ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

AZO-BENZOIN INITIATORS AND THEIR USE IN BLOCK COPOLYMERIZATION

Ph.D. THESIS

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to my mother, father and Ali,

PREFACE

Block copolymers may possess unique and novel properties for industrial applications. During the past 20 years they have sparked much interest; their potential has been realized in thermoplastic elastomers where the block copolymer is the principal constituent of the material and in applications where the block copolymer acts as a useful additive, eg, surfactants and viscosity improvers.

In this study an alternative procedure for block copolymer formation was introduced by the attachment of the structurally related benzoin and its derivatives to the polymer main chains.

In preparing this thesis I worked under supervision of Prof.Dr.Y.Yağcı, who supplied initial impetus for undertaking this task. I would like to thank for his kind interest and valuable suggestions throughout my research.

It is a pleasure for me to thank all of my colleagues, especially Drs. Ü.Tunca and M.H.Acar to whom I always benefit from their experiences. I extend personal thanks to Dr.M.Padmanaban and Mr.Y.Z.Menceloğlu for elemental analysis and NMR measurements.

Finally my sincere thanks are due to my parents and to Dr.A.Önen who has helped in many ways from suggestions to final drafts.

CONTENTS

SUMMARY

In this study new azo-benzoin initiators were synthesized by the condensation of 4,4'-azo-bis(4-cyano - pentanoyl chloride) (ACPC) with benzoin or α-methylol-benzoin methyl ether (MBME). The initiator structures were confirmed by IR and NMR spectroscopy as well as elemental analysis. The kinetics of bulk polymerization of styrene initiated by azo-benzoin initiators was investigated and the kinetic parameters evaluated. The initiation of polymerization of styrene by means of azo-benzoin initiators yields polymers with terminal photo-active benzoin or benzoin methyl ether groups. These photoactive prepolymers were employed in the second stage for the block copolymerization. The block copolymer structure was elucidated by means of extraction with appropriate solvents, GPC analysis, IR and NMR spectral measurements. Mechanisms for initiation and possible termination, for systems involving benzoin type initiators were discussed in the light of results from studies on the composition of the block copolymerization mixture. Structure and efficiency of block copolymerization greatly depend on both the relative reactivities of the photochemically derived radicals and termination mode of polymerization.

AZO-BENZOİN BAŞLATICILAR VE BLOK KOPOLIMERLEŞMEDE KULLANIMLARI

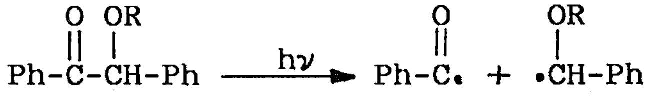
ÖZET

Polimer bilimi oldukça yeni bir dal olmasına rağmen son elli yılda çok hızlı bir şekilde gelişmiştir. Sentetik polimerler günlük yaşantımızda birçok alanda kullanılmakta ve endüstriyel olarak katlanan boyutlarda üretilmektedir. Bu tür maddeler metal, cam, seramik, odun, mukavva ve kağıt için giderek azalan doğal kaynaklar yüzünden alternatif malzemelerdir.

Günümüzde yeni polimerik malzemeler üretimi yerine varolan polimerlerin modifikasyonu bilimde ve endüstride önem kazanmaktadır. Bunun en önemli nedeni ekonomik oluşu ve varolan teknolojinin değerlendirilmesidir. Blok kopolimer sentezleri bu bakımdan yeni polimerik malzemelerin bilinen ticari polimerlerden üretilmelerine olanak sağlamaktadır.

İki veya daha fazla fonksiyonlu başlatıcıların blok kopolimer sentezinde kullanımı büyük bir uygulama alanı bulmaktadır. Bu tür bir teknoloji, başlatıcının aşamalı olarak bozunması prensibine dayanır. Aşamalı olarak bozunan başlatıcıların en yaygın kullanımda olanlarından biri de azo-peroksit başlatıcılardır. Bunların blok kopolimer sentezinde kullanımı sırasında her iki grubunda ısısal ve fotokimyasal aktiviteye sahip olması azo ve peroksit gruplarının aynı anda bozunmasına yol açar. Bu çalışmada bütünüyle farklı bozunma davranışına sahip fonksiyonel gruplar içeren başlatıcıların sentezi amaçlanmıştır.

Benzoin ve türevlerinin ışık etkisi altında α-bölünmesine uğrayarak serbest radikal polimerleşmesini başlattığı bilinmektedir.

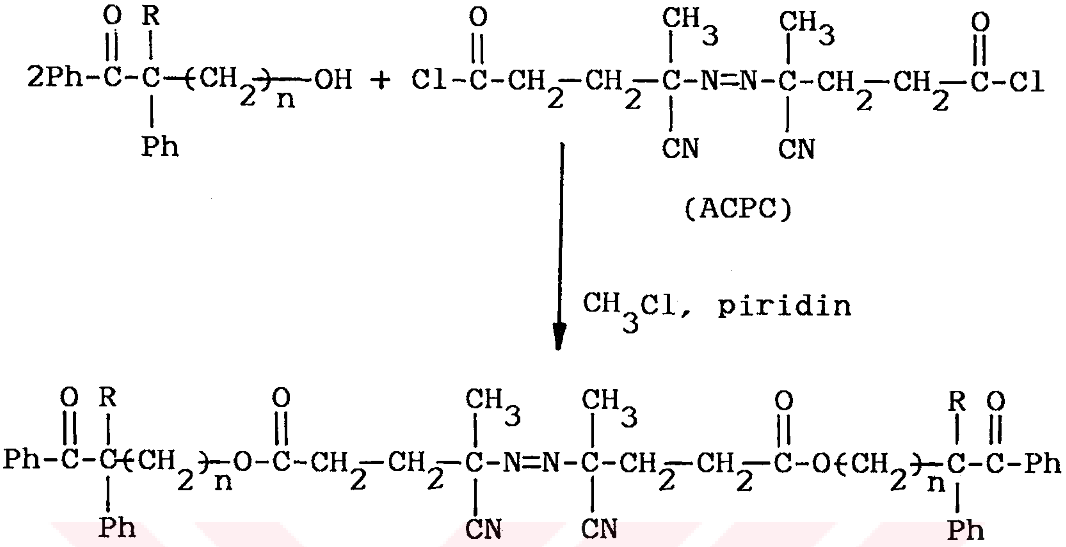


$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OR}{|}}{C}H{-}Ph} \xrightarrow{h\nu} \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}\bullet} + \mathrm{\bullet\overset{\overset{OR}{|}}{C}H{-}Ph}$$

Fotokimyasal aktif benzoin ve türevleri, polimer moleküllerinin ana ve yan zincirlerine bağlanarak blok ve graft kopolimer sentezine olanak sağlar.

Bu nedenle 4,4'-azo-bis-(4-siyanopentanoil klorür) ile benzoin ve α-metilolbenzoin metil eter'in (MBME) kondenzasyonu sonucu iki yeni azo-benzoin başlatıcısı, 4,4'-azo-bis-(4-siyanopentanoil)-bis-benzoin (ACPB) ve

4,4'-azo-bis-(4-siyanopentanoil)-bis-(α —metilolbenzoin metil eter) (ABME) sentez edilmiştir.



$$2Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{R}{C}}-(CH_2)_n-OH + Cl-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl$$

$$\xrightarrow{CH_3Cl,\ piridin} Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{R}{C}}(CH_2)_n-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O(CH_2)_n-\underset{Ph}{\overset{R}{C}}-\overset{O}{\overset{\|}{C}}-Ph$$

ACPB: R=H, n=0
ABME R= OCH_3, n=1

Bu başlatıcıların yapısı elementel analiz ve spektroskopik yöntemlerle kanıtlanmıştır. Başlatıcıların IR spektrumları karakteristik ester ve keto gruplarını göstermektedir. Ayrıca ^1H-NMR spektrumlarında ise fenil, CH_2O, OCH_3, CH_2 protonlarının varlığı görülmektedir.

Sentez edilen başlatıcıların ısısal bozunmaları DSC ile incelenmiş, bozunma hız sabitleri ve aktivasyon enerjileri hesaplanmıştır. Ayrıca bu başlatıcılar ile 60, 70, 80° C'de yapılan stiren polimerleşmesi sonucu elde edilen polimerleşme hızlarının logaritmaları - mutlak polimerleşme sıcaklıklarının tersleri diagramı (Arrhenius) çizilmiş ve elde edilen doğrunun eğiminden, polimerleşme aktivasyon enerjisi olarak ACPB için 75.89 kJ/mol, ABME için 71.63 kJ/mol değerleri hesaplanmıştır. ACPB örnek başlatıcı olarak ele alınıp, log R_p- log [M] ya da log [I] diyagramları çizilerek eğimlerinden,

$$R_p = K\,[M]^{1.13}\,[I]^{0.43}$$

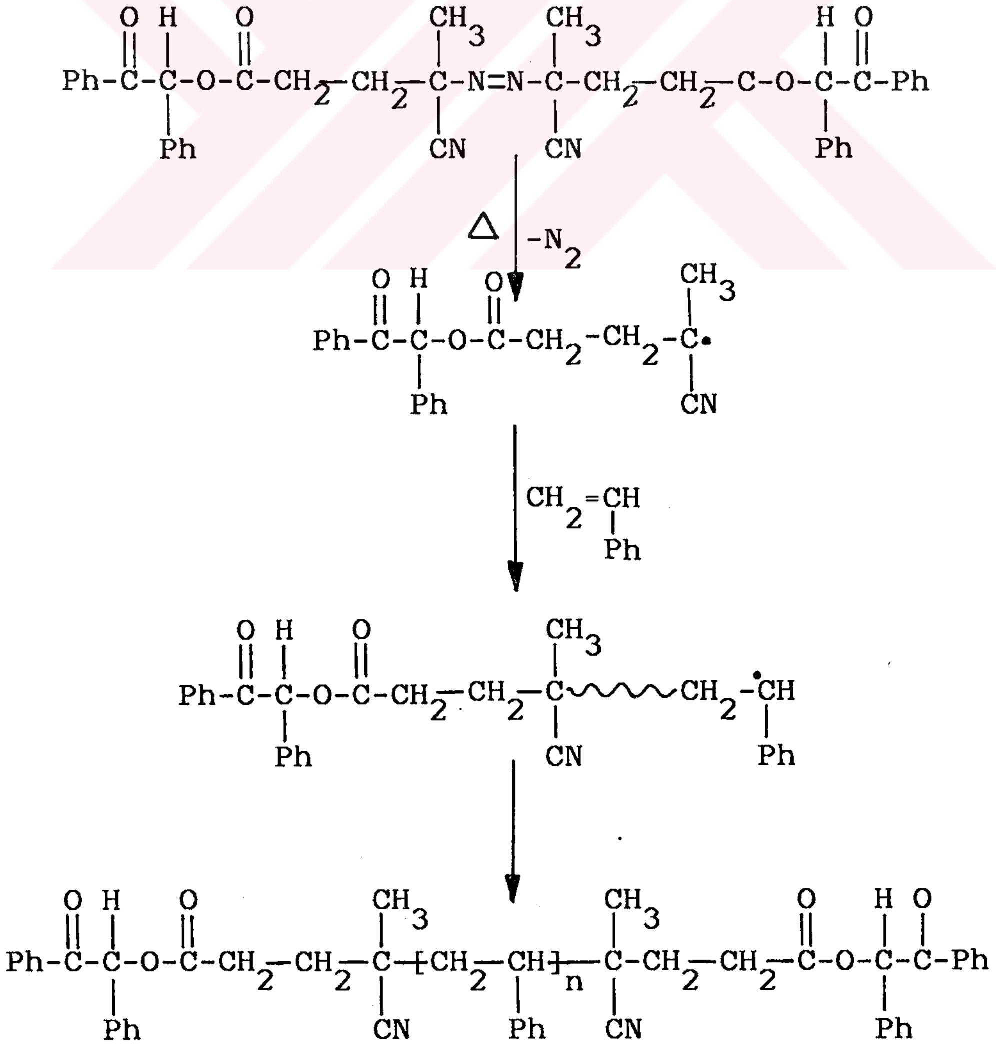
bulunmuştur.

Mayo denkleminden yararlanılarak ($1/\overline{P}_n$ — $[I]/R_p$) diyagramları çizilmiş ve bunların eğiminden fk_d değerleri bulunmuştur. $1/\overline{P}_n$ — $[I]/[M]$ diyagramlari çizilerek eğimlerinden C_I değerleri hesaplanmıştır.

Bütün kinetik veriler aşağıdaki tabloda, bilinen azo başlatıcılarla karşılaştırmalı olarak gösterilmiştir.

Azo başlatıcı	E_d (kJ/mol)	$k_d x10^5$	$fk_d x10^6$ (1/sn)	C_I
ACPB	-	-	2.44	0.416
ABME	99.77	1.92	7.36	0.906
AIBN	130	1.10	-	0.160
ACPA	108	1.33	8.16	-

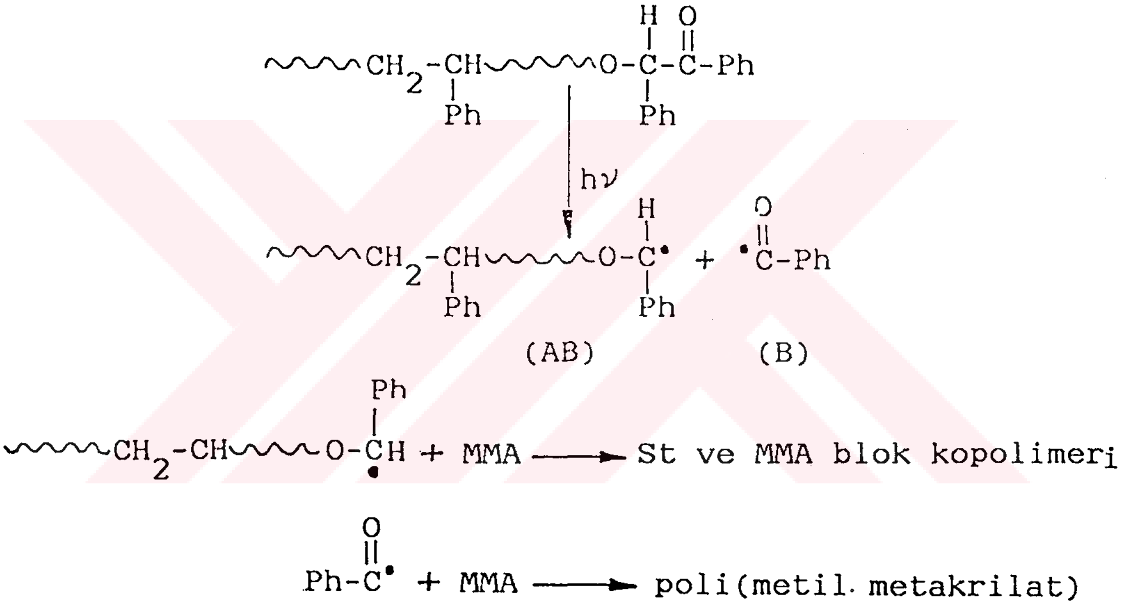
Azo-benzoin başlatıcılar kullanılarak elde edilen polimerler, sonlanma mekanizmasına bağlı olarak bir veya her iki ucunda benzoin grupları içerirler. Stiren polimerizasyonunda sonlanma aşaması başlıca birleşme mekanizması üzerinden gerçekleştiğine göre aşağıda gösterilen reaksiyonlar sonucu her iki uçta fotoaktif gruplar içeren polimerler elde edilebilir.



Bu reaksiyonlar sonucu elde edilen polistirenlerde (PSt) benzoin veya benzoin metil eter gruplarının yapıya bağlandığı deneysel olarak gösterilmiştir. Azobenzoin başlatıcılarla elde edilen polimerlerin UV spektrumları benzoin grubunun absorpladığı dalga boyunda absorpsiyona sahiptir.

Blok kopolimerleşme deneylerinde kullanilmak üzere farklı molekül ağırlığına sahip, benzoin veya benzoin metil eter uç gruplarını içeren bir seri polistiren sentez edilmiştir.

Bu prepolimerlerin UV ile ışıklandırılmaları sonucu benzoil (B) ve polimere bağlı alkoksi benzil (AB) radikalleri oluşur. Ortamda ikinci bir monomer varsa, polimerleşme koşullarına bağlı olarak bu radikallerden biri veya herikisi polimerleşmeyi başlatır.



Metil metakrilat (MMA), monomer olarak kullanıldığında her iki radikalinde (B ve AB) eşit derecede etkili olduğu bilinmektedir. Bu nedenle belirli bir oranda homopolimer oluşmaktadır. Uygun çözücü-çöktürücü sistemleri yardımıyla polimerleşme sonunda ele geçen reaksiyon karışımındaki blok kopolimer, homo-polistiren ve homo-polimetil metakrilat'dan ayrılmıştır. Jel geçirgenlik kromatografisi (GPC), refraktif indeks ve ultraviyole dedektörlerinin birlikte kullanılmasıyla polimer karakterizasyonunda güvenilir bir yöntemdir. Ayrılan homopolimerler ve blok kopolimer GPC ile karakterize edilmiştir. Homo-polimetil metakrilat, UV dedektörüne karşı duyarlı olmadığından saf blok kopolimerin UV kromatogramında gözlenen pik polistiren bloğundan kaynaklanmaktadır. Bu piklerin prepolistireninkilere kıyasla daha yüksek molekül ağırlığı bölgesinde olması blok kopolimer oluşumunun en açık kanıtıdır.

Kopolimerleşme reaksiyonlarında başlatıcı olarak kullanılan polistirenlerin molekül ağırlıkları ve konsantrasyonları reaksiyon sonunda ele geçen karışımdaki blok kopolimer oranını etkilemektedir. Bu nedenle prepolimer molekül ağırlığının etkisini incelemek için degişik molekül ağırlıklarında prepolistirenler kullanılarak bir seri deney yapılmış ve blok kopolimer oranının molekül ağırlığıyla arttığı görülmüştür. Prepolimer konsantrasyonunun etkisini incelemek için yapılan deneyler sonunda polistiren konsantrasyonu arttıkça blok kopolimer oranının arttığı gözlenmiştir.

