difficulties in obtaining a high degree of architectural and structural control in graft copolymers [19].

#### **2.4.2. General Methods On Block Copolymer Synthesis**

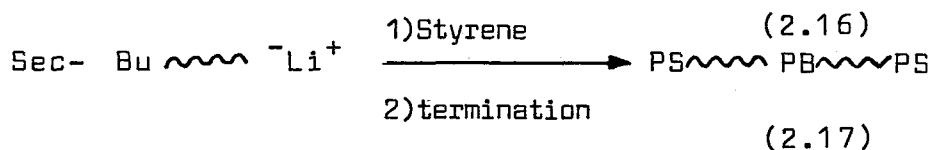
There are various methods for the synthesis of block copolymers with different mechanisms it is beyond the scope of this work to discuss all these procedures in detail. Therefore we would outline the general synthetic approaches to prepare block copolymer.

The methods of block polymerization will be discussed according to the classical scheme based on the type of the active centers. Five sections will be devoted to free radical, anionic, cationic, coordination, and step-growth polymerization.

##### **2.4.2.1. Anionic Living Polymerization**

The living polymeric carbanions are especially interesting because they can react with compounds which provide either functional end groups ready for subsequent reactions or the linking of the initial macromolecules to form star-branched polymers of precise structure.

Living macromolecules can initiate the polymerization of other monomers to produce well-defined block copolymers. In the anionic polymerization reactions it is the non-terminating character of the growing chains which can lead to an extremely narrow molecular weight distribution [20].

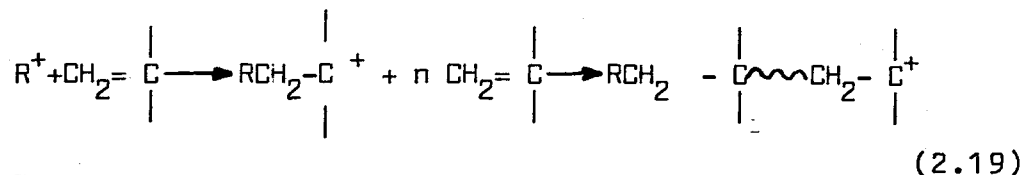


#### 2.4.2.2. Cationic Polymerization

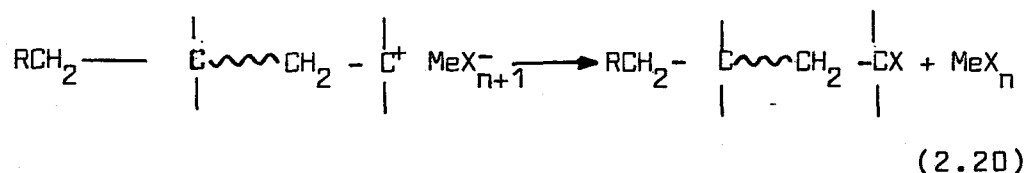
The cationic polymerization of olefin and vinyl monomers was generally restricted by chain transfer and chain termination, where as the living polymers prepared in cationic polymerization of cyclic ethers had too low electrophilicity to add the less basic olefin and vinyl monomers [21].



Cationation and propagation:

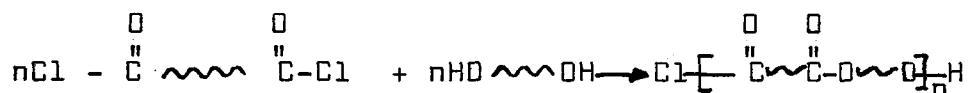


Termination:



### 2.4.2.3. Step-Growth Polymerization

The step growth block copolymers consist of low molecular weight sequence, usually arranged in a  $\langle A-B \rangle$  configuration, nevertheless A-B-A structures can also be generated. In this type of block copolymer, sequence having low solubility parameter are generally associated with highly polar sequences (polyester, polyamide, polycarbonate, polyuréthane) [22].



(2.21)

### 2.4.2.4. Coordination Polymerization

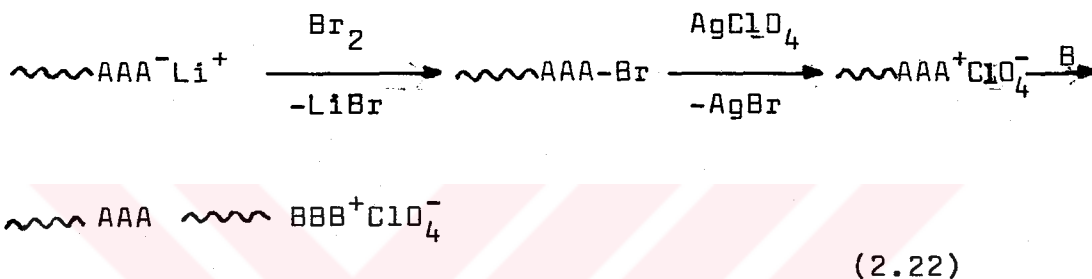
Coordination and especially Ziegler-Natta type catalysts are extremely helpful in controlling the chain growth processes and more specially the stereospecificity of polyolefins and some vinyl and methacrylate polymers. To prepare block copolymers, the catalyst must have a lifetime sufficient to permit sequencing of the monomers, particularly for  $(AB)_n$  and ABA type block copolymers and chain transfer reactions must be minimal. Otherwise, the reaction product will be at best, a mixture of homopolymers and block copolymer [23].

### 2.4.2.5. Free Radical Polymerization

The radical polymerization of a mixture of monomers usually does not lead to a block copolymer. However creation of free radical sites or radical generating species such as azo or peroxide on a given polymer can then initiate polymerization of a second monomer. This can be achieved in different ways. Various methods for the synthesis of block copolymers by radical mechanism have been treated recently by two review articles [24-26].

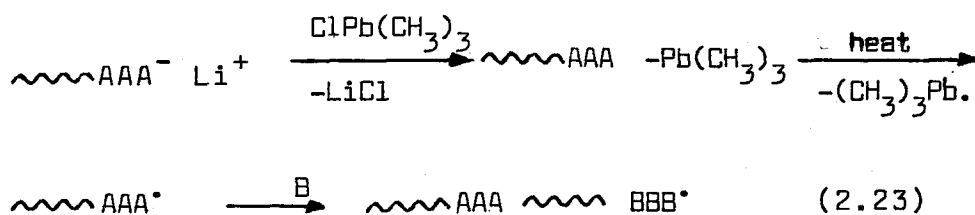
### 2.4.3. Transformation Reaction For Block Copolymer Synthesis

A unique approach to block copolymer synthesis involves changing the type of propagating center part way through the synthesis via a transformation reaction for example, anionic polymerization of monomer A is carried out as a living polymerization and then the carbanion centers transformed into carbenium ions by reaction with bromine followed by silver perchlorate [27].