Blok kopolimerleşme etkinliği ve oluşan kopolimerin yapısı büyük ölçüde polimerleşmenin sonlanma aşamasına bağlıdır. Ayrıca kullanılan monomerin oluşan küçük moleküllü ve polimerik radikallere olan seçiciliği blok kopolimerleşme etkinliğini belirleyici diğer bir unsurdur.

Sonuç olarak azo-benzoin başlatıcılardan yararlanarak iki aşamalı bir işlemle blok kopolimer elde etmek olasıdır. Bu tür başlatıcıların vinil polimerleşmesinde özellikle UV kaplamada toksik olmayan yapılarından dolayı kullanım alanı bulacağı açıktır ve bu yönde çalışmalar sürmektedir.

CHAPTER 1. OBJECTIVES OF THE WORK

In connection with the demand on novel materials possessing spesific physical properties research concerning the synthesis of block copolymers has recently become a widespread topic in polymer science.

Block copolymers consist of generally immiscible sequences, resulting in phase separation process which ultimately controls the colloidal and mechanical properties like surface activity, adhesion, elasticity and impact strength deserves great interest.

Another technological development focuses on polymer blends as heterophase polymeric materials [1], in which the useful properties of each polymeric partner can be combined at a very low cost to compete with block copolymers 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 processes. The synthesis of block copolymers with known composition and molecular weight by combining a large number of chemically different chains is therefore renewed challenge for polymer researchers.

Bi and polyfunctional initiators are of great interest because of their capacity to generate free radicals stepwise giving the possibility of using them in direct procedures to obtain block copolymers [2]. This process involves the sequential decomposition of the functional groups introduced in the initiator.

Benzoin and its derivatives are well known and extensively used photoinitiators which find commercial application in UV curable coatings [3]. Compared with other modes of initiation of free radical polymerization the light induced initiation has the great advantage of being applicable at low temperatures, preferably at room temperature.

For this reason, synthesis of bifunctional initiators having thermally labile azo group in the center and photochemically active benzoin or benzoin methyl ether groups at the each end of the molecule are aimed in this study. Upon heating these molecules produce free radicals without destroying the photosensitive groups, capable of initiating polymerization of vinyl monomers. The resultant polymers are expected to possess chromophoric groups which may cause subsequent polymerization of a second monomer when irradiated.

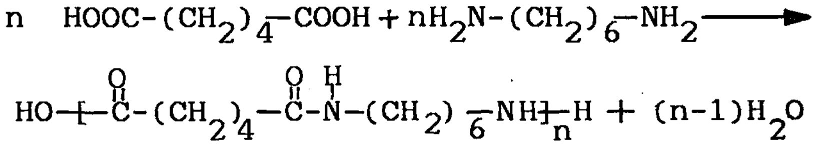
CHAPTER II. INTRODUCTION

II.1. POLYMERIZATION SYSTEMS

The classical subdivision of polymers into two main groups was made around 1929 by Carothers [4], who proposed that a distinction be made between polymers prepared by the stepwise reaction of monomers and those formed by chain reactions.

II.1.1. Condensation Polymerization

A condensation reaction that proceeds stepwise to produce a large molecule is called condensation polymerization. Whether a condensation reaction produces a polymer or a small molecule depends upon the functionality of the reactants. Functionality is the average number of reacting groups per reacting molecule. A functionality less than two produces a low molecular weight condensation product while a functionality of two ordinarily produces a linear polymer and a functionality greater than two allows branching and crosslinking. However, when one reactant is monofunctional, a low molecular weight compound invariably results regardless of the overall functionality of the system. A condensation polymerization starts by producing mainly bimolecular products; as the concentration of bimolecular products increases, further reactions, forming tri and tetramolecular products become important. This stepwise mechanism causes nearly complete conversion of original reactants to low molecular weight products early in the reaction. High polymer forms later and more slowly, because the concentration of reactive groups decreases as the length of chain increases. The reaction of diacid with diamine to yield a linear polyamide is a typical example of condensation polymerization.



$$n\ HOOC\text{-}(CH_2)_4\text{-}COOH + nH_2N\text{-}(CH_2)_6\text{-}NH_2 \longrightarrow HO\text{-}[\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{N}}\text{-}(CH_2)_6\text{-}NH]_n\text{-}H + (n-1)H_2O \qquad (2.1)$$

II.1.2. Addition Polymerization

The difunctionality necessary to form a linear macromolecule is achieved by opening the multiple bonds or strained rings. Such reactions invariably proceed by a chain reaction mechanism and resulting polymers have a repeat unit which is identical in composition to the monomer and are formed without loss of any portion of the monomer molecules. Polymerization usually begins with the addition of an initiator which is capable of producing an active species. The active species then reacts with the monomer to produce an activated molecule. Polymerization then proceeds by successive addition of further monomer molecules to the activated end of the growing chain. The addition of monomer molecules to the activated chain end will proceed until the reactive center is destroyed by chemical reaction or until the supply of monomer is exhausted.

Addition polymerization is classified into free radical and ionic polymerization according to the structure of active growing species which may be either a radical or an ion.

II.1.2.1. Free Radical Polymerization

A free radical is an atomic or molecular species whose normal bonding system has been modified such that an unpaired electron remains associated with the new structure. 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 [5].

The complete polymerization proceeds in three distinc stages: initiation, propagation, termination. At the first stage free radicals, produced by decomposition of the initiator (I), reacts with the monomer molecule (M) to produce the chain initiating species,

$$\begin{aligned} I &\xrightarrow{k_d} 2R^\bullet \\ R^\bullet + M &\xrightarrow{k_i} M_1^\bullet \end{aligned} \qquad (2.2)$$

where k_d and k_i are the rate constants of the initiator decomposition and initiation step respectively. Although the decomposition of an initiator molecule can be quantitative, chain initiation may be less than 100 percent efficient. Most initiators in typical vinyl polymerization have efficiencies between o.6 and 1.0, i.e. between 60 and 100 % of all radicals formed ultimately initiate polymerization of the chains. The major cause of low efficiencies is recombination of radical pairs before they move apart (cage effect) [6].

Propagation contains the growth of $M_1^\bullet$ by adding to another monomer and this step repeats increasing the chain by one monomer unit at a time,

$$M_n^\bullet + M \xrightarrow{k_p} M_{n+1} \qquad (2.3)$$

where k_p is the rate constant of propagation. The value of k_p is in the range of 10^2-10^4 liter/mole-sec. In theory the chain could continue to propagate until all monomer in the system had been consumed. But for the fact that free radicals are particularly reactive species and interact quickly to form inactive covalent bonds. This means that short chains are produced if the radical concentration is high, as the probability of radical interaction is correspondingly high and the radical concentration should be kept small if long chains are required.

Termination of chains can take place in several ways, but the most important termination reaction is the interaction of two active chain ends. In this case termination can take place in two ways,

1. Combination where two chain ends couple together to form one long chain.

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{tc}} M_{n+m} \qquad (2.4)$$

2. Disproportionation with hydrogen abstraction from one end to give an unsaturated group and two dead polymer chains,

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{td}} M_n + M_m \qquad (2.5)$$

where k_{tc} and k_{td} are the rate constants of termination by coupling and disproportionation respectively.

One or both processes may be active in any system depending on the monomer and polymerization conditions. Studies [7] show that polystyrene terminates predominantly by combination where as poly(methyl methacrylate) terminates entirely by disproportionation at polymerization temperatures above 60^{o}C and partly by each mechanism at lower temperatures. Typical termination rate constants are in the range of 10^{6}-10^{8} liter/mole-sec. or orders of magnitude greater than the propagation rate constants. The much greater value of k_t compared to k_p does not prevent propagation because the radical species are present in very low concentrations and the polymerization rate is dependent only the one-half power of k_t.

II.1.2.2. Kinetics of Radical Polymerization

The overall rate of polymerization as well as the length of the polymeric chains formed in addition polymerization are determined by the rates of the individual processes of initiation, propagation and termination. The overall mechanism for the conversion of monomer to polymer by use of a typical free radical initiator, I, can be described by the following set of rate equations.

$$I \xrightarrow{k_d} 2R^{\bullet}$$

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet} \qquad (2.6)$$

chain propagation,

$$RM^{\bullet} + M \xrightarrow{k_p} RMM^{\bullet}$$

$$RMM^{\bullet} + M \xrightarrow{k_p} RMMM^{\bullet} \qquad (2.7)$$

$$RM^{\bullet}_{n-1} + M \xrightarrow{k_p} RM^{\bullet}_{n}$$

if we assume that both termination reactions are kinetically equivalent we may then write a generalized equation for the rate of termination process as

$$M^{\bullet}_{n} + M^{\bullet}_{m} \xrightarrow{k_t} P \qquad (2.8)$$

In the above equations I is an initiator ; $R^{\bullet}$ is a low molecular weight radical; M is a molecule of monomer and M_n is a polymeric radical with n monomer units in the chain; k_d, k_i, k_p and k_t are the individual rate constants for the above reactions.

By making several assumptions relatively simple expressions for the rate of polymerization (R_p) and degree of polymerization ($\overline{DP}$) may be obtained.

1- The rate of formation of free radicals is equal to the rate of consumption of free radicals.

2- In the propagation step the rate constant is invariant after the initial addition reaction so rate of propagation includes only one rate constant (k_p).

3- The rate of production of chain radicals is equal to the rate of termination of chain radicals.

$$d[RM^{\bullet}_{n}]\ /dt = 0$$

4 - The rate of polymerization is equal to the rate of propagation since the number of monomer molecules consumed by initiation is small compared with the number consumed during propagation.

The rates of each step can be written as follows.

$$R_d = 2k_d[I] \qquad (2.9)$$

$$R_i = k_i[R^\bullet][M] \qquad (2.10)$$

$$R_p = k_p[M^\bullet][M] \qquad (2.11)$$

$$R_t = 2\,k_t[M^\bullet]^2 \qquad (2.12)$$

Taking into account assumption 1, R_d may set equal to R_i, so that

$$R_i = 2k_d[I]$$

and as $R_i = R_t$

$$2k_d[I] = 2k_t[M^\bullet]^2 \qquad (2.13)$$

$$[M^\bullet] = (k_d/k_t)^{1/2}\ [I]^{1/2} \qquad (2.14)$$

is obtained. By substituting the value of $[M^\bullet]$ into the equation (2.11) and considering the initiator efficiency,

$$R_p = k_p(fk_d/k_t)^{1/2}\ [I]^{1/2}[M] \qquad (2.15)$$

$$K = k_p(fk_d/k_t)^{1/2}$$

$$R_p = K\ [I]^{1/2}[M] \qquad (2.16)$$

Thus the overall rate of polymerization should be proportional to the square root of the initiator concentration and if f is independent of [M], to the first power of the monomer concentration. This is true if the initiator efficiency is high; with very low efficiency, f may be proportional to [M], making R_p proportional to $[M]^{3/2}$ [8].

These rate equations can be adapted further to indicate the effect of different reaction variables on the degree of polymerization of the polymeric products. The kinetic chain length, is the number of molecules consumed by each primary radical,

$$\nu = \frac{R_p}{R_i} = \frac{k_p[M]}{2k_t[M^{\cdot}]} \qquad (2.17)$$

substituting for $[M^{\bullet}]$ from the equation (2.14), equation (2.17) becomes

$$\nu = \frac{k_p}{2(fk_dk_t)^{\frac{1}{2}}} \; \frac{[M]}{[I]^{\frac{1}{2}}} \qquad (2.18)$$

It can be seen from equation (2.17) that the kinetic chain length is inversely proportional to the rate of initiation. The actual size of the polymer molecule depends on the mechanism of termination whereas kinetic chain length is independent of termination mechanism. Thus if termination occurs by coupling the number of monomer units in the average polymer molecule (Pn) is twice the kinetic chain length ($P_n = 2\nu$). If termination occurs by disproportionation, the degree of polymerization is equal to the kinetic chain length. In the presence of a solvent or other chain transfer agent the degree of polymerization can be arrived at by the following kinetic treatment.

$$M_x^{\bullet} + XP \longrightarrow M_xX + P^{\bullet} \qquad (2,19)$$

$$P^{\bullet} + M \longrightarrow PM^{\bullet}, \text{ etc.} \qquad (2.20)$$

where P may be monomer, initiator, solvent or other added chain transfer agent.

The degree of polymerization is therefore

$$\bar{P}_n = \frac{\text{rate of growth}}{\text{rates of all reactions leading to dead polymer}}$$

$$\bar{P}_n = \frac{R_p}{fk_d[I]+k_{tr,M}[M][M^{\bullet}]+k_{tr,s}[S][M^{\bullet}]+k_{tr,I}[I][M^{\bullet}]} \qquad (2.21)$$

this equation is true for the termination by combination, if termination is by disproportionation the first term becomes $2fk_d[I]$. If transfer constants are defined as,

$$C_M = \frac{k_{tr,M}}{k_p} \qquad C_S = \frac{k_{tr,S}}{k_p} \qquad C_I = \frac{k_{tr,I}}{k_p}$$

then,

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p^2}\,\frac{R_p}{[M]^2} + C_M + C_S\,\frac{[S]}{[M]} + C_I\,\frac{k_t}{k_p^2 fk_d}\,\frac{R_p^2}{[M]^3} \qquad (2.22)$$

The above analysis assumes that the radical formed in the transfer process is approximately as reactive as the original chain radical, otherwise retardation or inhibition results.

II.2 GENERAL PRINCIPLES OF PHOTOCHEMISTRY

All photochemical reactions occur as a result of electronically excited states which have a definite energy structure and lifetime.

The Jablonsky diagram, as shown in Figure (2.1), represents the electronic transitions involved in a molecule, following light excitations. Most molecules in their ground state possess an even number of electrons which are spin-paired, and the electrons remain spin-paired in the excited states directly populated by light absorption. However, following light absorption spin-unpairing may occur with facility, particularly in the case of aromatic ketones. The number of spin-unpaired electrons in a particular state is known as spin multiplicity. Thus, light absorption by ground state singlets produces excited state singlets which may undergo spin unpairing to yield excited state triplets. Such transformations between states of different spin-multiplicity are known as intersystem crossing.

Photochemical reactions are known to occur from both singlet and triplet excited states and generally occur from the lowest excited singlet (S_1) and triplet (T_1) states which are formed after absorption of a photon and mainly by radiationless transition intersystem crossing from the lowest excited singlet state. However, due to the short lifetimes of S_1 states, many photochemical reactions and particularly intermolecular processes occur only via the T_1 states which are longer-lived.

Consequently, population of chemically reactive state in photoinitiation may require intersystem crossing, a factor which should be taken into account with regard to the overall efficiency of photoinitiation. Aryl, alkyl ketones such as benzoin ethers and its derivatives are also known to undergo intersystem crossing with high efficiency and probably react via the T_1 state.

A second important consideration is the orbital nature of the excited states. For photoinitiator systems, the states of most interest are n,π^* and π,π^* which signify that an electron has been promoted from a non-bonding (n) or bonding (π) orbital, respectively, to an antibonding (π^*) orbital of particular importance is the orbital nature of the reactive excited state, which is generally T state. The T state of most aromatic ketones is n,π^*.

The Jablonsky diagram is shown in Figure (2.1) where,

S_0= Ground State
S_1, S_2 = Excited Singlet States
T_1, T_2 = Excited Triplet States
⟶ = Radiative process

⇝ Radiationless process
a) Light absorption
b) Singlet Decay (Radiationless)
c) Singlet Decay (Fluorescence)
d) Intersystem crossing
e) Triplet Decay (Radiationless)
f) Triplet Decay (Phosphorescence)

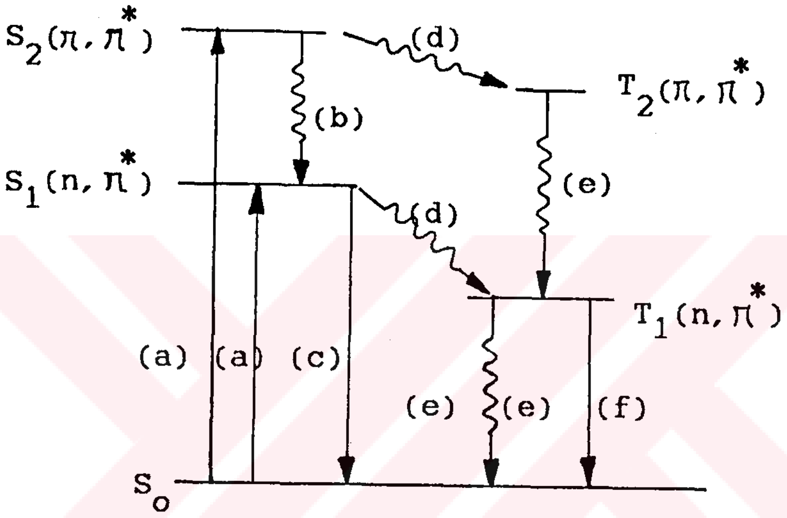


Figure 2.1. Jablonsky Diagram

II.2.1. Photochemistry of the Aromatic Carbonyl Group

Aromatic carbonyl compounds may, under appropriate circumstances, function as photosensitizers or photochemically active initiators for free radical vinyl polymerization

There are five distinct mechanisms by which a photoexcited molecule (A^*) can initiate polymerization.