The carbenium ions are then used to polymerize monomer B.

Anionic propagating centers are transformed into radical centers by reaction with trimethyl lead chloride, followed by heating in the presence of a second monomer.



Transformation reactions offer the potential for synthesizing a wider range of block copolymers. Anionic polymerization is limited to forming copolymers only from those monomers which undergo anionic propagation, cationic is limited to those which propagate through carbenium ion centers. Whether this potential is

realized depends on whether various side reactions can be controlled. A side reaction in the anionic-to-cationic transformation is the Wurtz-type coupling between lithium and bromine containing molecules. The anionic-to-radical transformation involves the formation of trimethyllead radical, which can initiate the homopolymerization of monomer B. However, the living anionic polymerization technique, although attractive, has some limitations [1]:

i)- It is limited to monomers which are sensitive to nucleophilic attack, i.e to non-polar monomers like styrene and derivatives, butadiene and isoprene, acrylic monomers, and heterocycles such as ethylene oxide. Therefore, it excludes all monomers which polymerise by radical mechanism, such as VCM, vinyl acetate, etc or monomers such as THF and isobutene which are sensitive only to cationic initiation.

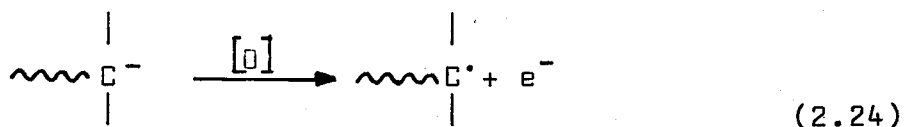
ii)- Success of the anionic technique is dependent on the reactivity of the anion generated for example the polystyryl carbanion can initiate the polymerization of butadiene and vice versa but with the polymerization of ethylene oxide, the alkoxide ion generated is too stable to initiate the polymerization of styrene.

So the combination of monomers which may be converted into block copolymers by the anionic mechanism is consequently limited.

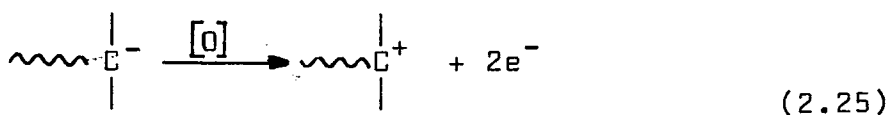
One of Richards mayor achievement was to overcome these difficulties and to propose a general method which allows multiple combinations of monomers. Among these alternatives are;



i)- Converting carbanions to free radicals by a one-electron oxidation step:

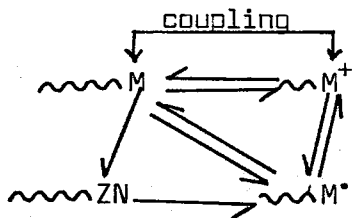


ii)- Changing carbanions to carbenium ions by a two-electron oxidation process:



Therefore the range of attainable block copolymers can be greatly extended if this convenient process, i.e. changing the active species after the propagation step of the first monomer to one best suited to the propagation of the second is correctly achieved. Such a process requires three distinct stages.

The transformation of the propagating end from that employed with the first monomer to that best suited to propagate the second monomer, permits all kinds of combinations of monomers.



The interest in such research consists in developing routes to new specifically structured block copolymers for example, an ABC polybutadiene-b-tetrahydrofuran-c-styrene may be synthesized by (i) oxidation of a living

cationic polybutadiene, (ii) initiation and polymerization of a tetrahydrofuran sequence to produce a cationic AB block copolymer and (iii) titration of the living solution with monofunctional living polystyrene.

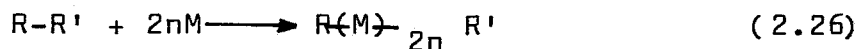
Stage 1: Polymerization of the first monomer capping of the propagating ends with stable but potentially reactive functional groups and isolation of the resulting polymer A or leaving it in situ.

Stage 2: Dissolution of polymer A and comonomer in a solvent system suitable for copolymerization.

Stage 3: Reaction or change of conditions resulting in transformation of the functional end groups of polymer A into propagating species which polymerize the comonomer by a different mechanism to that used in stage 1 to produce block copolymer.

## 2.5. Iniferter Process

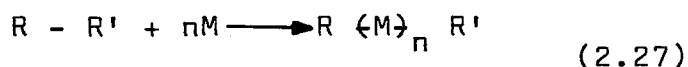
Polymer formation in radical polymerization of a vinyl monomer (M) initiated by an initiator (R-R') is expressed by scheme (2.26) if no chain transfer (CT) reaction occur and ordinary bimolecular terminations proceed only by recombination (R=R').



In this case, radical polymerization gives a polymer with two initiator fragments at its chain ends. However, usually in radical polymerization, termination by disproportionation and CT reactions are known to be important and hence the number of the initiator fragments per polymer molecule is always  $< 2$ . At the present

time, it is impossible to control the mode of these terminations.

So if we use initiators which have very high reactivities for CT reaction to the initiator and/or primary radical termination (PRT) i.e. ordinary bimolecular termination is neglected, it is expected that a polymer with two initiator fragments at its chain ends will be obtained (Scheme 2).



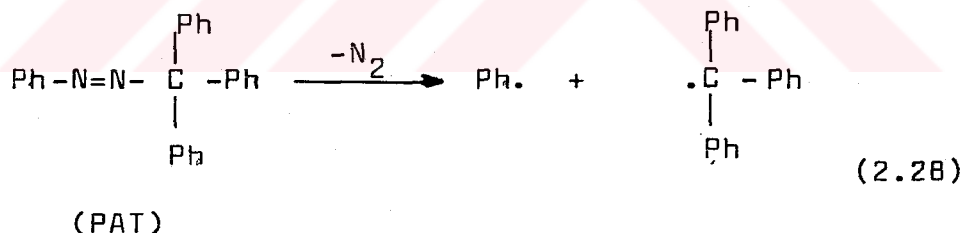
Therefore, these radical polymerizations may simply be considered as an insertion reaction of monomer molecules into the R-R' bond of the initiator leading to a polymer with two initiator fragments, similar to telomerization of ethylene with carbon tetrachloride as a telogen. For initiators with these functions to the name "iniferter". Many radical initiators having somewhat low initiating reactivities would be expected to serve as iniferters, if the monomers and polymerization conditions used are selected carefully. Some organic sulphur compounds, phenylazotriphenylmethane and azobisdiphenylmethane or tetraphenylethane derivatives were found to serve as iniferters for the polymerization of styrene (St) and methyl methacrylate (MMA).