1- Direct addition of A to monomer, to form a biradical or dipolar species.

$$A^* + M \longrightarrow {}^{\bullet}A\text{-}M^{\bullet} \text{ or } {}^{+}A\text{-}M^{-} \text{ or } {}^{-}A\text{-}M^{+} \qquad (2.23)$$

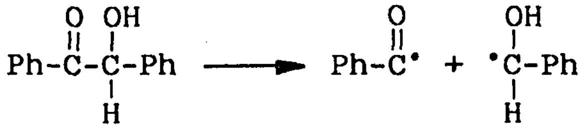
2- Energy transfer from (mainly) triplet excited states to monomer.

$$A^*(T_1) + M(S_0) \longrightarrow A(S_0) + M^*(T_1) \qquad (2.24)$$

3- Homolytic dissociation of the photoexcited molecule,

$$AB^* \longrightarrow A^\bullet + B^\bullet \qquad 2.25$$

e.g. aromatic carbonyl compounds of benzoin type [9].



$$\text{Ph-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{-Ph} \longrightarrow \text{Ph-}\overset{\overset{\displaystyle O}{\|}}{C}{}^\bullet + {}^\bullet\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\text{-Ph} \qquad (2.26)$$

4- Hydrogen abstraction by A^* from monomer or solvent.

$$A^* + {}^\bullet RH \longrightarrow {}^\bullet AH + R^\bullet \qquad (2.27)$$

5- Electron transfer between A^* and monomer, solvent etc. to produce a pair of ion radicals.

$$A^* + M^+ \longrightarrow M^+,\ A^- \ \text{or}\ M^-,\ A^+ \qquad (2.28)$$

The biradical intermediates from mechanisms 1 and 2 easily undergo cyclisation, consequently these systems are highly inefficient initiating systems. Mechanisms 3, 4 and 5 however, can be used with great efficiency to initiate free radical polymerization.

The orbitals associated with the aromatic carbonyl group are shown in Figure (2.2) .

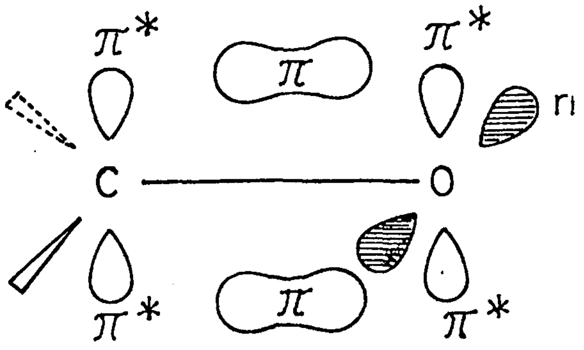


Figure 2.2: Carbonyl group orbitals

The group has electrons in non-bonding (n) orbitals associated with the oxygen atom, each n orbital containing two electrons. On excitation, one of these electrons may be promoted to either a σ^* or π^* orbital. For most molecules the ordering of the orbital energies is, $\sigma < \pi < n < \pi^* < \sigma^*$ and consequently the most readily observed transitions are $n \longrightarrow \pi^*$ transitions and $\pi \longrightarrow \pi^*$. Usually the $n \longrightarrow \pi^*$ transitions are of lower energy than the corresponding $\pi \longrightarrow \pi^*$ transitions although this order may be reversed in molecules with a high degree of conjugation i.e. where the π orbitals are of higher energy than the n orbitals.

Important differences are found both in electronic structures and chemical reactivities of (n,π^*) and (π,π^*)excited states. On looking at the orbitals of the carbonyl group it can be seen that electron density is removed from the oxygen atom on promotion of an electron from an n orbital to a π^* orbital. Therefore (n,π^*) excited states display reactivity similar to that of alkoxy radicals, e.g. in the case of hydrogen abstraction reactions conversely (π,π^*) excited states have a greater electron density on the oxygen atom and as a result the carbonyl group becomes more polar in nature.

Solvent polarity can also have a great effect on the type of transition encountered. Increasing solvent polarity causes a decrease in the energy of $\pi \longrightarrow \pi^*$ transitions and a long wavelength shift occurs due to the stabilization of the more polar excited state. For an $n \longrightarrow \pi^*$ transition increasing solvent polarity causes an increase in the energy for the transition as the n orbital is stabilised by increased hydrogen bonding or other dipolar interaction.

Consequently, for aromatic carbonyl compounds with small energy separation between their highest n and π orbitals, the lowest excited state may be (n,π^*) or (π,π^*) in character depending on solvent polarity.

Typically $n \longrightarrow \pi^*$ transitions have lower molar extinction coefficients than $\pi \longrightarrow \pi^*$ transitions. This is a consequence of the poor spatial overlap of the n and

π orbitals and this may be seen in Figure (2.2), $n \longrightarrow \pi^*$ transitions are therefore partially forbidden by the selection rules while $\pi \longrightarrow \pi^*$ transitions are allowed. Finally, another important difference between (n,π^*) and (π,π^*) states is that intersystem crossing, S_1-T_1, occurs more readily with (n,π^*) states and this is practically significant as we have seen that the triplet state is important as a photochemical intermediate due to its relatively long lifetime.

The reasons for this greater ease of triplet formation are two-fold,

1- The initial $n \longrightarrow \pi^*$ transition is partially forbidden as is the reverse process. This confers a greater lifetime on the S_1 (n,π^*) than the S_1 (π,π^*) and hence a greater probability of forming the triplet state.

2- The $S_1 \longrightarrow T_1$ conversion is easier due to the smaller energy separation between the two states. For (n,π^*) states the separation is 1500cm^{-1} but for (π,π^*) states it is 10000-15000cm^{-1}.

II.2.1.1 Carbonyl compounds whose lowest excited states are of the (n,π^*) type

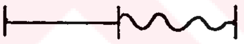
Of the readily available compounds benzophenone and its derivatives are the most important. Their high intersystem crossing efficiency and consequently their ready triplet state formation give them many uses in organic photochemistry, particularly in the role of sensitisers. They undergo reactions typical of the (n,π^*) state, e.g. hydrogen abstraction from alcohols and ethers and these have been extensively studied [10,11]. The quantum yields for photoreduction approach the maximum theoretical value of 2 but these systems have found little use as initiators for vinyl polymerization because of complicating side reactions including termination by the semipinacol radicals [12,13].

II.2.1.2. Carbonyl compounds whose lowest excited states are of the (π,π^*) type

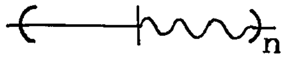
Some aromatic carbonyl compounds more highly conjugated than benzophenone have lowest excited states with (π,π^*) character. Fluorenone and its derivatives appear to belong to this class. Unlike benzophenone, aromatic carbonyl compounds with (π,π^*) T_1 states are not photoreduced by hydrogen donors such as alcohols but are readily reduced by electron donors.

II.3. BLOCK COPOLYMERS

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)- systems possessing many segments as shown below schematically.

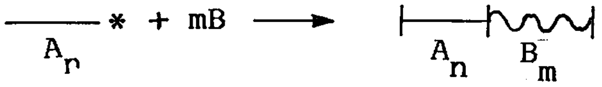
A B block copolymer,  (2.29)

A-B-A block copolymer,  (2.30)

$-(A-B)_n-$ block copolymer  (2.31)

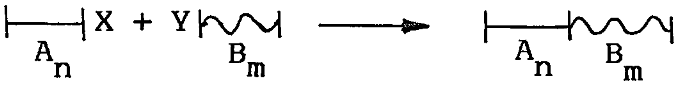
The first synthesis of block copolymers was carried out by Bolland and Melville [14] via living macro radicals in 1938. But block copolymers assumed great industrial importance after Szwarc et.al. [15] synthesized well defined block copolymers via living macroanions in 1956. The increasing importance and interest in block copolymers arises mainly from their unique properties in solution and in the solid state which are consequence of their molecular structure. In particular, sequences of different chemical composition are usually incompatible and therefore have a tendency to segregate in space.

There are two general methods for the synthesis of block copolymers. In the first, active sites on a macromolecular chain are created which then initiate the polymerization of a monomer. The polymerization may be radical, anionic or cationic and for one active site, can be represented as shown below.



(2.32)

The second method, which is usually called condensation, is the reaction between chemical functional groups present at the ends of different polymers. Schematically,



(2.33)

With difunctional species, the reactions lead to multiblock copolymers, also called segmented copolymers [16, 17,18,19].

II.3.1. Preparation of Block Copolymers by Anionic Living Polymerization

Since Szwarc et al. [20] discovered that living polymers of predictable molecular weight could be produced in an anionic pathway, major advances were reported in the mastering of this type of polymerization mechanism leading to the production of new and sometimes high performance materials. 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. Above all, living macromolecules can initiate the polymerization of other monomers to produce well-defined block copolymers. Well defined diblock, triblock and also star shaped copolymers were synthesized either to improve the knowledge of their colloidal and morphological behavior in relation to structure or to discover new sequential structures which take maximum advantage of specific capabilities of block copolymers i.e. in the surface coating area, in adhesive, biomedical and alloying applications.

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. This same characteristic also provides the best method for creating block copolymers by the sequential addition of different monomers. Among the anionic block copolymers the most interesting and important ones have been the triblock variety, of the ABA type, since these gave rise to the rapid development of a new class of materials, the "thermoplastic elastomers". The three stage process leading to ABA block copolymers can be shown schematically as below in the case seconder butyl lithium is an initiator.

$$\text{sec-BuLi} + \text{Styrene} \longrightarrow \underset{\text{Polystyryl anion}}{\text{sec-Bu}\sim\sim\sim^{-}\text{Li}^{+}} \qquad (2.34)$$

$$\text{polystyryl anion} + \text{butadiene} \longrightarrow \text{sec-Bu}\sim\sim\text{---}^{-}\text{Li}^{+} \qquad (2.35)$$

$$\text{sec-Bu}\sim\sim\text{---}^{-}\text{Li}^{+} \xrightarrow[\text{2) termination}]{\text{1) Styrene}} \text{PS}\sim\sim\text{PB}\sim\sim\text{PS} \qquad (2.36)$$

II.3.2. Preparation of Block Copolymers by Cationic Polymerization

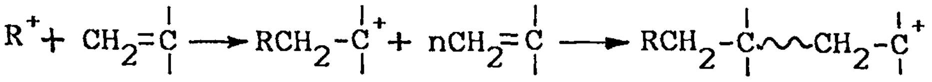
For many years, the copolymers prepared by cationic polymerization were ill-defined in structure and contamined by a large amount of homopolymers, that's why until recently block copolymerization by cationic processes was largely disregarded. The cationic polymerization of olefin and vinyl monomers was 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. However since 1960, studies [21,22,23] concentrated on cationic polymerization and in the last 10 years rapid and definite progress has been made and new concepts developed. To the conventional mechanistic sequence of cationic polymerization of olefins

Kennedy has substituted a scheme combining controlled initiation with uninterrupted propagation followed by controlled termination [22].

Ion generation:

$$RX + MeX_n \rightleftharpoons R^+MeX^-_{n+1} \qquad (2.37)$$

Cationation and propagation:



$$R^+ + CH_2{=}\overset{|}{\underset{|}{C}} \longrightarrow RCH_2{-}\overset{|}{\underset{|}{C}}{}^+ + nCH_2{=}\overset{|}{\underset{|}{C}} \longrightarrow RCH_2{-}\overset{|}{\underset{|}{C}}{\sim\sim}CH_2{-}\overset{|}{\underset{|}{C}}{}^+ \qquad (2.38)$$

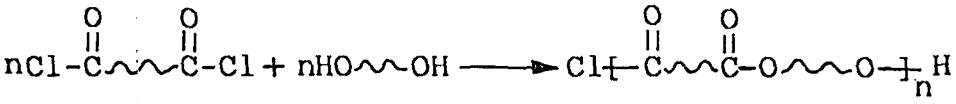
Termination:

$$RCH_2{\sim\sim}\overset{|}{\underset{|}{C}}{\sim\sim}CH_2{-}\overset{|}{\underset{|}{C}}{}^+MeX^-_{n+1} \longrightarrow RCH_2{-}\overset{|}{\underset{|}{C}}{\sim\sim}CH_2{-}\overset{|}{\underset{|}{C}}X + MeX_n \qquad (2.39)$$

The disadvantages of the usual chain transfer to monomer were overcome by the inifer concept [22,24]. It involves controlled initiation as well as chain transfer using special functional initiating and transfer agents (inifers) which may be mono, bi, tri or multi functional species.

II.3.3. Preparation of Block Copolymers by Step-Growth Polymerization

The synthesis of block copolymers by step growth processes has been extensively discussed in recent years. The step growth block copolymers consist of low molecular weight sequences, usually arranged in a -(A-B)- configuration, nevertheless A-B-A structures can also be generated. In this type of block copolymer, sequences having low solubility parameter are generally associated with highly polar sequences (polyester, polyamide, polycarbonate, polyurethane), the strong interaction of which are responsible for phase separation even though the block molecular weights are limited to a few thousands. Step growth polymerizations give block copolymers having sequences with predictable molecular weight, and a pure reaction medium is not necessary for block copolymerization. As a typical example we can consider esterification of acid chlorides with alcohols. For this poly(oxyethylene), polystyrene or polybutadiene with dicarboxylic acid chloride terminal groups are mainly reacted with polyethers, aromatic or aliphatic polyesters with hydroxyl terminal groups and hydroxyl terminated polystyrene [25,26,27,28].



$$nCl-\overset{O}{\overset{\parallel}{C}}\sim\sim\overset{O}{\overset{\parallel}{C}}-Cl + nHO\sim\sim OH \longrightarrow Cl\left[-\overset{O}{\overset{\parallel}{C}}\sim\sim\overset{O}{\overset{\parallel}{C}}-O\sim\sim O-\right]_n H \qquad (2.40)$$

II.3.4. Preparation of Block Copolymers by 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 [29]. To prepare block copolymers, the catalyst must have a lifetime sufficient to permit sequenching 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 homo polymers and block copolymer. In spite of their great interest for homopolymerization and random copolymerization the application of these catalysts in block copolymerization is difficult and gives disappointing results. The explanation is to be found in the too short active lifetime of the growing chains. The most important olefins polymerized using Ziegler-Natta catalysts are ethylene and propylene [30].

II.3.5. Preparation of Block Copolymers by Coupling Reactions

In the synthesis of block copolymers, a combination of polymerization types has been used successfully. This route involves the coupling of polymer anion, the coupling of polymer cation and coupling reactions of polymer anion to polymer cation. An example for coupling reactions of polymer anions is conversion of polystyryl anion to polystyrene having carboxyl terminated groups by coupling with CO_2. Carboxylate terminated polystyrene can be used in the block copolymer synthesis via step growth polymerization [31,32].

II.3.6. Preparation of Block Copolymers by Radical Polymerization

The free radical mechanism has been very early evidenced as a typical chain process by which unsaturated monomers are converted to polymers of high molecular weight [33]. The initiation of radical polymerizations, various transfer, as well as termination reactions all lead to a variety of products and the make-up of the mixture can only be slightly influenced by varying the reaction conditions or the monomer concentration, the initiator or the solvent. Furthermore, radical block copolymerization leads inevitably to more or less homopolymer so that the products require careful separation before the block copolymer can be characterized. Nevertheless the synthesis of block copolymers via radical mechanism has several important advantages:

1- Almost all monomers can be polymerized radically and thus a wide choice of monomer combinations are available

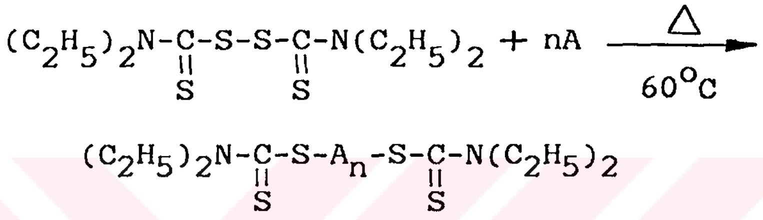
2- Radical polymerizations are considerably less sensitive to impurities than are ionic techniques.

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.

II.3.6.1 Active End Groups

Initiator end groups can be fixed to a polymer. Thus polystyrene-block-poly(oxyethylene glycol)-block-polystyrene can be obtained by capping the hydroxyl groups of the poly(oxyethylene glycol) with a percarbonate, which upon heating generates radicals able to initiate styrene polymerization [34].

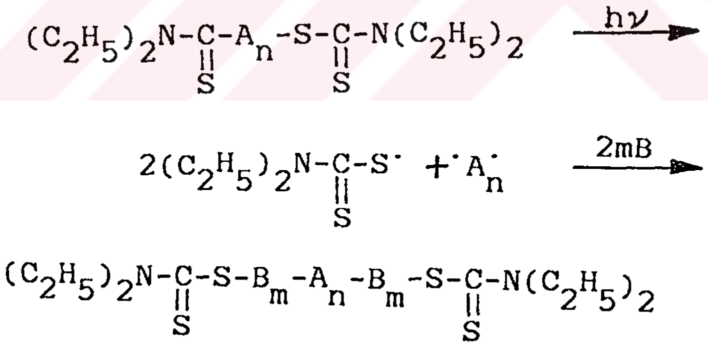
One approach involving active end groups uses iniferters defined as initiator transfer agents (inifers) and initiator terminators (initers) [35,36]. Thus by using tetraethylthiuram disulfide as a thermal initiator, α, w- bifunctional oligomers are obtained according to the scheme



$$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2 + nA \xrightarrow[60^oC]{\Delta}$$

$$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S-A_n-S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2 \qquad (2.41)$$

The S-A bond is photolabile. In the second step these oligomers are photolysed in the presence of a second monomer.



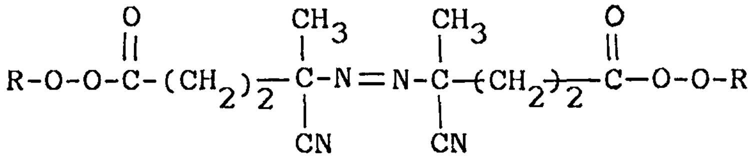
$$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-A_n-S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2 \xrightarrow{h\nu}$$

$$2(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S^{\cdot} + {}^{\cdot}A_n^{\cdot} \xrightarrow{2mB}$$

$$(C_2H_5)_2N-\underset{\underset{S}{\|}}{C}-S-B_m-A_n-B_m-S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2 \qquad (2.42)$$

chain propagation of monomer B occurs only on the macroradical, where as the microradical terminates the chain.

Another technique to generate functionalized precursor prepolymer is to use radical initiators which at least has two different initiating groups. These groups can be of different types, e.g. peroxide and azo, or of the same type, but with different rates of decomposition. For example initiators containing azo and peroxide functions of general formula



$$R\text{-}O\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}N{=}N\text{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}(CH_2)_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}R \qquad (2.43)$$

where R=t–butyl [37,38], benzoyl [39] p-nitrobenzoyl or m-chloro benzoyl [40] have been used to synthesize block copolymers containing methyl methacrylate.

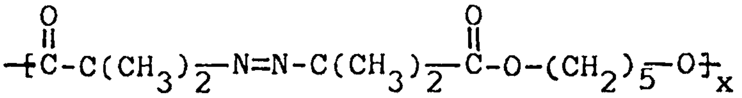
The use of polymers with end groups that can be converted into radicals by organometallic compounds is another effective approach. Manganese and rhenium carbonyls with additives like tetrafluoroethylene have been used to prepare a functionalized polymethacrylate by photopolymerization in a first step [41]. Then the polymerization of acrylonitrile is thermally initiated according to the scheme below.

$$nA + \tfrac{1}{2}Mn_2(CO)_{10} + CF_2{=}CF_2 \longrightarrow A_n\text{—}CF_2\text{—}CF_2\text{—}Mn(CO)_5 \longrightarrow$$

$$\longrightarrow A_n\text{—}CF_2\text{—}CF_2^{\bullet} \xrightarrow{mB} A_n\text{—}CF_2\text{—}CF_2\text{—}B_m \qquad (2.44)$$

II.3.6.2. Polyinitiators

Polyinitiators, eg, polyazo derivatives, in which the initiating groups are in the chain rather than the end groups, can be used for the synthesis of block copolymers. The general formula of such initiators is $\text{-}\!\!(R\text{-}N{=}N\text{-}R\text{-}N{=}N)_x$, where R may be of low molecular weight, or a precursor sequence of the block copolymer. A typical example of a polyinitiator where R is small is the following polyazoester [42].

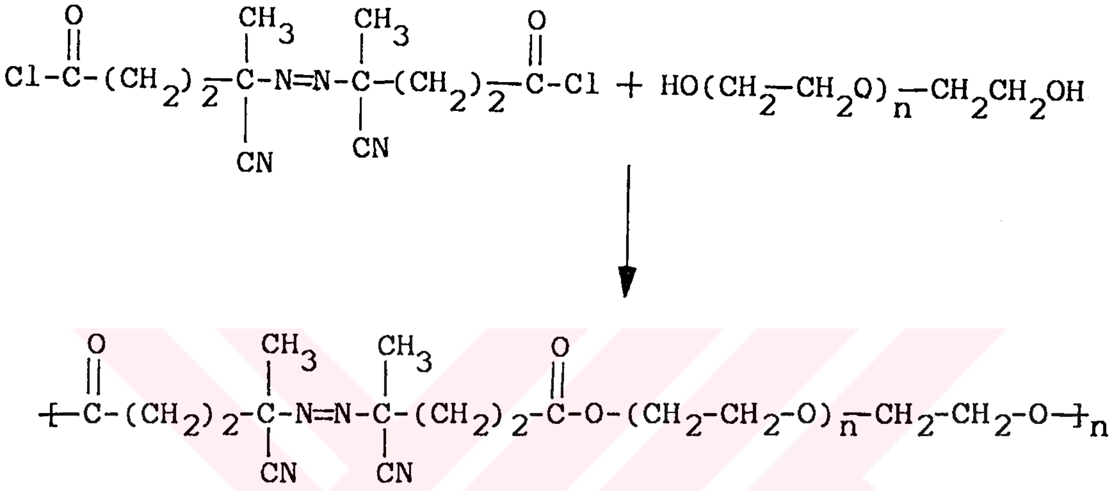


$$\text{-}\!\!\left(\overset{\overset{O}{\|}}{C}\text{-}C(CH_3)_2\text{-}N{=}N\text{-}C(CH_3)_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}(CH_2)_5\text{-}O\right)_x \qquad (2.45)$$

This reacts with a monomer in a first step by partial decomposition according to the scheme

$$\text{-}\!\!(R\text{-}N{=}N\text{-}R\text{-}N{=}N)\text{-} \xrightarrow[-N_2]{\Delta} \text{-}R\text{-}N{=}N\text{-}R^{\bullet} \xrightarrow{nA} \text{-}R\text{-}N{=}N\text{-}R\text{-}A_n \qquad (2.46)$$

The decomposition of the remaining azo groups of this prepolymer in the presence of a second monomer leads to block copolymers. An example of a polyinitiator in which R is a polymeric one obtained by capping hydroxyl terminated poly(ethyleneoxide) with 4,4'azo-bis(4-cyanovaleryl chloride) according to the following scheme



$$\mathrm{Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-Cl} + \mathrm{HO(CH_2-CH_2O)_n-CH_2CH_2OH}$$

$$\downarrow$$

$$\left[\mathrm{\overset{O}{\overset{\|}{C}}-(CH_2)_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2-CH_2-O)_n-CH_2-CH_2-O}\right]_n$$

II.3.6.3. Photolysis and Mechanical Degradation of Polymers

When polymer chains are broken by the application of large stresses, macroradicals are produced and can be used in block copolymer synthesis. These mechanical processes include high speed stirring and ultrasonic waves to produce macroradicals.

Block copolymers can also be prepared photochemically by copolymerizing vinyl monomers with partially substituted N-nitroso peptide chains [43]. These polymers are unstable under UV light and generate azo groups in the chain which photochemically initiate the polymerization of monomers. Photochemical preparation of block copolymers will be discussed in more detail as an individual section.

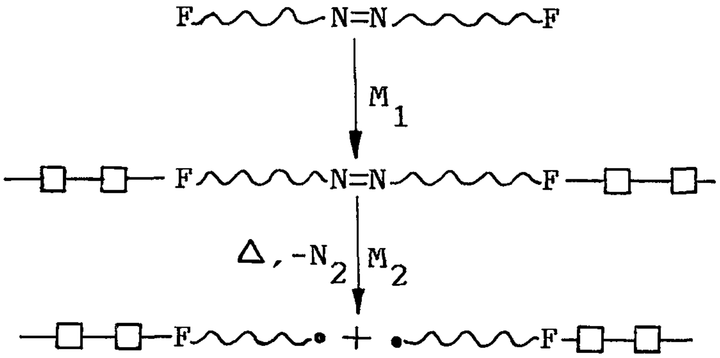
II.3.6.4. Living Radicals

The preparation of block copolymers using living radicals is based on the fact that some polymers are in soluble in their monomers and occluded macroradicals are produced when they are polymerized in bulk or in a poor solvent. For example the macroradical occlusion phenomenon was also reported during photopolymerization of methyl methacrylate in a hydroalcoholic medium [44]. The encagement of macroradicals was favoured by high solution viscosity, where as their ability to initiate a postpolymerization was depending on the medium fluidity controlling the monomer diffusion. The postpolymerization of these polymers proves the existence of encaged radicals able to react with acrylonitrile to form a block copolymer.

The methods of block copolymer synthesis via free radical mechanism provide a great variety of block copolymers because of the large number of monomers that can be polymerized by free radical mechanisms and are especially useful for polar monomers that can not be polymerized by anionic mechanisms. However this methods result in products that are generally polydisperse in molecular weight, composition and structure and include significant percentage of homopolymers.

II.4. THE USE OF AZO COMPOUNDS IN THE SYNTHESIS OF BLOCK COPOLYMERS

Bi- and polyfunctional initiators are of great interest because of their broad application in the synthesis of block copolymers. This process involves sequential decomposition of the functional groups introduced in the initiator. The first stage is the formation of a macromolecular initiator which is capable of forming block copolymers in the presence of a second monomer. A general scheme of this mechanism can be shown as below, where F represents a functional group, M_1 represents a monomer polymerized by means of functional groups, M_2 represents a monomer polymerized by decomposition of an azo group.



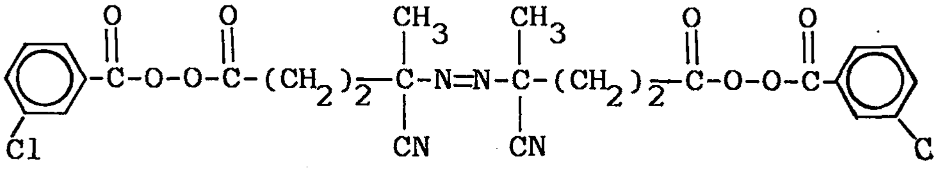
(2.48)

A different sequence of the same procedure may also be employed where decomposition of the azo group takes place in the first stage.

One of the recent studies [45] on this subject is based on the use of a bifunctional low molar mass initiator containing two chromophoric groups, namely azo and peroxide groups, that differ in optical activity.

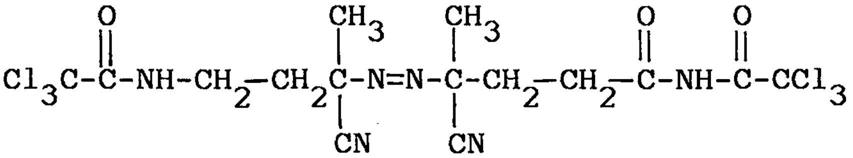
$$R\text{-}O\text{-}O\text{-}X\text{-}N{=}N\text{-}X\text{-}O\text{-}O\text{-}R \qquad (2.49)$$

The most effective usage of these initiators was made by photolysis of azo groups in the presence of monomer A and a subsequent thermal decomposition of the peroxidic groups in the presence of a monomer B. The synthesis of 4,4'-azo-bis-(4-cyanovaleryl)-bis-(m-chlorobenzoyl)diperoxide initiator was reported [45,46].



(2.50)

Another bifunctional initiator, used in the same manner as above mentioned one i.e. in the photochemical to thermal radical transformation polymerizations was reported by Yagci et all [47].



$$Cl_3C-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N{=}N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{O}{\|}}{C}-CCl_3 \qquad (2.51)$$

4,4'-azo-bis-(4-cyanopentane-trichloroacetylamide)

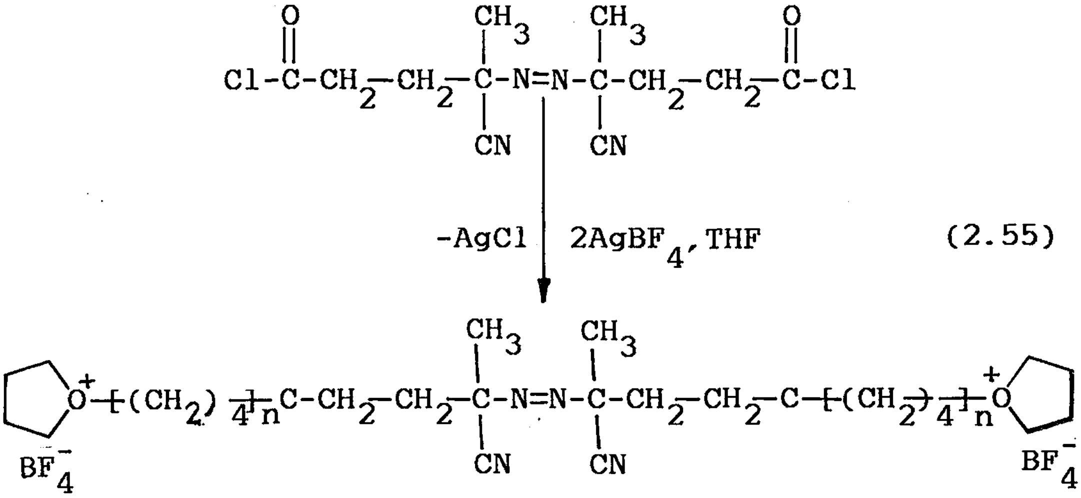
When this initiator is heated in the presence of monomer A, polymer containing terminal CCl_3 groups of the structure is formed. With the aid of this polymer, block copolymers can be obtained by applying a method proposed by Bamford [48].

$$Mn_2(CO)_{10} + h\nu \longrightarrow 2Mn(CO)_5 \qquad (2.52)$$

$$A_n{-}CCl_3 + Mn(CO)_5 \longrightarrow A_n{-}{}^{\bullet}CCl_2 + Mn(CO)_5{-}Cl \qquad (2.53)$$

$$A_n{-}{}^{\bullet}CCl_2 + mB \longrightarrow A_n{-}CCl_2{-}B_m \qquad (2.54)$$

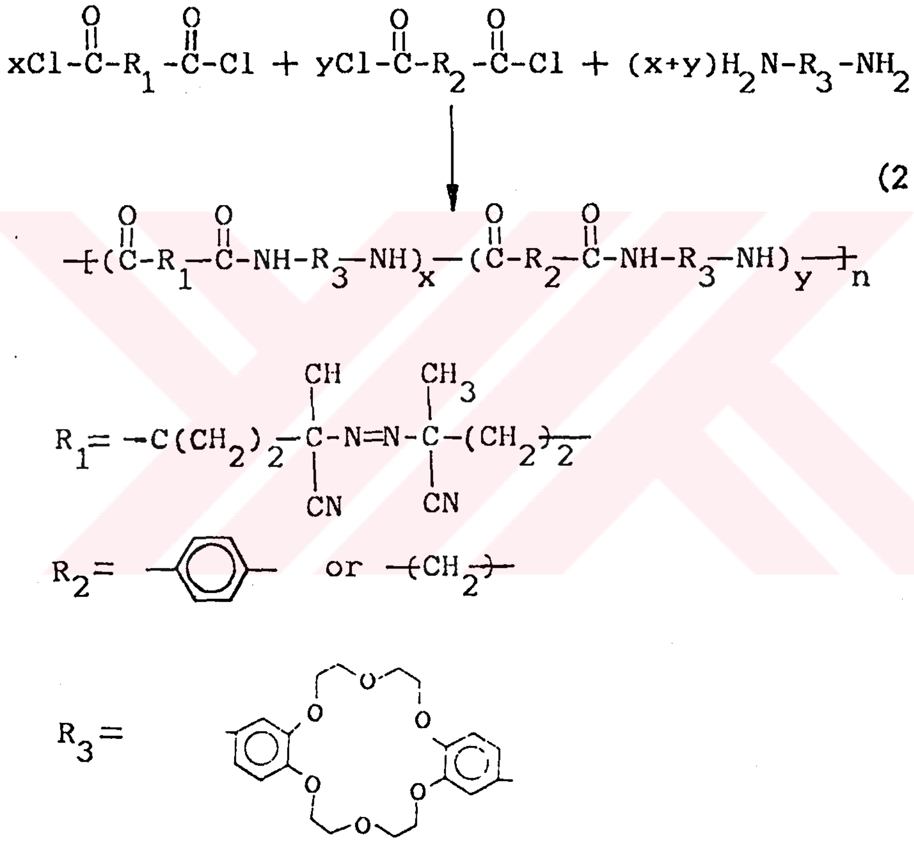
Recently a new conceptual approach to prepare block copolymers by cation to radical and reverse transformation polymerization is presented [49,50,51,52]. First synthesis of tetrahydrofuran containing one azo linkage in the main chain by use of a difunctional azo-oxocarbenium initiator is achieved.



(2.55)

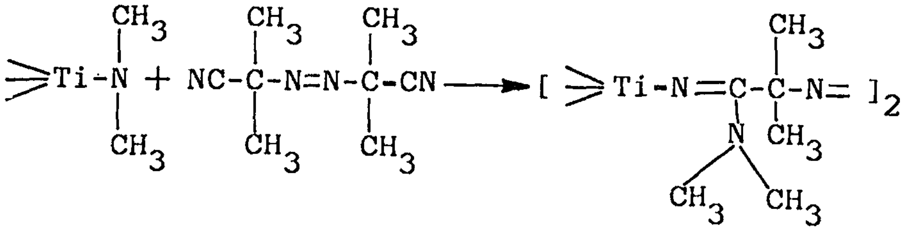
and then thermal decomposition of the azo linkage produces two polymeric radicals per chain which gives rise to the formation of block copolymers in the presence of a new monomer.

Macroazonitriles [53,54,55] containing crown ether moieties and various amounts of -N=N- units in the main chain were prepared by solution polycondensation between cis-diamino dibenzo-18-crown-6 (DADC) and adipoyl chloride (AC) or terephtaloyl chloride (TPC) with the addition of 4,4'-azo-bis(4-cyanopentanoyl chloride) (ACPC).



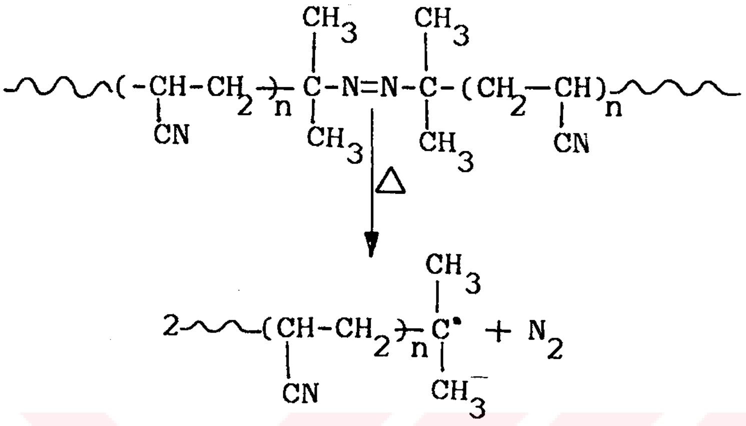
(2.56)

Polyacrylonitrile containing azo linkage in the main chain was achieved by anionic insertion polymerization [56].