From a viewpoint of tailor-made polymer synthesis, iniferters can be classified into several types; mono-di, tri, or poly-functional iniferters, thermal or photoiniferters; monomeric, polymeric or polymer-gel iniferters; monomer-or macromer-iniferters etc. Among the iniferters used, some sulfur compounds having N,N diethyldithiocarbamate groups were found to serve as an excellent photoiniferters for the controlled synthesis

of various monofunctional telechelic, block star, graft and cross-linked polymers, if photoiniferters with the functional groups were used [12].

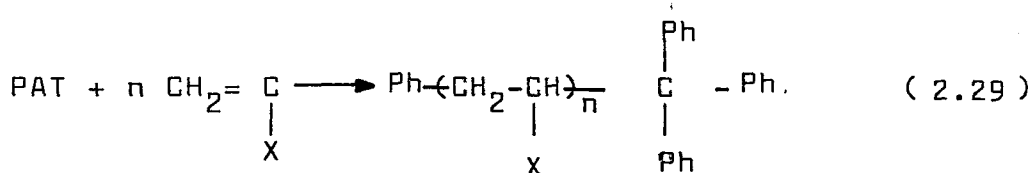
Radical polymerization of methyl methacrylate (MMA), with phenylazotriphenylmethane (PAT) was found to give the polymer with a trityl group bonded at its  $\alpha$ -chain end which could further dissociate into propagating and trityl radicals. Therefore, it was confirmed that PAT served as a thermal iniferter for polymerization of MMA, which proceeded via a living radical mechanism, i.e. yield and molecular weight of the polymers increased with reaction time. When the polymer thus obtained was used as a polymeric iniferter for the polymerization of styrene (St), the block copolymer was obtained.

PAT has been known to decompose into a highly reactive phenyl radical and an unreactive trityl radical, according to Eq.(2:28)



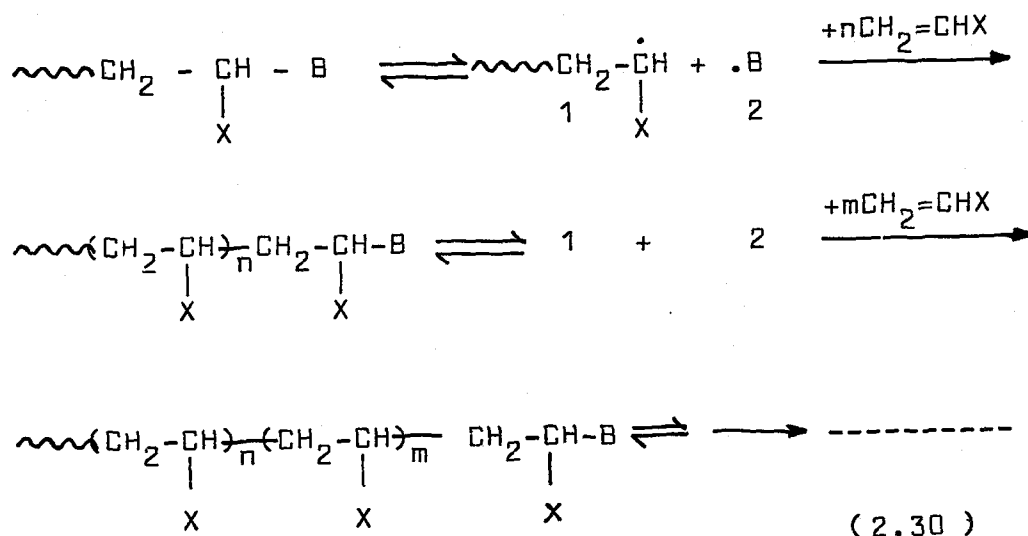
In 1940's, PAT was examined as an initiator having a modifier function in radical polymerization of butadiene, similar to diazothioethers and diazoaminobenzenes. However, the experiment did not give good result, because the activity of PAT as an initiator was low. After that some studies on the decomposition of PAT and its initiator activity have been performed. PAT is now used as a source of phenyl radical in physical organic chemistry.

In radical polymerization with PAT, it is expected that phenyl radical in Eq.(2.28) can easily add to the monomer to initiate polymerization, and trityl radical reacts only with the propagating radical. If the above reactions occur preferentially in radical polymerization of vinyl monomers with PAT, the polymer with phenyl and trityl groups at its  $\omega$  and  $\alpha$  ends, respectively, may be produced as shown in Eq. (2.29)



From these viewpoints, Otsu has proposed in 1982 a concept of initiator-transfer agent-terminator (iniferter) to design of the structure of polymer chain end in radical polymerization. As reported previously the photopolymerizations of St and MMA with some organic sulfur compounds as an iniferter were confirmed to proceed via a mechanism close to this concept, i.e. the resulting polymers have to iniferter fragments bonded at both chain ends. Moreover, if the end group of the polymers obtained with such iniferters can further induce radical polymerization as a polymeric iniferter, these radical polymerization may be considered to proceed via a new mechanism, i.e. yield and molecular weight of the polymers increase with reaction time.

Therefore, Otsu has also proposed in 1982 an ideal model for living radical polymerization in homogeneous system as shown in Eq (2.30)

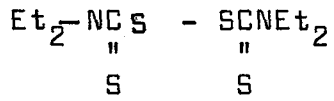


Namely the C-B bond in the propagating chain end dissociates into radicals in which 1 is reactive propagating radical and 2 is an unreactive small radical which does not enter the initiation, but undergoes readily primary radical termination to give the identical C-B bond.