(2.57)

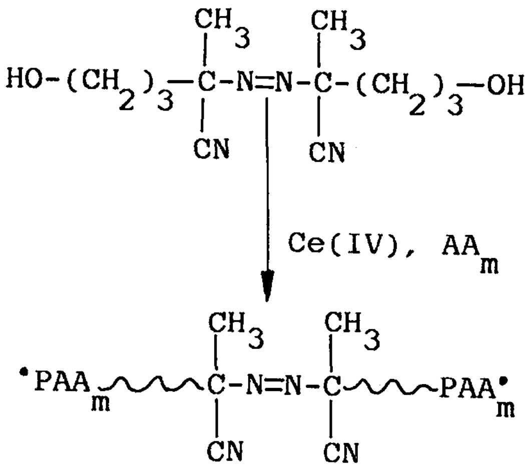
The polymerization of acrylonitrile initiated by preformed adduct leads to a polymer with -N=N- groups in the main chain. Polyacrylonitrile functionalized in this way will decompose on heating and forms two radicals in a similar way to AIBN.



$$\sim\!(\text{-CH(CN)-CH}_2\text{-})_n\text{-C(CH}_3)_2\text{-N=N-C(CH}_3)_2\text{-(CH}_2\text{-CH(CN))}_n\!\sim \xrightarrow{\Delta} 2\sim\!(\text{CH(CN)-CH}_2)_n\text{-C}^{\bullet}(\text{CH}_3)_2 + \text{N}_2$$

(2.58)

Redox polymerization systems also has great importance for the synthesis of block copolymers. The advantage of being applicable at low temperatures, azo containing prepolymers can be obtained at the first stage. Recently [57] the polymerization of acrylamide was carried out by a redox system consisting of ceric ions and an azo initiator having alcoholic hydroxyl groups according to the following reactions.



$$\text{HO-(CH}_2)_3\text{-C(CH}_3)(\text{CN})\text{-N=N-C(CH}_3)(\text{CN})\text{-(CH}_2)_3\text{-OH} \xrightarrow{\text{Ce(IV), AA}_m} {}^{\bullet}\text{PAA}_m\!\sim\!\text{C(CH}_3)(\text{CN})\text{-N=N-C(CH}_3)(\text{CN})\!\sim\!\text{PAA}_m^{\bullet}$$

(2.59)

Polyacrylamide (PAA_m) functionalized in this way will decompose on heating and forms radicals in a similar way to the low molar mass azo initiators.

II.5. PHOTOCHEMICAL SYNTHESIS OF BLOCK COPOLYMERS

If a molecule absorps electromagnetic radiation in the visible and UV region, its energy is momentarly increased and the molecule is said to be in an excited state. This energy rich molecule can either dissociate into reactive free radicals or dissipate its energy by fluorescence, phosphorescence or collisional deactivation. For a polymer former process can lead to a formation of free radical sites on the polymer backbone which can be used to initiate block or graft copolymerization. If none of the bonds in the polymer are ruptured by the radiation, the process can be promoted by the addition of photosensitizers. Upon absorption of UV or visible energy, a photosensitizer itself can decompose into active radicals or transfer its energy to other molecules in the system, thereby promoting the copolymerization reaction. Compared with other modes of initiation of free radical polymerization the light induced initiation has the great advantage of being applicable at low temperatures, preferably at room temperature. Moreover, because of the selective absorptivity of certain groups (chromophores) it is possible to produce reactive sites at definite positions of the macromolecule.

There are generally, two quite different photochemical methods for the preparation of block copolymers, both of them starting with a homopolymer A_n, containing n repeating units of type A per macromolecule.

1- Addition of monomer B to A_n. In this case, the polymer A_n is activated by UV light, where by the polymerization of B is initiated. The site of activation can be either located in the chain or at the chain end. The mechanism is shown schematically as below for the case the site of activation is in the chain.

$$-\!(A)_{n}\!-X\text{-}Y\!-\!(A)_{n'} \xrightarrow{h\nu} -\!(A)_{n}\!-X^{\bullet} + {}^{\bullet}Y\!-\!(A)_{n'}\!- \qquad (2.60)$$

$$-\!(A)_{n}\!-X^{\bullet} + mB \longrightarrow -\!(A)_{n}\!-X\!\sim\!\sim\!(B)_{m}\!-\!-^{\bullet} \qquad (2.61)$$

$$-(A)_{n'}-Y^{\bullet} + mB \longrightarrow -(A)_{n'}-Y\sim\sim(B)_{n}-\bullet \qquad (2.62)$$

$$2(A)_n\text{-}X\sim\sim(B)_m-\bullet- \begin{cases} \longrightarrow (A)_n\text{-}X\sim\sim(B)_m\sim\sim(B)_m\sim\sim X(A)_n & (2.63)\\ \qquad \text{Combination} & \\ \longrightarrow 2(A)_n\text{-}X\sim\sim(B)_m- & (2.64)\\ \qquad \text{Disproportionation} & \end{cases}$$

$$2(A)_{n'}-Y\sim\sim(B)_m\bullet- \begin{cases} \longrightarrow (A)_{n'}-Y\sim\sim(B)_m\sim\sim(B)_m\sim\sim Y-(A)_{n'} & (2.65)\\ \qquad \text{Combination} & \\ \longrightarrow 2(A)_{n'}\text{-}Y\sim\sim(B)_m & (2.66)\\ \qquad \text{Disproportionation} & \end{cases}$$

Schematical representation of the copolymerization reactions as in the case the site of activation is at the chain end,

$$-(A)_n\text{-}X\text{-}Y \xrightarrow{h\nu} -(A)_n X^{\bullet} + {}^{\bullet}Y \qquad (2.67)$$

$$-(A)_n\text{-}X^{\bullet} + mB \longrightarrow -(A)_n\text{-}X\sim\sim(B)_m-\bullet \qquad (2.68)$$

$$2(A)_n X\sim\sim(B)_m-\bullet- \begin{cases} \longrightarrow (A)_n\text{-}X\sim\sim(B)_m\sim\sim(B)_m\sim\sim X(A)_n & (2.69)\\ \qquad \text{Combination} & \\ \longrightarrow 2(A)_n X\sim\sim(B)_m & (2.70)\\ \qquad \text{Disproportionation} & \end{cases}$$

$$Y^{\bullet} + mB \longrightarrow Y\text{-}(B)_{m}^{\bullet} \qquad (2.71)$$

$$2Y\text{-}(B)_{m}^{\bullet} \begin{cases} \longrightarrow Y(B)_{m}\sim\sim\sim(B)_{m}\text{-}Y & (2.72) \\ \quad \text{Combination} & \\ \longrightarrow 2Y\text{-}(B)_{m}\text{-} & (2.73) \\ \quad \text{Disproportionation} & \end{cases}$$

Notably homopolymerization of B can be initiated in the second case as is indicated by reactions (2.71) and (2.73) if radical Y is reactive towards monomer B, which applies to many systems. Consequently, the resulting product is a mixture of block and homopolymer. If the fragment macroradicals generated by reactions (2.60) and (2.67) are deactivated by hydrogen abstraction such as by the following reaction

$$\text{-}(A)_{n}\text{-}X^{\bullet} + RH \longrightarrow \text{-}(A)_{n}\text{-}XH + R^{\bullet} \qquad (2.74)$$

blocking of B onto $\text{-}(A)_{n}$ will be prevented. Moreover, homopolymerization of B might be initiated by $R^{\bullet}$.

These considerations shed light upon an important problem connected with the synthesis of block copolymers via free radical mechanisms. Actually it is very difficult to prevent homopolymerization in this case.

Regarding the chemical nature of the final product it must be pointed out that in free radical polymerization chain termination can occur either by combination or by disproportionation, as also indicated in the above reaction schemes combination results in a three block structure. If both modes of termination reactions are likely to occur the final product will be inhomogeneous regarding its chemical composition.

2- Homopolymer A_n is coupled photochemically with homopolymer B_m. In this case, photoreactive groups must be located at one chain end of each of the polymers.

These groups must be capable of combining chemically upon absorption of a photon.

$$-(A)_n-X \xrightarrow{h\nu} -(A)_n-X^*$$

then two routes are possible, in the first one the end groups of both homopolymers are chemically identical,

$$-(A)_n-X^* + X-(B)_m \longrightarrow -(A)_n-X-X-(B)_m \tag{2.75}$$

$$-(A)_n-X^* + X-(A)_n \longrightarrow -(A)_n-X-X-(A)_n \tag{2.76}$$

in the second case, the end groups of the two homopolymers are of different nature.

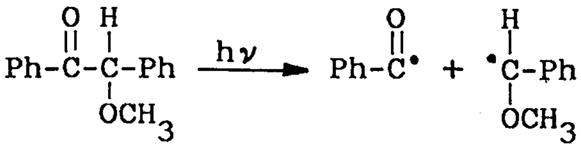
$$-(A)_n-X^* + Y-(B)_m \longrightarrow -(A)_n-X-Y-(B)_m \tag{2.77}$$

Regarding the first case, it is to be noted that, quite frequently reaction (2.75) will compete with reaction (2.76). Therefore the final product will contain in addition to the non-reacted macromolecules, chains of the structures,

$$-(A)_n-X-X-(A)_n \quad \text{and} \quad -(A)_n-X-X-(B)_m$$

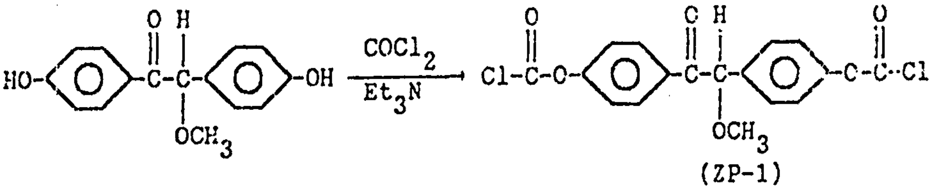
when polymeric initiators having photolabile groups in the main chain are used in the block copolymerization the availability of this method depends greatly on the availability of synthetic procedures appropriate to incorporate photolabile groups into the main chain of polymer. Polymers containing carbonyl groups, keto-oxime ester group, benzoin methyl ether groups, N-nitroso groups,disulfide groups can be used for this purpose.

It is already known that benzoin methyl ether undergoes photofragmentation [9,58] upon UV irradiation.

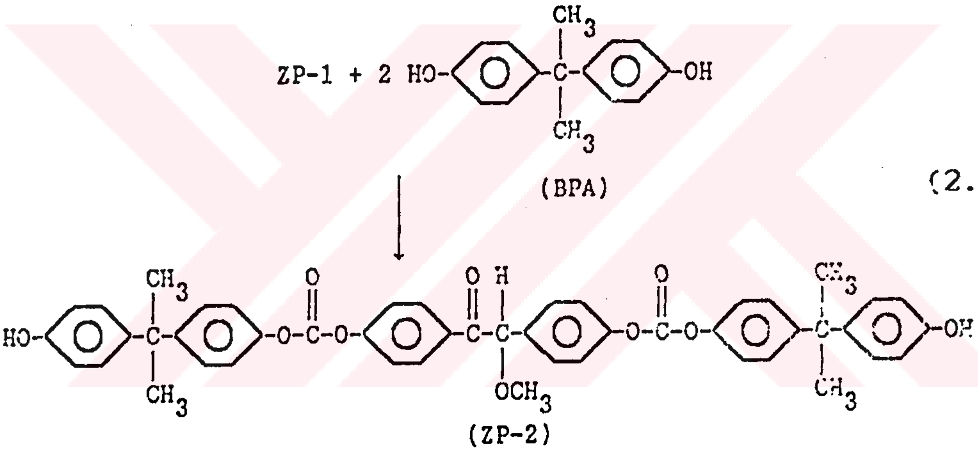


$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle OCH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}Ph} \xrightarrow{h\nu} \mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}^{\bullet}} + \mathrm{{}^{\bullet}\underset{\underset{\displaystyle OCH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}Ph} \qquad (2.78)$$

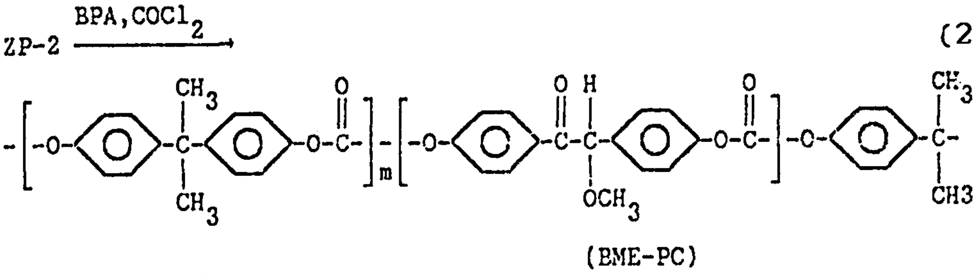
Smets [59] incorporated benzoin methyl ether groups into polycarbonate by performing the polycondensation of bisphenol A with phosgene in the presence of 6,6'-dihydroxy benzoin methyl ether as illustrated by reactions below.



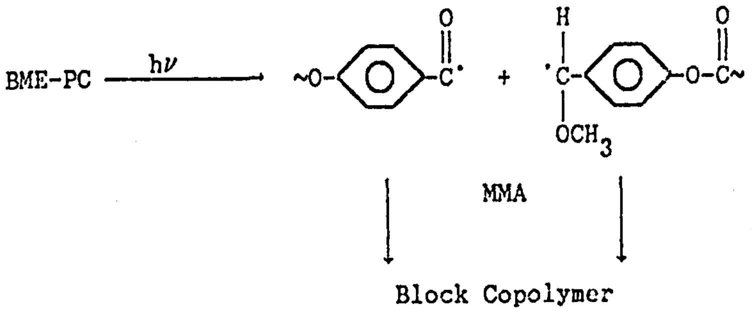
(2.79)



(2.80)



(2.81)

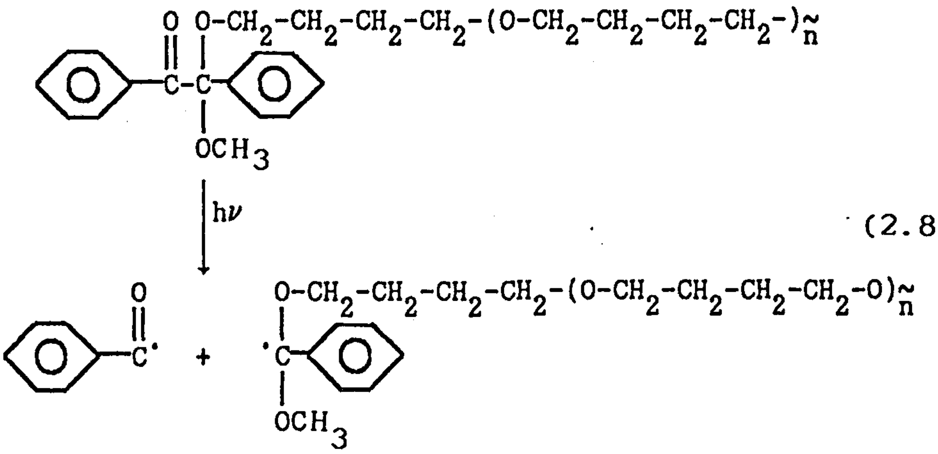


(2.82)

(2.83)

When photolabile groups are incorporated at the chain ends of polymeric initiators the photolysis of terminal groups leads to pairs of radicals, one of which is low molar mass. If the latter is capable of initiating the polymerization of the monomer, homopolymer is to be formed simultaneously with block copolymer. If metal carbonyls are photochemically reacted with halogen containing polymers, homopolymerization is avoided. Polymers having halogen containing end groups, polymers having amine end groups, iniferter systems and polymers having terminal benzoin methyl ether groups are reported for the purpose of preparing block copolymers up to date.

One of recent studies involves the preparation of polytetrahydrofuran containing benzoin methyl ether end groups. When cationic polymerization of THF is performed in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) degradative chain transfer occurs and both polytetrahydrofuran with and without photoreactive end groups is formed [60]. UV irradiation of the polymer formed according to the reaction below resulted in generation of a pair of radicals.



(2.84)

Both radicals are capable of initiating the polymerization of olefinic monomers such as styrene and methyl methacrylate[60]. By this means a mixture of homopolymer and block copolymer is produced.

CHAPTER III. EXPERIMENTAL

III.1. PURIFICATION OF MATERIALS

Benzene (Merck)

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

n-Hexane (Merck)

Treated with small portions of conc. H_2SO_4 until the acid layer remains colorless, then washed with water, aq. 10 % Na_2CO_3, water and dried with $CaCl_2$ and distilled over sodium wire (68.7°C/760 mm Hg).

Dichloromethane (Merck)

Shaken with portions of conc. H_2SO_4, then washed with water, aq. 5 % Na_2CO_3, then water again. Predried with $CaCl_2$ and distilled over P_2O_5 (40°C/760 mm Hg).

Chloroform (Merck)

Can be shaken with several portions of conc. H_2SO_4, washed throughly with water, and dried with $CaCl_2$ before filtering and distilling (61°C/760 mm Hg).

Dimethyl sulphoxide (Merck)

Dried with CaH_2 and fractionally distilled under reduced pressure (75.6-75.8°C/12 mm Hg).

Tetrahydrofuran (Merck)

Refluxed over KOH to remove the peroxides. Then distilled over sodium wire (66.5^{o}C/760 mm Hg).

Styrene (Petkim)

Washed with aq. 5 % NaCH to remove inhibitors, then with water, dried with $CaCl_2$ and distilled under reduced pressure (50^{o}C/25 mm Hg). Middle fraction is collected and immediately used.

Methyl methacrylate

Washed twice with aq. 5 % NaOH to remove inhibitors and twice with water. Dried with $CaCl_2$ and distilled under reduced pressure (46^{o}C/100 mm Hg), middle fraction is collected and immediately used.

Others

4,4'-Azo-bis(4-cyanopentanoic acid) (Fluka), Paraformaldehyde (Fluka), Benzoin (Aldrich), Benzoin methyl ether (Aldrich), Pyridine (Merck), Phosphorus pentachloride (Merck), Cyclohexane (Merck), Acetonitrile (Merck), Methanol used without further purification.

III.2. PREPARATION OF MATERIALS

III.2.1. 4,4'-Azo-bis(4-cyanopentanoyl chloride) (ACPC)

4,4'-Azo-bis(4-cyanopentanoic acid) (ACPA) was converted to its acid chloride by the modified procedure of Simionescu [45]. 10 g of ACPA was suspended in 100 ml of anhydrous benzene and stirred until dissolution. 20 g of phosphorus penta chloride was added to the solution in portions within 30 minutes under cooling with ice. The stirring was continued for another 1.5-2 h at 0°C and then the reaction mixture was allowed to stand 2h and protected from light. After filtering, the clear solution was distilled under vacuum and nitrogen not exceeding 30 °C for removal of benzene and phosphorus oxychloride. The resulting yellow solid was dissolved in 10 ml of CH_2Cl_2 under nitrogen followed by the addition of a cooled non polar solvent, 30 ml of n-hexane until the appearance of turbidity. After keeping at low temperature, solvent was removed by syringe and the acid chloride was dried and stored under nitrogen in refrigerator mp:94-96.5 °C. In all these operations, contact with atmospheric moisture and temperatures above 30 °C were avoided. IR spectra of ACPC is shown in Figure (3.1).

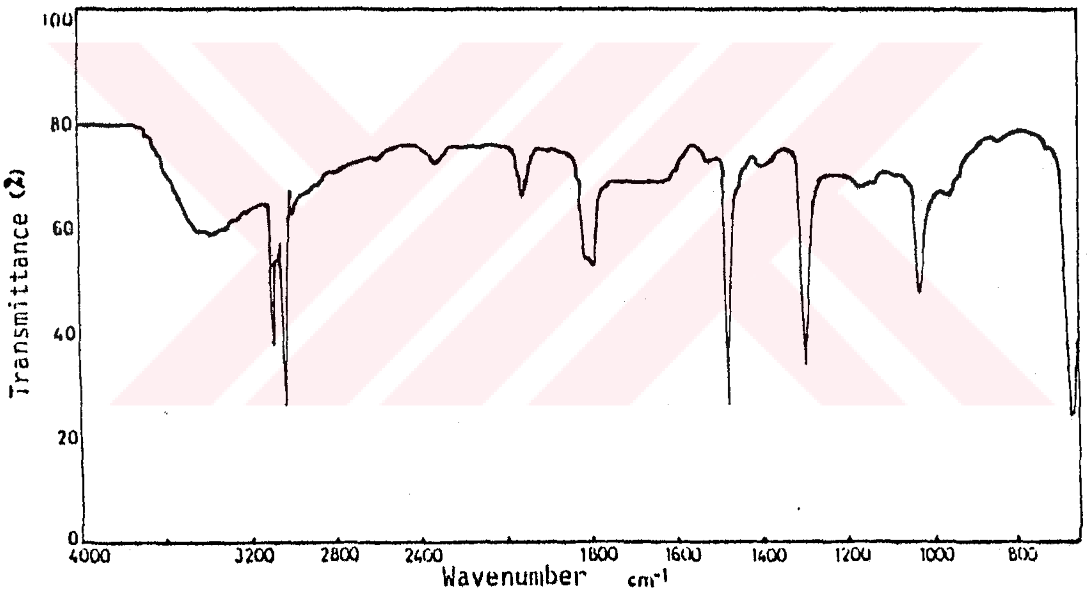
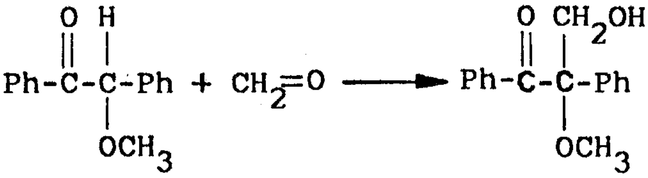


Figure 3.1. IR spectra of ACPC on KBr disc.

III.2.2. α- Methylol benzoin methyl ether (MBME)

MBME was prepared according to the modified method of Ahn et. all. [61]. 1.66 g of paraformaldehyde was added to a stirred solution of 10.3 g benzoin methyl ether dissolved in 50 ml dimethyl sulpoxide containing 0.1 g KOH dissolved in 5 ml ethanol. The reaction was performed under nitrogen at 40 °C for 3 h. The reaction mixture was cooled to room temperature, neutralized with dilute HCl and then diluted to 120 ml by addition of a saturated sodium chloride solution. The mixture was then extracted with ethyl acetate and the extract was washed three times with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure to give a pale yellow oil, which was crystallized slowly in a refrigerator to give colorless crystals of α-methylol benzoin methyl ether in a yield of 55 %, mp: 70-73^oC.



$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{OCH_3}{|}}{\overset{\overset{H}{|}}{C}}{-}Ph} + \mathrm{CH_2{=}O} \longrightarrow \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{OCH_3}{|}}{\overset{\overset{CH_2OH}{|}}{C}}{-}Ph} \qquad (3.1)$$

Figure (3.2) shows NMR spectra of MBME where 8.1-7.9 ppm (2H of benzoyl), 7.6-7.2 ppm (8H of phenyl), 4.6-4.0 ppm (2H of $-CH_2-O-$), 3.5 ppm (3H of $O-CH_3$).

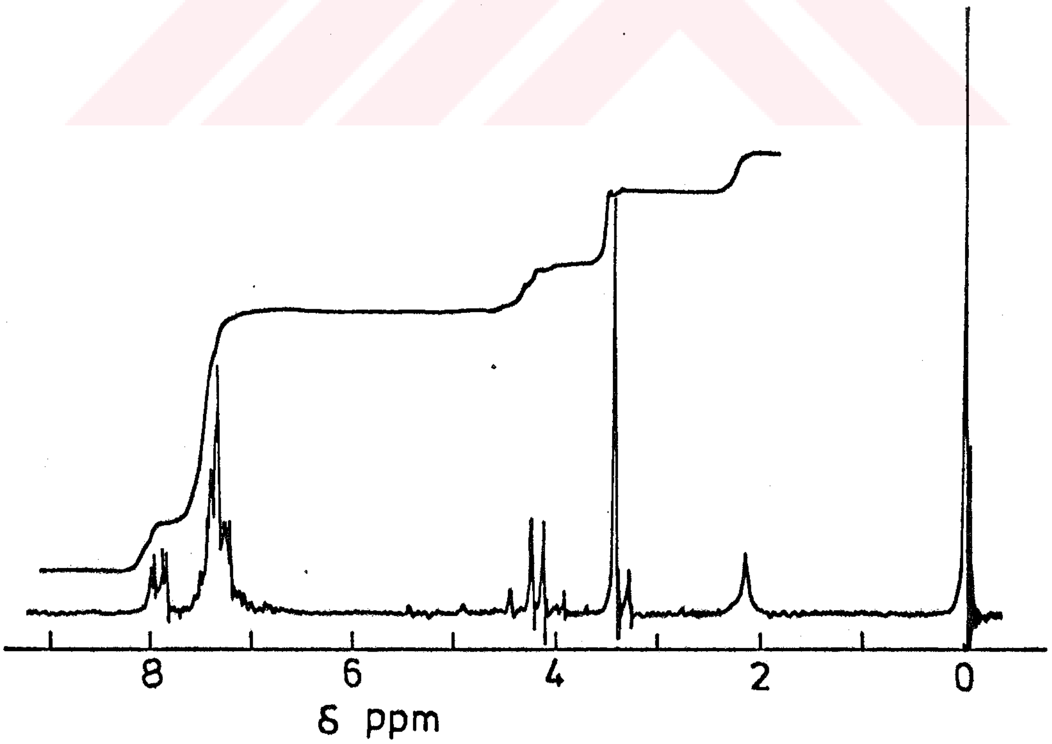


Figure 3.2. ^{1}H-NMR spectrum of MBME in $CDCl_3$

III.2.3. 4,4'-Azo-bis(4-cyanopentanoyl)-bis benzoin (ACPB)

In a three-neck flask fitted with a stirrer and nitrogen inlet, 2.75 g benzoin in 50 ml chloroform were introduced and treated with 1.00 g pyridine with cooling at 0°C. From a dropping funnel, 2.02 g of ACPC dissolved in 25 ml chloroform were added under nitrogen at a temperature not exceeding 5°C. The mixture was stirred for another 5 h at this temperature and allowed to stand overnight. The solution was concentrated by evaporating chloroform under vacuum and the initiator then precipitated in methanol at -70°C giving white crystals of ACPB in a yield of 20 %, mp:128°C.

III.2.4. 4,4'-Azo-bis(4-cyanopentanoyl)-bis(α-methylol benzoin methyl ether) (ABME)

ABME was prepared by the reaction of MBME and ACPC in a similar way described for ACPB. Yellowish crystals were obtained with a yield of 18 %, mp:44°C.

III.3. TECHNIQUES

III.3.1 Thermal Polymerization

Bulk styrene containing a known amount of ACPB or ABME charged into a pyrex polymerization tubes with standart socket joints. The tubes are fitted to high vacuum apparatus by means of manifold with standard sockets. Polymerization tubes are then placed in a Dewar flask containing liquid nitrogen and after their contents are frozen are degassed. After thawing they are frozen again. This freeze-thaw technique is repeated three times before sealing the tubes. These samples are polymerized by placing them into a constant temperature bath. After the required time, the tubes are quickly dipped into the cold water and are opened by applying hot point. The contents of samples are poured into the excess amount of methanol to precipitate the polymer. The precipitates are filtered off, dried in a vacuum and weighed. % Conversion is calculated from the equation below.

$$\text{Conversion } \% = \frac{\text{Weight of obtained polymer (g)}}{\text{Weight of monomer (g)}} \qquad (3.2)$$

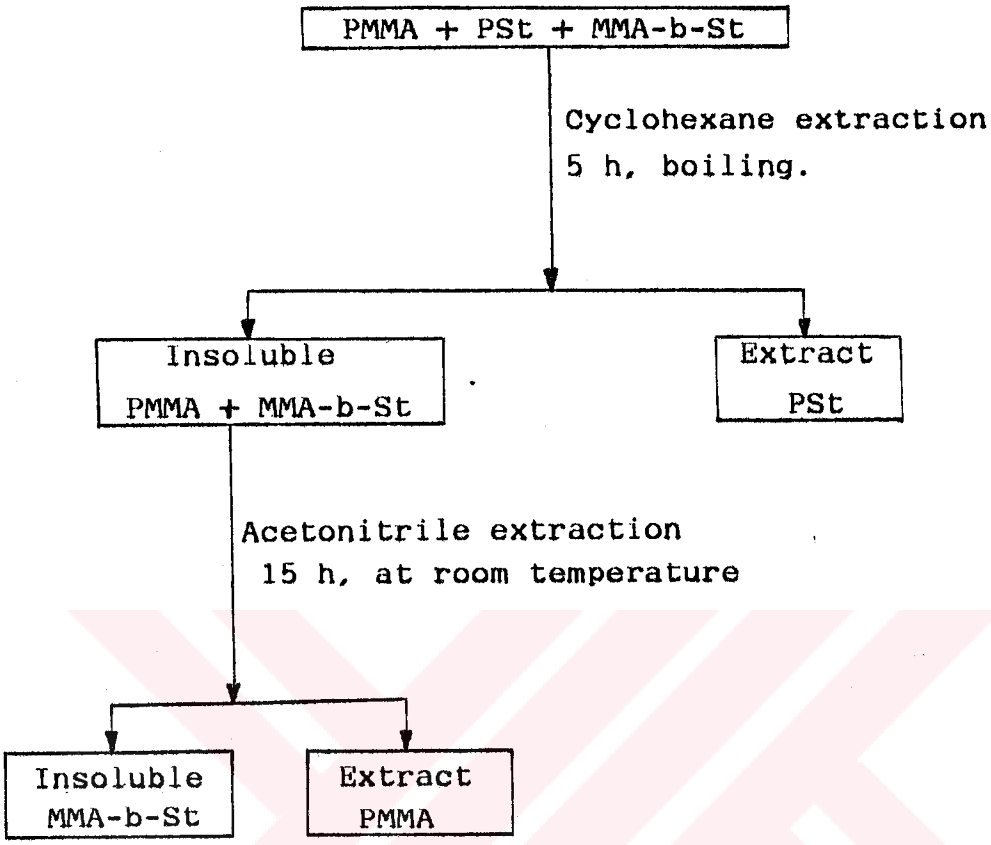
Rate of polymerization (R_p) is calculated by

$$R_p = \frac{W}{m} \times \frac{1000}{V} \times \frac{1}{t} \qquad (3.3)$$

W= weight of polymer obtained (g)
m= molecular weight of monomer (g/mol)
V= volume of reaction mixture (L)
t= time (sec.)

III.3.2. Photochemical Block Copolymerization

Appropriate solutions of obtained prepolymers and methyl methacrylate were contained in pyrex tubes. The mixture was degassed in the usual manner prior to irradiation with Annular type photoreactor (Applied photophysics) equipped with lamps emitting at 350 nm at 25°C. At the end of the given time, polymers were obtained from the reaction mixture by precipitation into methanol. The mixture of block copolymer and homopolymers was separated by successive extraction in boiling cyclohexane and acetonitrile according to the scheme below, Then the extracted homopolymers were precipitated into methanol and dried to constant weight.



III.4. APPARATUS

High Vacuum Apparatus

A pyrex high vacuum line contains B-14 sockets, mercury diffusion pump, Edwards two-stage rotary oil pump and two liquid nitrogen cold traps, one between diffusion pump and manifold, the other between diffusion and backing pumps. System is divided into several sections by means of teflon taps for multipurpose uses. The vacuum obtained is usually about 10^{-4} torr . Schematic representation of high vacuum system is shown in Figure (3.3).

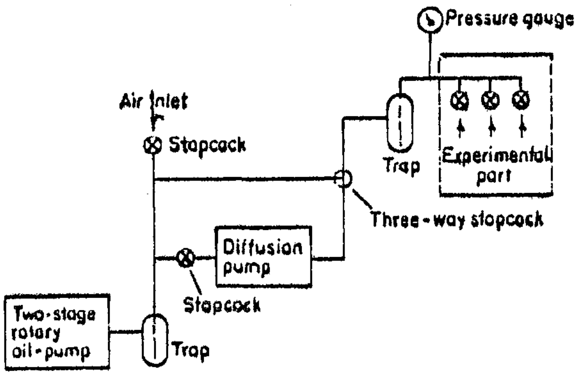


Fig.3.3. Schematic representation of high vacuum system

^{1}H-NMR Spectroscopy

^{1}H-NMR spectra were recorded on JNM-FX-1000 Fourier Transform NMR (110 MHz) in $CDCL_3$, using tetramethylsilane as internal standart.

IR Spectroscopy

IR spectra were recorded on a Jasco FT/IR-3 and Shimadzu IR-400 infrared spectrometers.

UV Spectroscopy

UV spectra were recorded on a Perkin Elmer 550S UV-Vis spectrophotometer, using THF as a solvent.

Elemental Analysis

Elemental analysis was carried out with a Yanaco-CHN Corder MT-3 instrument.

Differential Scanning Calorimetry

Perkin Elmer DSC-II type instrument was employed to determine the thermal and kinetic data of azo-benzoin initiators. Approximately 1 mg of sample was put directly to the standart aluminium pan. A slow current of nitrogen passed over the sample holders during the measurement at a heating rate of 8°C/min.

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 1 ml/min at 25°C.

Annular Photoreactor

Photochemical block copolymerization experiments were carried out by using Annular photoreactor APQ 40, equipped with 400 W medium pressure lamp emitting at 350 nm. Figure (3.4) shows schematical representation of annular reactor.

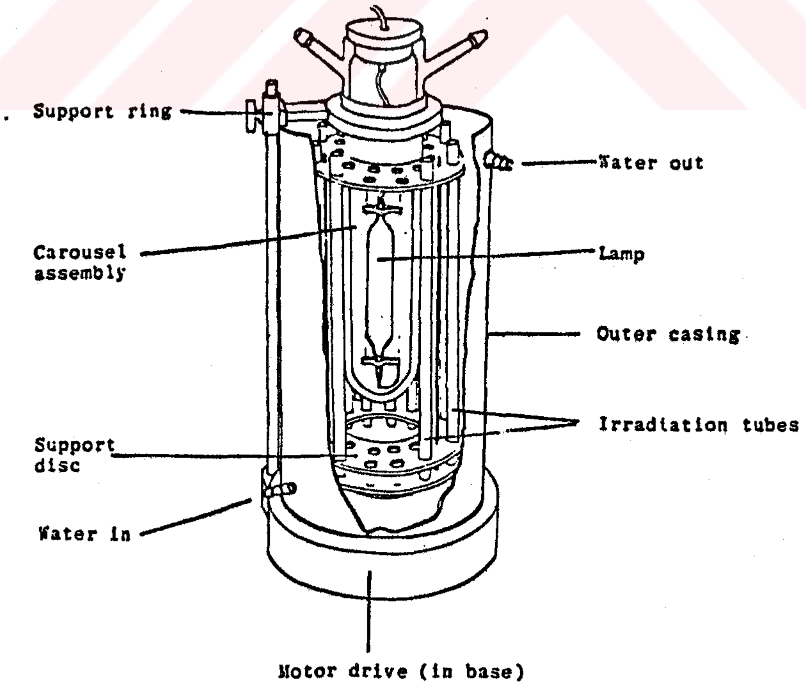
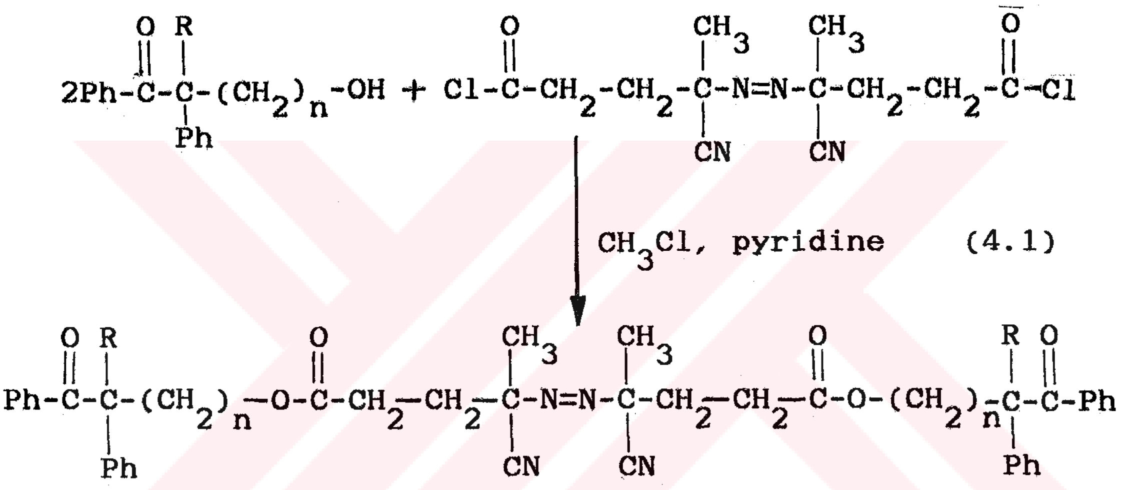


Figure 3.4. Schematic representation of annular reactor.