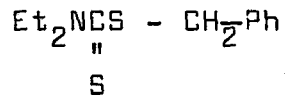
Accordingly, if the polymerization proceeds via the repetition of dissociation at the chain end, addition of the monomer to 1, and primary radical termination with 2 such polymerization may proceed via a living radical mechanism according to Eq.(2.30) As described above, the polymerizations of St and MMA with sulfur compounds as a photoiniferter were found to be performed by a mechanism close to Eq. [28].

TABLE: 2.1. . . The Iniferter Molecules Which are Used in Block Copolymer . Synthesis.

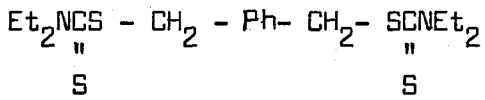
Compound	Type of iniferter	Monomer	Reference
PAT (Phenylazotriphenylmethane)	Thermal, photo	MMA	28
BDC (Benzyl N,Ndiethylthiocarbamate)	Photo	St, MMA	29
XDC (p-xylene bis(N,N,diethyldithiocarbamate)	Thermal	St, MMA	29
DDC (Tetrakis(N,Ndiethylthiocarbamate) benzen)	Thermal	St, MMA	29
TD (Tetraethylthiuram disulphide)	Thermal, photo	St, MMA	29
DPD (Diphenyldisulfide)	Photo	St, MMA	29
PEDC(2 phenylethyldiethylthiocarbamate)	Photo	St, MMA	29
TPSN(1,2 di cyano tetraphenylethane)	Thermal	MMA	30
DBD (Di benzoildisulfide)	Thermal	St, MMA	31



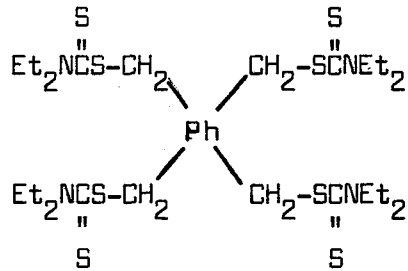
(TD)



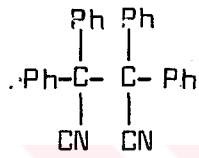
(BDC)



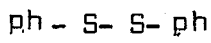
(XDC)



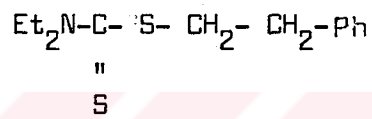
(DDC)



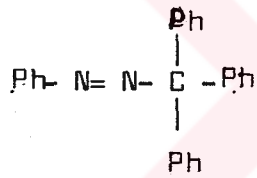
TPSN



(DPD)



(PEDC)



(PAT)



(DBD)



## CHAPTER 3. EXPERIMENTAL PART

### 3.1. Purification Of Materials

#### Styrene:

Washed with aq. 5%NaOH to remove inhibitors, then with water, dried for several hours with  $\text{CaCl}_2$  and distilled under reduced pressure ( $50^\circ\text{C}/25$  mmHg), middle fraction is collected and immediately used.

#### Methyl methacrylate:

Washed twice with aq. 5%NaOH to remove inhibitors and twice with water. Dried with  $\text{CaCl}_2$  and distilled under reduced pressure ( $46^\circ\text{C}/100$ mmHg), middle fraction is collected and immediately used.

#### AIBN (Azobisisobutyronitrile)

Crystallized from acetone, Dried under vacuum at room temperature and stored in the dark under vacuum, mp  $101-101.5^\circ\text{C}$ .

#### TPMM (Triphenylmethyl Mercaptane)

Triphenylmethyl mercaptane (TPMM) was used as purchased.

### 3.2. Techniques

#### Preparation of triphenylmethyl group terminated polymers

Bulk monomers containing a known amount of AIBN and TPMM was outgassed in the usual manner and placed in a constant temperature bath at 70°C. At the end of reaction, the mixtures were poured into ten-fold excess of methanol, and precipitated polymers then filtered and dried.

#### Block Copolymerization

Bulk monomers containing above obtained triphenylmethyl terminated polymers were degassed and heated at 70°C. After polymerization for a given time, the content of the tubes was poured into methanol. The separation of the polymers obtained from block copolymerization was carried out by extracting them with appropriate solvents.

### 3.3. Analysis

#### Gel Permeation Chromatography

The  $\bar{P}_n$  values of obtained polymers were calculated from GPC chromatograms according to polystyrene standart samples. Using Knauer M-64 instrument and THF as the eluent at a flow rate of 1ml/min at 25°C.

#### <sup>1</sup>H NMR Spectroscopy

<sup>1</sup>H-NMR spectra were recorded on Bruker 200 Spectrometer in CDCl<sub>3</sub> solution with tetramethylsilane as internal standard.

### UV Spectroscopy

UV spectra were recorded on a UV 160 A Shimadzu UV-Vis spectrophotometer, using  $\text{CH}_2\text{Cl}_2$  as a solvent.

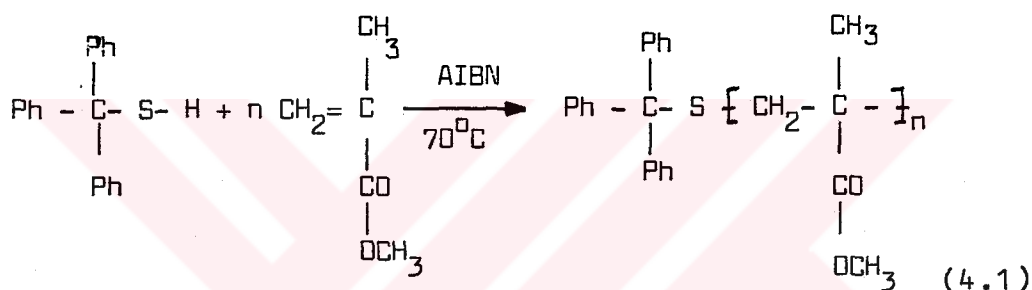
### IR Spectroscopy

IR spectra were recorded on a Shimadzu IR-400 model spectrophotometer.