CHAPTER IV. RESULTS AND DISCUSSION

IV.1. SYNTHESIS OF AZO-BENZOIN INITIATORS

New azo-benzoin initiators were synthesized [62] by reactions of benzoin (B) or the α-methylolbenzoin methyl ether with the diacid chloride (ACPC) as shown in reaction (4.1).



$$2Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{R}{C}}-(CH_2)_n-OH + Cl-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{CH_3Cl,\ pyridine} \quad (4.1)$$

$$Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{R}{C}}-(CH_2)_n-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-\underset{Ph}{\overset{R}{C}}-\overset{O}{\overset{\|}{C}}-Ph$$

ACPB: R=H, n=0

ABME: R=$-OCH_3$, n=1

The structure of the new azo benzoin–initiators was confirmed by elemental analysis as well as spectroscopic investigations. The IR spectra contain the characteristic CO ester band and CO keto group of benzoin at 1725 and 1680 cm^{-1}, respectively (Figure 4.1). The ^1H-NMR spectra, recorded in $CDCl_3$, evidence resonance signals of the phenyl, OH, CH_2O, OCH_3, CH_2 and CH_3 protons of relative intensities corresponding to the number and type of protons (Figures 4.2 and 4.3). Elemental analysis were in agreement with the proposed structures as can be seen from the Table (4.1).

Table 4.1. Elemental Analysis of Azo-benzoin Initiators

Azo-benzoin initiator	Calculated			Found		
	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
ACPB	71.85	5.38	8.39	68.97	5.65	8.54
ABME	69.84	5.82	7.40	68.30	5.88	6.87

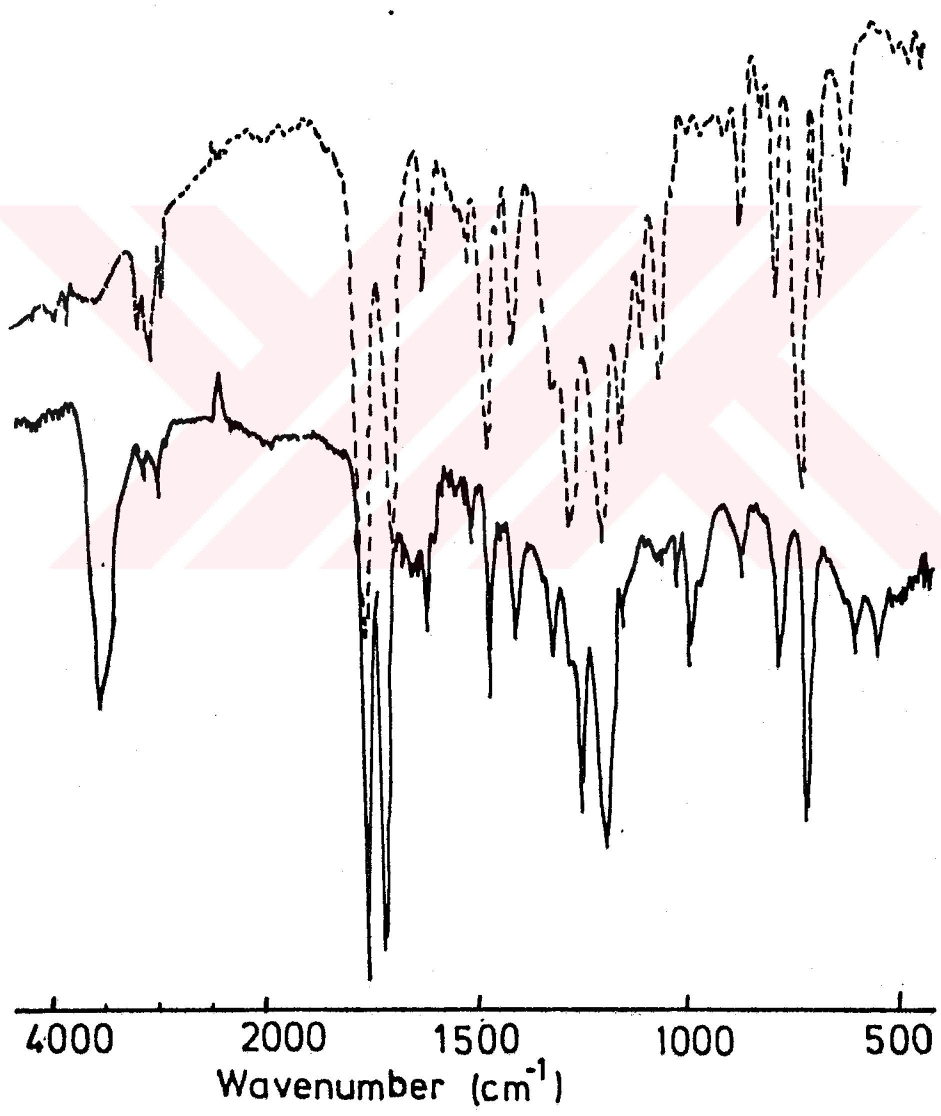


Figure 4.1. IR spectra of azo-benzoin initiators
a) ACPB (———) b) ABME (-----)

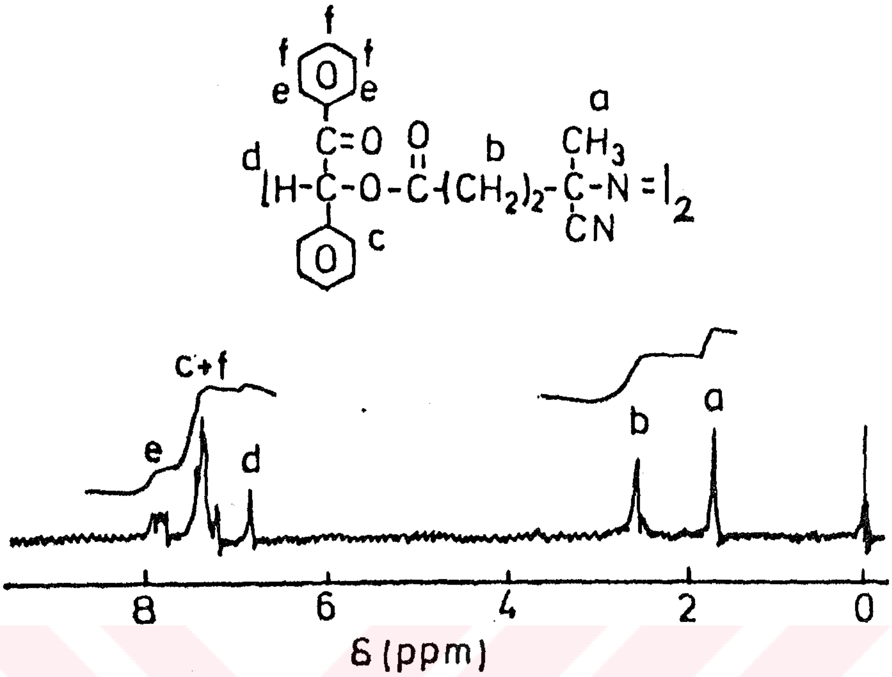


Figure 4.2. ^{1}H-NMR spectra of ACPB in $CDCl_3$

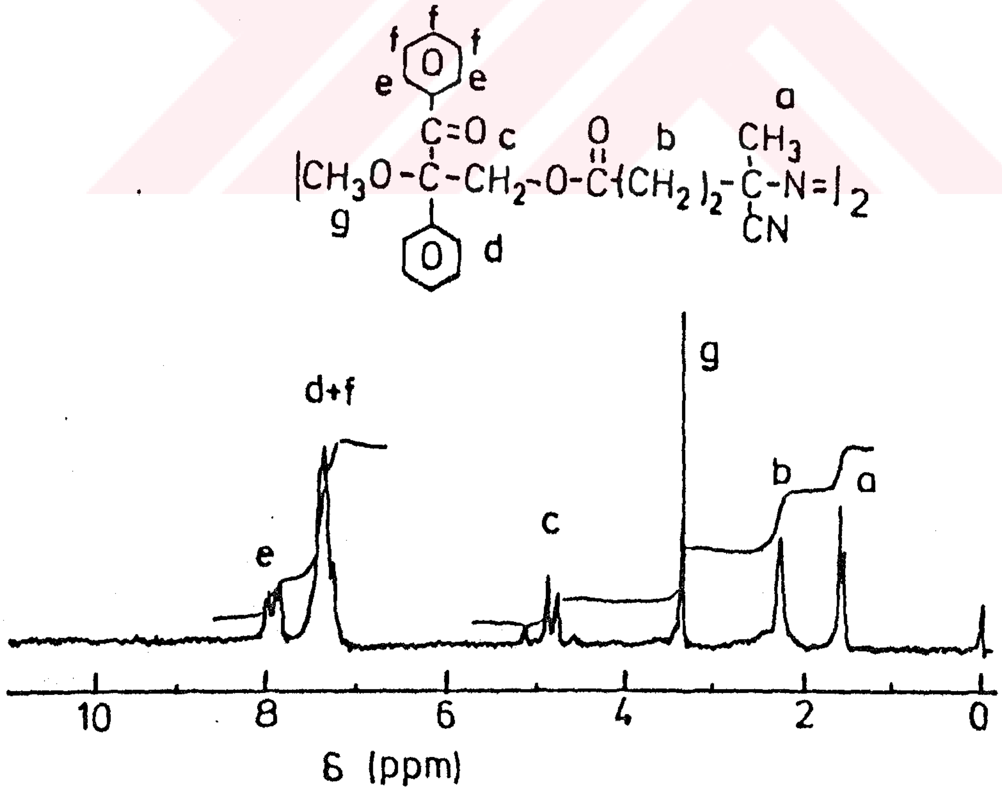


Figure 4.3. ^{1}H-NMR spectra of ABME in $CDCl_3$

IV.2. DECOMPOSITION OF AZO-BENZOIN INITIATORS

Decomposition of the azo-linkage of azo-benzoin initiators were studied by DSC. Figure (4.4) shows typical DSC trace for the decomposition of ABME. As can be seen, there is no secondary reaction beside the decomposition of the azo function in the temperature range studied. The azo-benzoin initiator (ABME) melts at 44° C and is in liquid form above this temperature which provides homogenity and good heat transfer during the measurement. The rate constant for the decomposition (k_d) was determined at various temperatures and exhibited first order kinetics, as can be seen from the Arrhenius plot in Figure (4.5). Activation energy for the decomposition was estimated to be 99.77 kJ/mole which is in good agreement with the literature value given for common azo compounds. Decomposition rate constant for ACPB could not be clearly determined due to the interference of secondary reactions observed in the studied temperature range. However, related DSC thermogram is presented in Figure (4.6). For this reason, kinetic consideration with this respect is limited only for ABME and assumed that ACPB behaves in the similar manner.

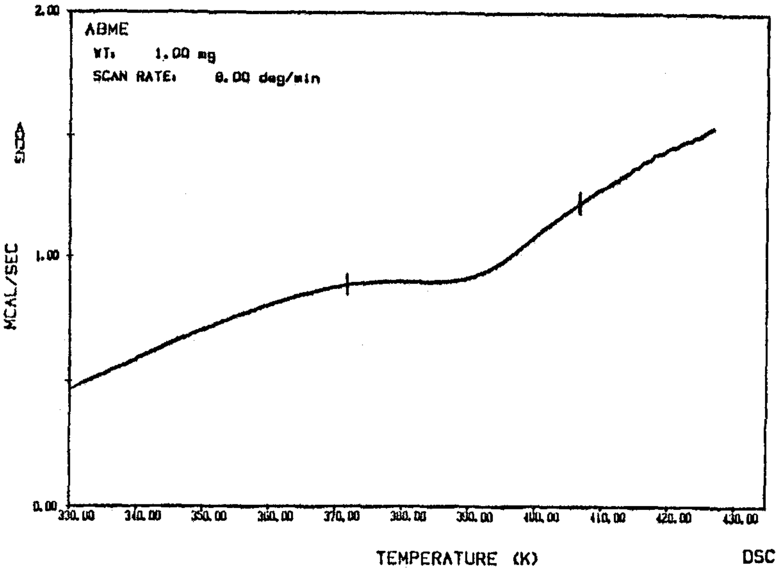


Figure 4.4. DSC trace for the decomposition of ABME

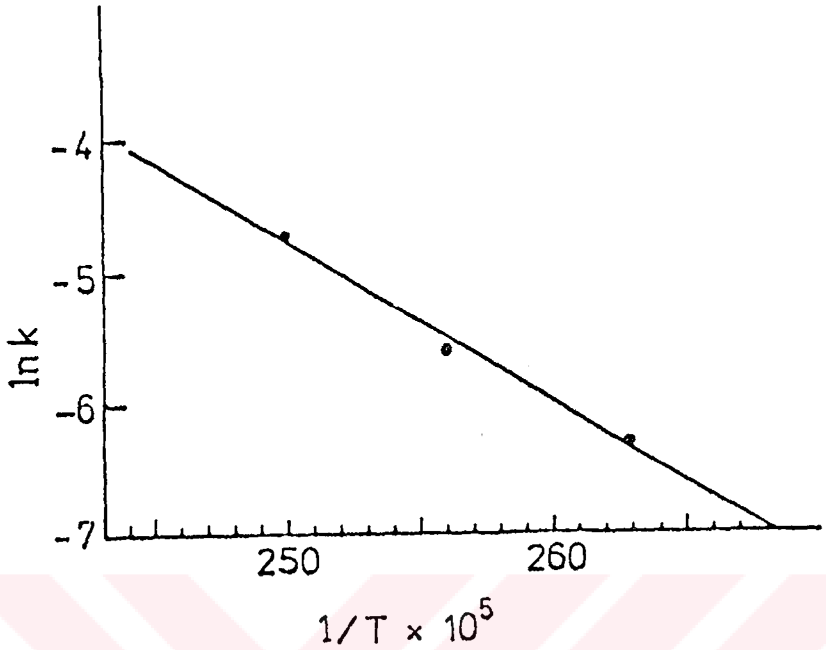


Figure 4.5. Arrhenius plot for the decomposition of ABME

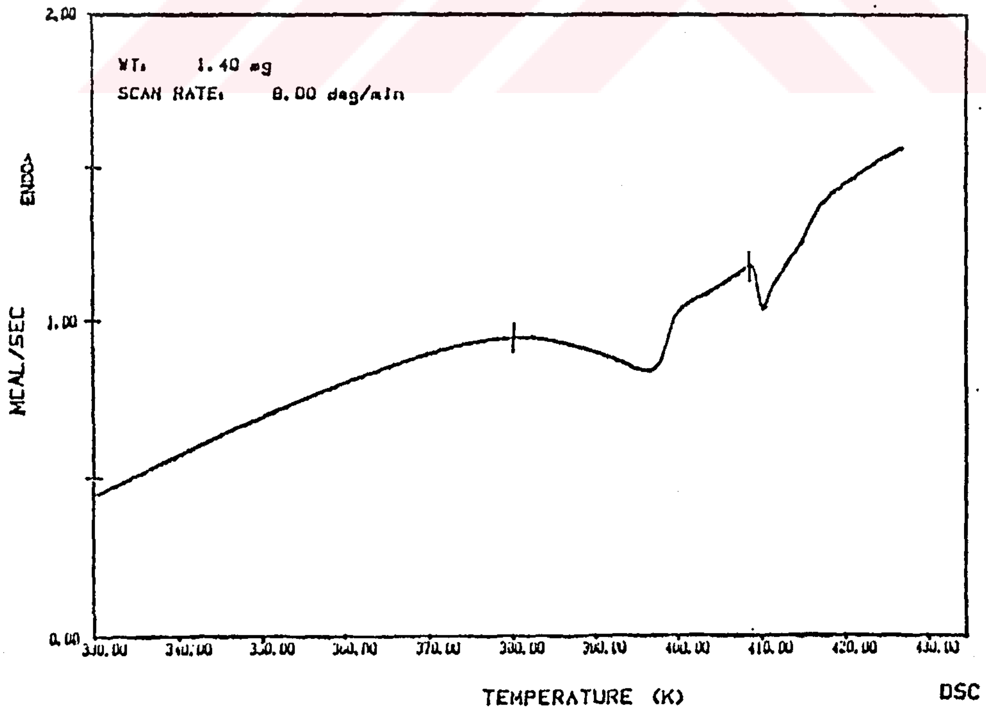


Figure 4.6. DSC trace for the decomposition of ACPB

IV.3. KINETICS OF LOW CONVERSION POLYMERIZATION OF STYRENE INITIATED BY AZO-BENZOIN INITIATORS

Both azo-benzoin initiators were used as free radical initiator for the polymerization of styrene in bulk [62,63]. Typical results for ACPB and ABME are shown in Tables (4.2) and (4.3), respectively. The conversion versus time plots of polymerizations at 60, 70 and 80 ^{o}C are presented in Figures (4.7) and (4.8). The logarithm of the rates of polymerization is plotted against the reciprocal of the absolute temperature and Arrhenius-type diagrams (Figures 4.9 and 4.10) are obtained in which activation energies of 75.89 kJ/mole and 71.63 kJ/mole are calculated for ACPB and ABME respectively in the 60-80^{o}C range.

For the polymerization of a vinyl monomer such as styrene, in which termination occurs exclusively by combination, the rate of polymerization is given by eq.(2.16) Dependence of the order of the overall rate of polymerization on both monomer and initiator concentration was determined only for ACPB initiated polymerization.

A plot of log R_p against log [M] at constant [I] is shown in Figure (4.11) where the slope which refers to the order of the rate in monomer concentration is equal to the theoretical value of unity. George and Ward [64] have reported a value of 1.16 as the order of monomer concentration for polymerization of styrene initiated by poly(bisphenol A -4,4'-azobis-4-cyanopentanoate) in DMF.

A plot of log R_p versus log [I] at constant [M] is also shown in Figure (4.12). There is a gradient of 0.43 which exhibits general behavior of this type of initiation.