## CHAPTER 4. RESULT AND DISCUSSION

Styrene (St) and methylmethacrylate (MMA) were polymerized in the presence of 2,2'-azobisisobutyronitrile (AIBN) and triphenylmethyl mercaptane (TPMM) as initiator and chain transfer agent, respectively, yielding polymers with trityl end groups as depicted below, i.e. for MMA polymerization;



Typical IR spectra of TPMM and trityl terminated PMMA (TPM-PMMA) are illustrated in Figure 4.1. The stretching band at  $2570 \text{ cm}^{-1}$  due to S-H group disappeared in the polymer Figure 4.1 (b) also shows trityl moiety together with the peaks for MMA. The introduction of trityl groups into PMMA was also supported by  $^1\text{H-NMR}$

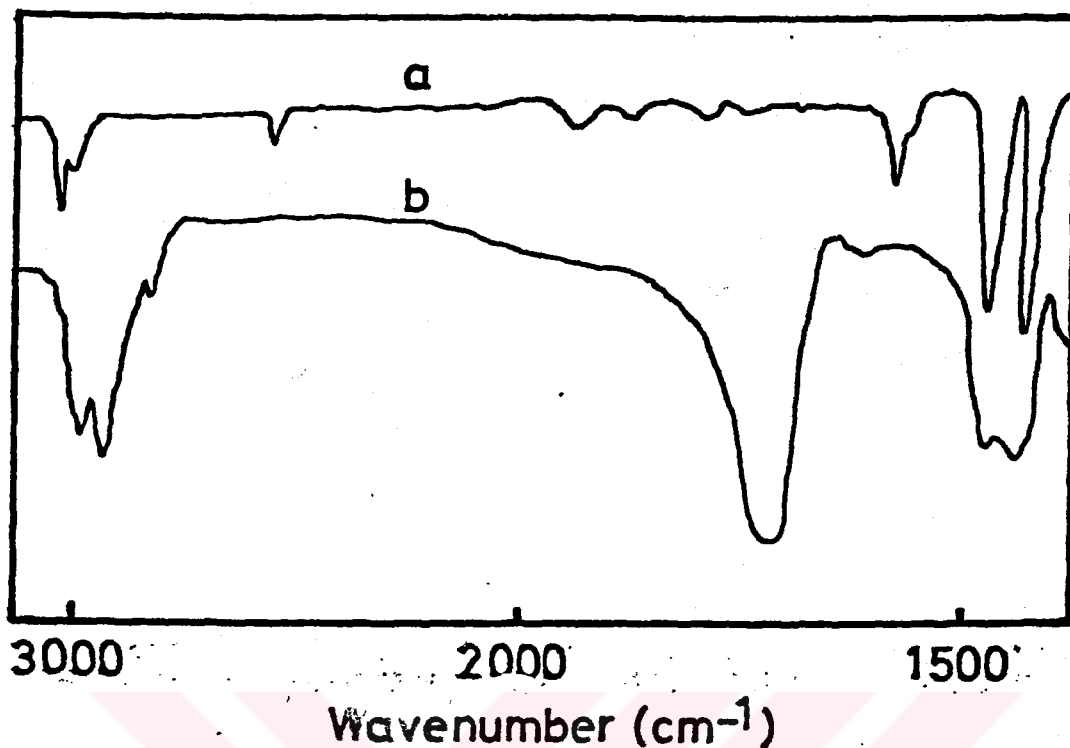


FIGURE: 4.1. IR Spectra of (a) TPMM and (b) TPM-PMMA

As can be seen from Figure 4.2 aromatic protons appear in 7,2 ppm region in addition to peaks at 3.6 and 1.4-2.0 ppm for  $\text{OCH}_3$  and vinyl protons, respectively. UV spektrum of the polymer possesses an absorption band at around 330nm region indicating attachment of trityl end groups. In addition, GPC analysis shows no contamination of physically entrained TPMM in the polymer.

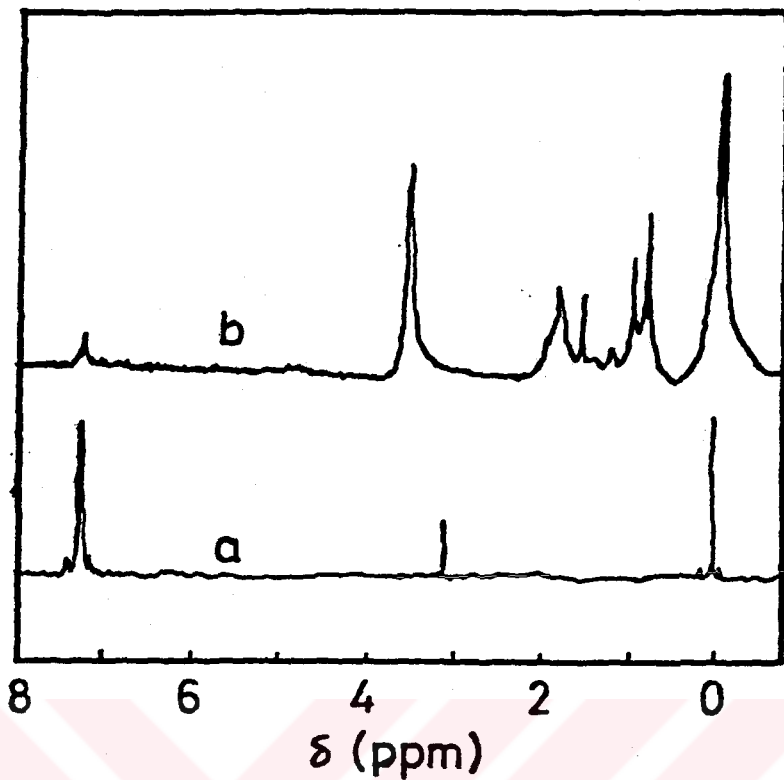


FIGURE: 4.2. <sup>1</sup>H-NMR Spectra of (a) TPMM and (b) TPM-PMMA

TPMM was shown to be an efficient transfer agent in the polymerization of St and MMA. Transfer constants were found to be 17.8 and 0.71 for St and MMA, respectively, from the slope of  $1/\bar{P}_n$  against  $[S]/[M]$  as shown in Figure 4.3. Notably, chain transfer constant for St is higher than that for MMA polymerization.

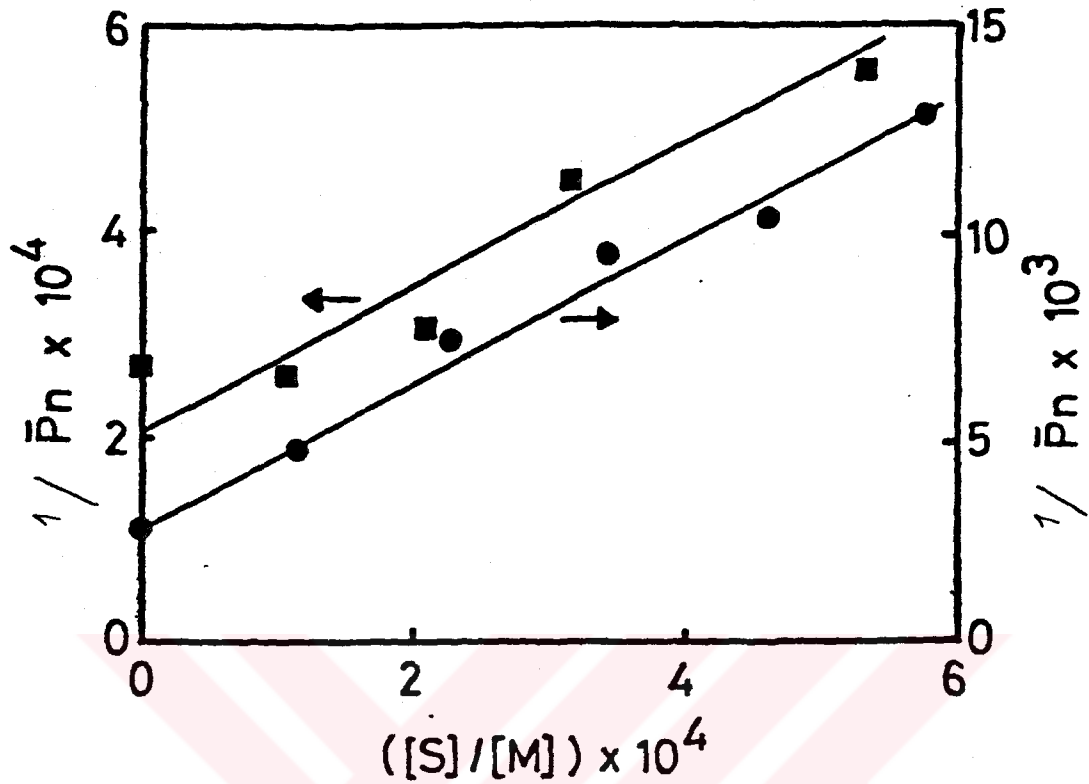


FIGURE: 4.3. Plots Of Reciprocal Degree Of Polymerization Versus  $[S]/[M]$  For(●) St And [■] MMA Polymerization, S=TPMM

In general, the same behaviour was observed with common chain transfer agents. The polymer with the desired molar mass can be prepared by controlling the feed ratio of the monomer to the chain transfer agent, TPMM (Tables 4.1 and 4.2).

TABLE: 4.1. Polymerization of St Initiated by AIBN in the Presence of TPMM at 70°C<sup>a)</sup>,

TPMM x 10 <sup>3</sup> (mol/l)	Conversion (%)	$\bar{M}_n \times 10^{-3}$ <sup>b)</sup> (g/mol)	$\bar{M}_w \times 10^{-3}$ <sup>b)</sup> (g/mol)
0	14.0	37	99
1	6.0	22	55
2	6.2	14	30
3	1.5	11	26
4	2.8	10	19
5	3.4	8	16

a) Polym. time: 2h, |St|=8.7mol/l, |AIBN|=5x10<sup>-3</sup>mol/l

b) Determined by GPC

TABLE: 4.2. Polymerization of MMA Initiated by AIBN in the Presence of TPMM at 70°C<sup>a)</sup>

TPMM x 10 <sup>3</sup> (mol/l)	Conversion (%)	$\bar{M}_n \times 10^{-4}$ <sup>b)</sup> (g/mol)	$\bar{M}_w \times 10^{-4}$ <sup>b)</sup> (g/mol)
0	8.5	36.7	76.4
1	6.9	38.4	54.5
2	7.1	32.6	50.0
3	3.2	22.2	46.3
5	5.6	17.6	46.6

a) Polym. time: 0.5h, |MMA|=9.4 mol/l, |AIBN|=10<sup>-3</sup>mol/l

b) Determined by GPC



### Radical Polymerization With Polymeric Thermal Iniferter:

The obtained polymer has a trityl moiety at one end. Trityl terminated polystyrene (TPM-PSt) was used as a thermal iniferter in the polymerization of St. The plot of molecular weight ( $\bar{M}_n$ ) of the polymers against the conversion is shown in Figure 4.4. As can be seen  $\bar{M}_n$  of the polymers increased linearly with conversion which indicates that this polymerization proceeds via a quasi-living radical mechanism in a manner proposed by Otsu [12].

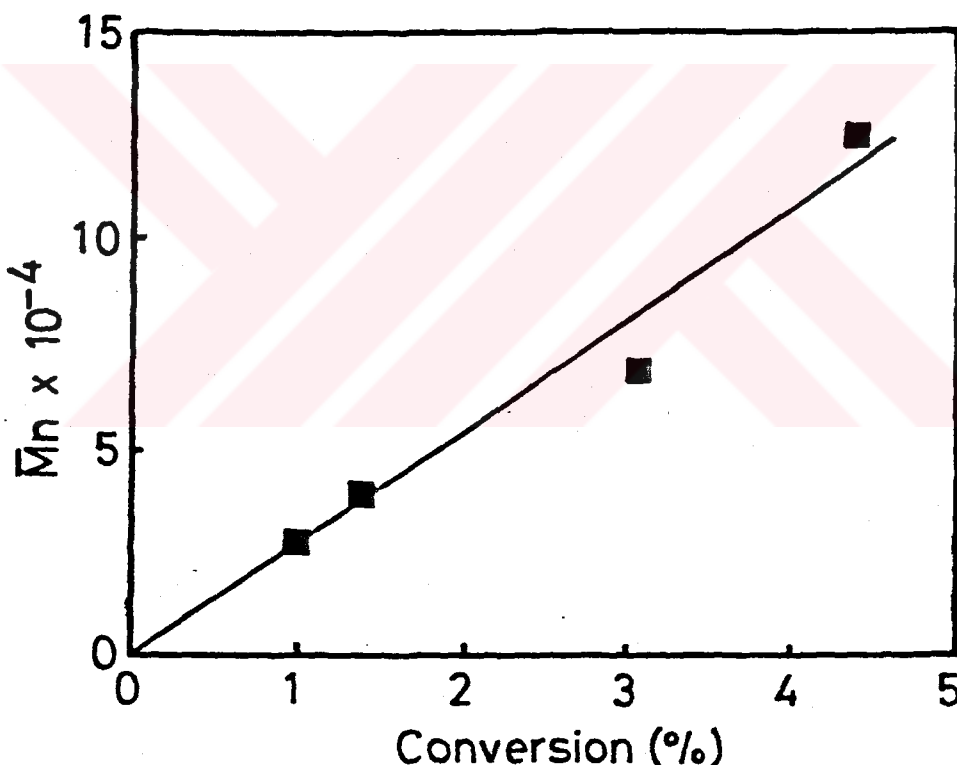


FIGURE: 4.4. Polymerization of St With TPM-PSt at 70°C [St] = 8.7 mol/l, [TPM-PSt] = 20 g/l

Figure 4.5. shows the GPC traces recorded with polymer isolated at various reaction times in bulk polymerization of St with TPM-PSt. The GPC trace of TPM-PSt showed unimodal molecular weight distribution but that formed thereafter become a bimodal molecular weight polymer appeared and it shifted to higher molecular weight side with time.

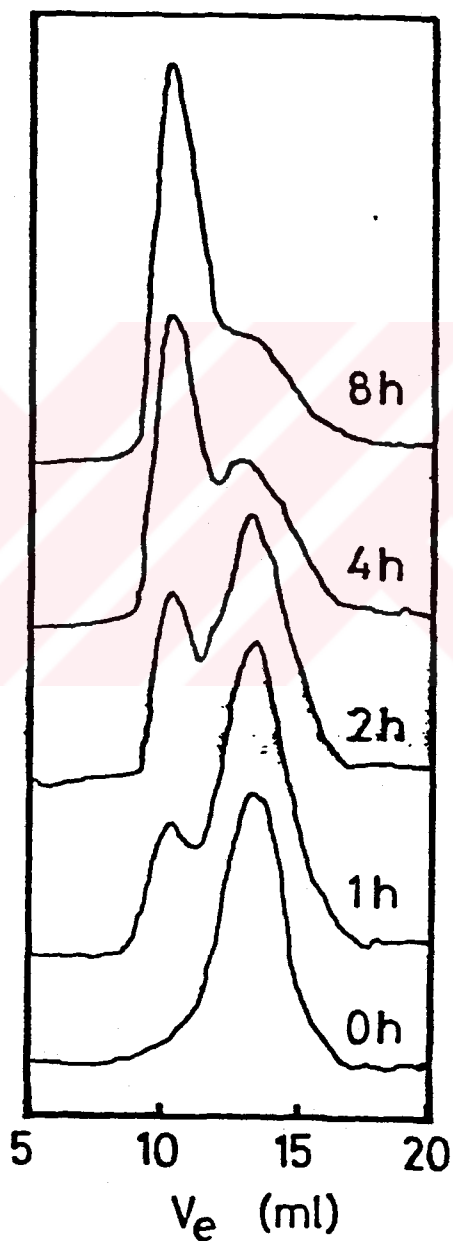
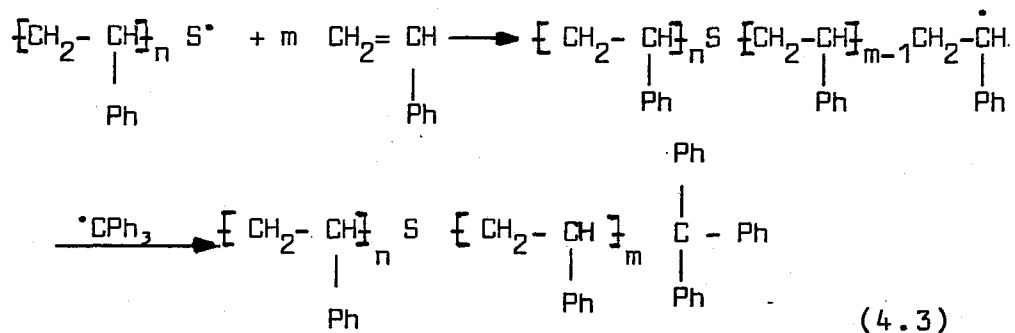
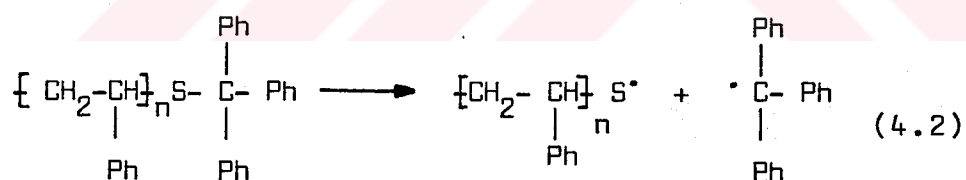


FIGURE: 4.5. GPC Traces For Polystyrene Polymerized In Bulk With TPM-PSt At Each Time.

In relation to this, the peak of lower weight polymer decreased and that of higher molecular weight polymer increased.

Thermal instability of trityl terminated polymers was proved by heating this polymer in boiling benzene for 3h. The resulting polymer showed no initiation activity for styrene polymerization and molecular weight of the polymer did not change indicating that the polymer obtained by using TPMM as chain transfer agent was stabilized by such treatment and initiation functionality is due to trityl end groups.

Polymerization involves dissociation of trityl terminated polymer into radicals to give chain extended high molecular weight polymer. Bond dissociation is expected to occur preferentially at the S-CPh<sub>3</sub> bond since tertiary bonds ease the decomposition. The thiyl radical reacts with the monomer whereas trityl radical reacts only with the propagating radical.



Similarly, if the polymers thus obtained were used as polymeric iniferter of the polymerization of second monomer, block copolymers must be produced. The results of block copolymerization of St with TPM-PMMA and MMA with TPM-PSt are summarized in Table 4.3. Polymer molecules which for any reasons fail to acquire trityl groups during the chain transfer polymerization contribute to the formation of non-blocked components. Several deactivation reactions leading to the formation of homopolymers were discussed in detail elsewhere [28].

TABLE: 4.3. Block Copolymerization By Using Polymeric Iniferters

Polym. inifer. (g/l)	Monomer (mol/l)	Time (h)	Yield (g)	Fractions		Extracted Block (%)
				PSt (%)	PMMA (%)	
TPM-PSt,80 (49800)	MMA.9.4	3	0.72	22	26	52 (110700)
TPM-PMMA,40 (110600)	St, 8.7	2	0.52	22	16	62 (142500)
TPM-PMMA,40 (106800)	St, 8.7	2	0.56	15	19	66 (145800)

Numbers in paranthesis show the  $\bar{M}_n$  values

Representative GPC traces for TPM-PSt and after polymerization with MMA are shown in Figure 4.6. The peak at higher molecular weight is ascribed to the block copolymer.

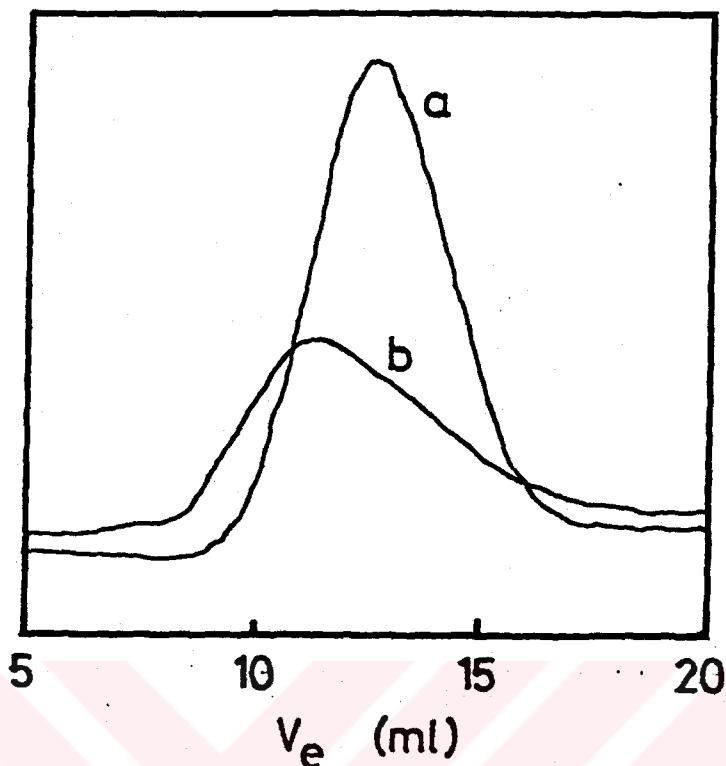


FIGURE: 4.6. GPC Traces for (a) TPM-PSt and (b) Block Copolymer of St and MMA

<sup>1</sup>H-NMR data are in agreement with the block copolymer structure. The spectrum of the block copolymer (Figure 4.7) displays methyl groups of varying tacticity of poly (methyl methacrylate) block at highest field of 0.85-1.1 ppm. The corresponding methylene group resonances appear in the chemical shift range from 1.4 to 2.0 ppm overlapping with those of the polystyrene block.

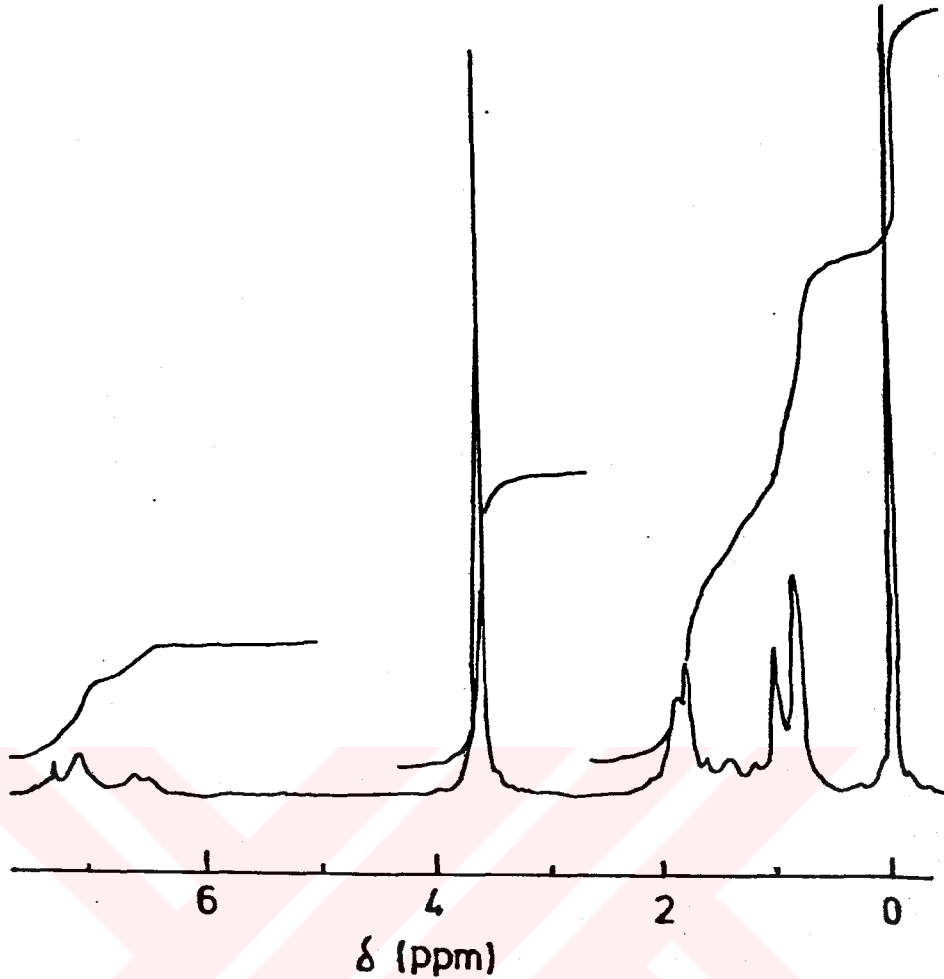


FIGURE: 4.7.  $^1\text{H}$ -NMR Spectrum of the Block Copolymer.

The methyl ester protons resonate at 3.6 ppm. The aromatic ring hydrogens appear as two bands at 6.55 and 7.05 ppm which suggests that the styrene units are grouped in blocks.

In conclusion, these results indicate that combination of chain transfer polymerization and iniferter technique can be applied to produce block copolymer of monomers that are prone to free radical polymerization. This method pertains to trityl groups attached to the polymer ends by means of high chain transfer reactions and subsequent thermolysis of these groups in the presence of monomers [32].

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## BIDGRAPHY

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