For free radical polymerization the inverse degree of polymerization ($1/\overline{P}_n$) is related to the rate of polymerization (R_p) by

Table 4.2. Bulk Polymerization of Styrene Initiated by ACPB at 60°C

Run No	$[I]\times10^3$ (mol/l)	Time (min)	Yield (%)	$R_p\times10^5$ (mol/l.s)	$(1/\overline{P}_n)\times10^4$
1	7	120	4.44	5.34	5.80
2	5	180	5.22	4.18	3.90
3	3	240	5.61	3.38	3.16
4	1	360	5.75	2.30	1.98
5	0.5	480	5.08	1.54	1.82

[M]=8.71 mol/l

Table 4.3. Bulk Polymerization of Styrene Initiated by ABME at 60°C

Run No	$[I]\times10^3$ (mol/l)	Time (min)	Yield (%)	$R_p\times10^5$ (mol/l.s)	$(1/\overline{P}_n)\times10^4$
1	5	120	4.77	5.76	7.98
2	4	150	6.49	6.27	5.33
3	3	180	6.15	6.59	4.04
4	2	210	4.97	5.27	3.34
5	0.5	300	2.10	3.89	1.58

[M]=8.71 mol/l

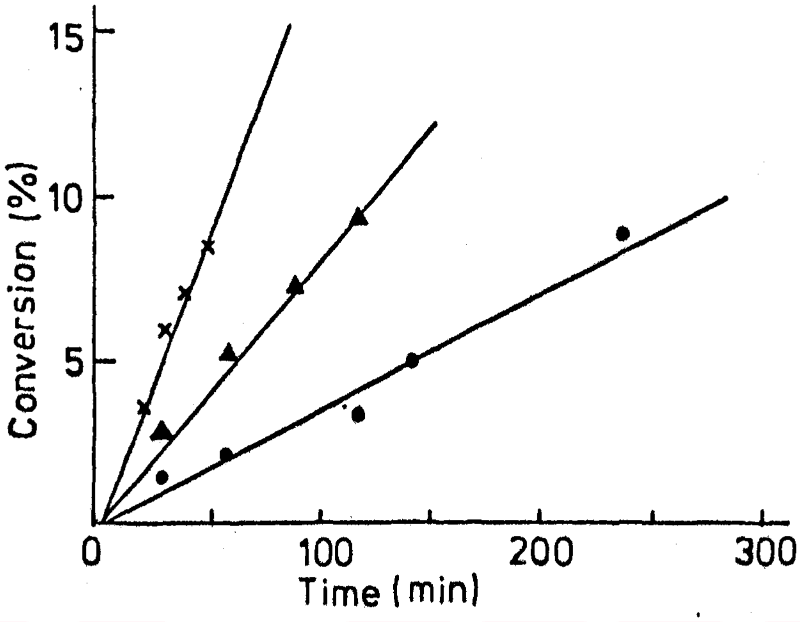


Figure 4.7. Time-conversion curves for the bulk polymerization of styrene initiated by ACPB at various temperatures, [ACPB]= 5×10^{-3} mol/l, [M]= 8.71 mol/l, (●) 60°C, (▲) 70°C, (×) 80°C.

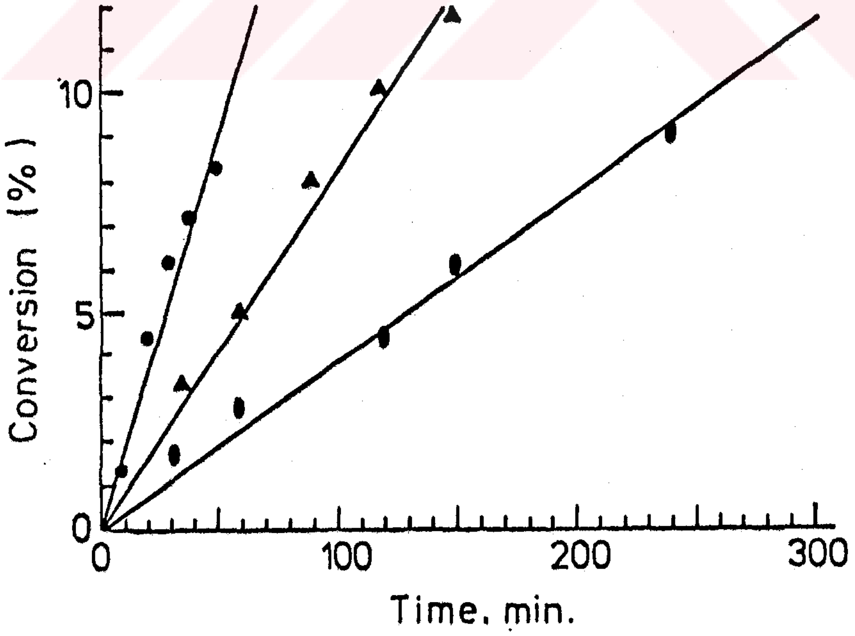


Figure 4.8. Time-conversion curves for the bulk polymerization of styrene initiated by ABME at various temperatures, [ABME]= 5×10^{-3} mol/l, [M]= 8.71 mol/l, (⬮) 60°C, (▲) 70°C, (●)80°C.

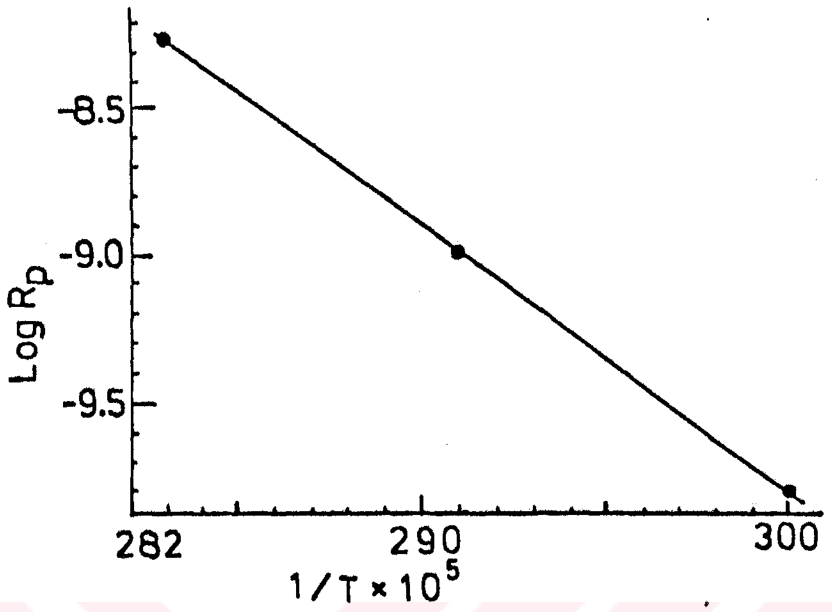


Figure 4.9. Plot of log R_p versus 1/T for the bulk polymerization of styrene initiated by ACPB.

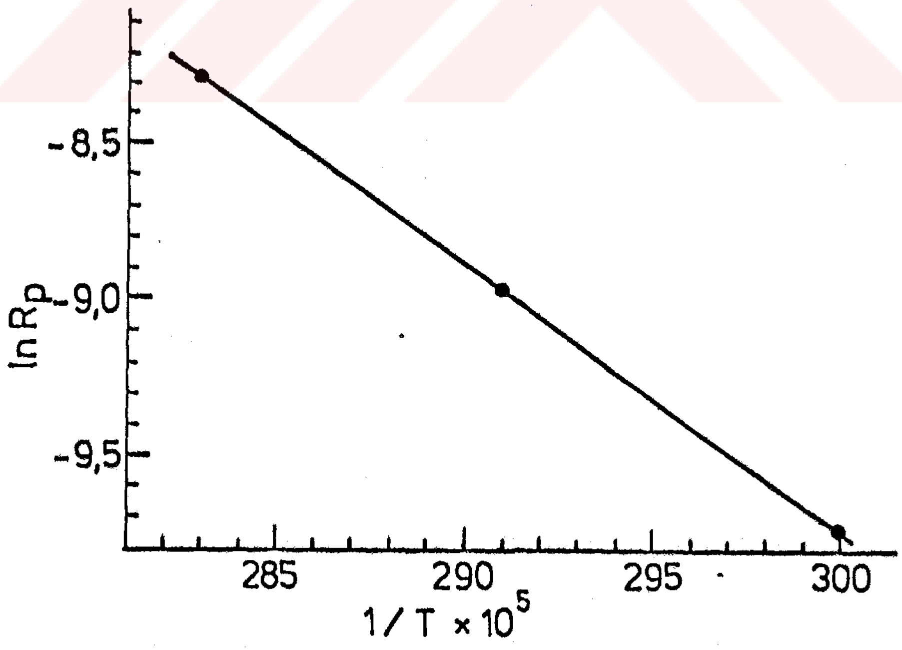


Figure 4.10. Plot of log R_p versus 1/T for the bulk polymerization of styrene initiated by ABME

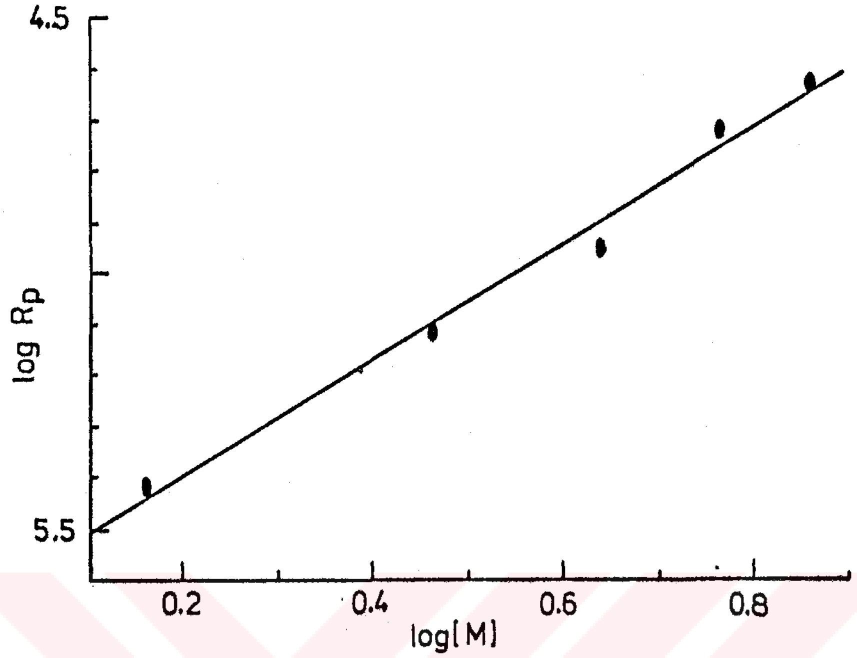


Figure 4.11 Plot of log R_p versus log [M] for polymerization of styrene initiated by ACPB.

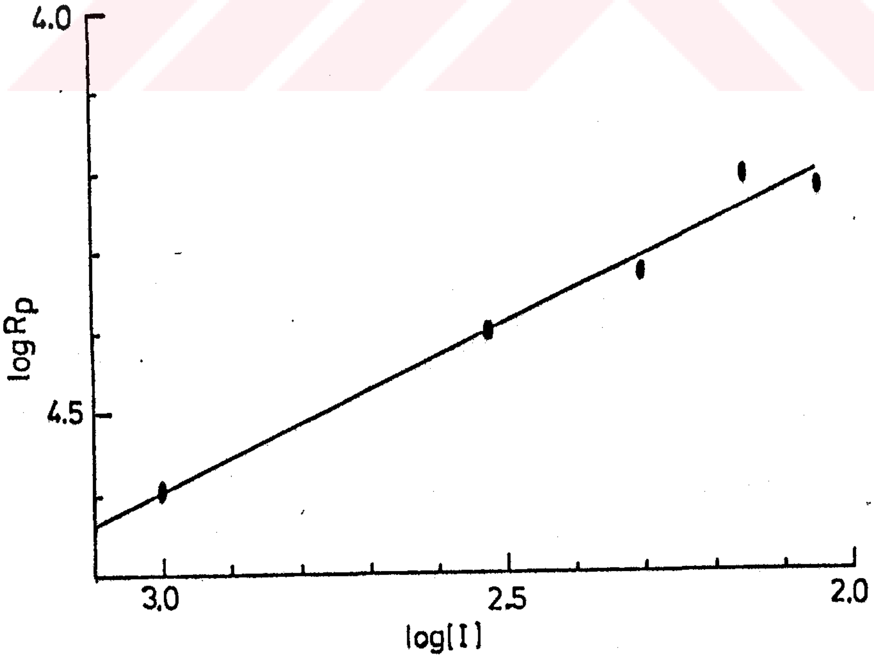


Figure 4.12. Plot of log R_p versus log [I] for polymerization of styrene initiated by ACPB.

$$1/\overline{P}_n = (fk_d[I]/R_p) + C_M + C_I([I]/[M]) \quad (4.2)$$

in which C_I and C_M are transfer constants to initiator and monomer respectively; k_d is the thermal decomposition rate constant and f is the initiator efficiency.

A plot of the reciprocal number average degree of polymerization ($1/\overline{P}_n$) against [I]/[M] is shown in Figures (4.13) and (4.14). The C_I values for both azo-benzoin initiators were calculated from the slope of the straight line and were found to be C_I=0.416 and C_I=0.9 for ACPB and ABME respectively.

Figures (4.15) and (4.16) show plot of ($1/\overline{P}_n$) against ($[I]/R_p$) from which the values of fk_d for ACPB and ABME was calculated to be 2.44×10^{-6} sec^{-1} and 7.36×10^{-6} sec^{-1} respectively. Kinetic parameters for both ACPB and ABME together with the commercial azo initiators such as 2,2'-azobis(isobutyronitrile) (AIBN) and 4,4'-azobis (-4-cyanopentanoic acid) (ACPA) from which azo-benzoin initiators derived, are collected in Table (4.4).

Table 4.4. Kinetic Parameters of Azo Initiators

Azo Initiator	E_d (kJ/mol)	$k_d \times 10^5$	$fk_d \times 10^6$ (1/sec)	C_I
ACPB	-	-	2.44	0.416
ABME	99.77	1.92	7.36	0.906
AIBN	130	1.10	-	0.160
ACPA	108	1.33	8.16	-

As can be seen from the Table (4.4), azo-benzoin initiators exhibit initiator properties similar to that of common azo initiators except their participation in transfer reactions. However, in our case the benzoin groups attached to the azo-initiator may contribute to the relatively higher value of C_I. This effect is more pronounced in the case of ABME which possesses additional OCH_3 and spacer CH_2 groups in the structure.

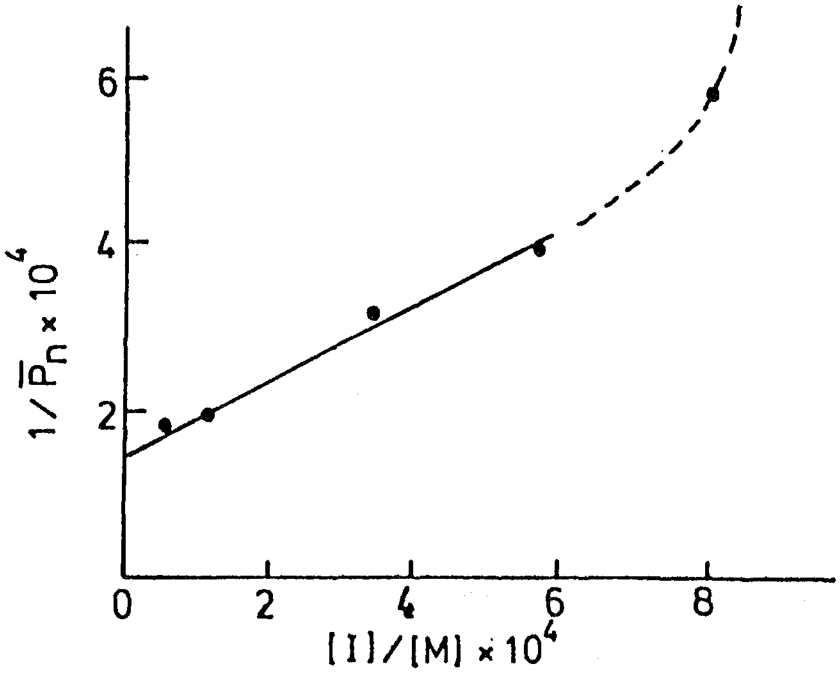


Figure 4.13. Plot of the reciprocal degree of polymerization ($1/\bar{P}_n$) versus [I]/[M] for styrene polymerization in bulk at 60°C initiated by ACPB.

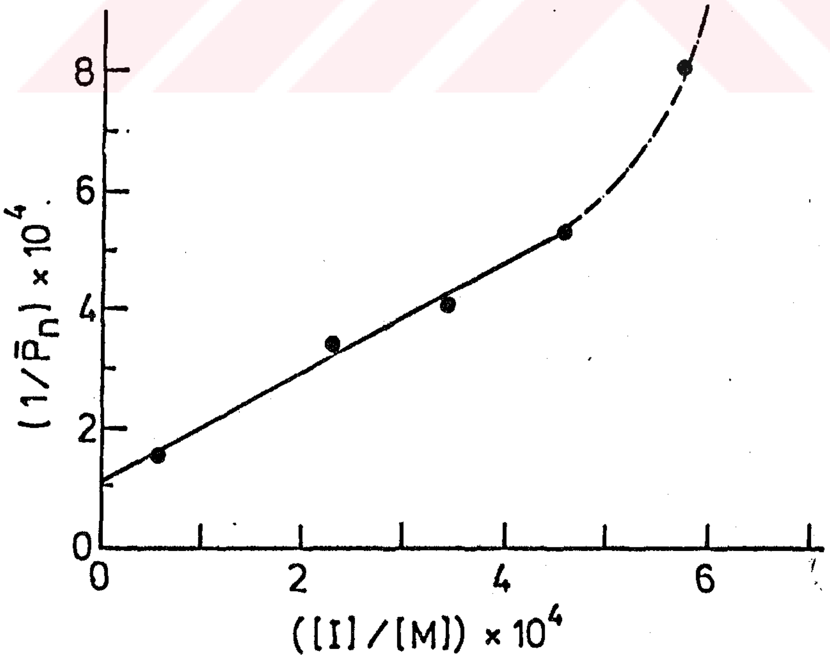


Figure 4.14. Plot of the reciprocal degree of polymerization ($1/\bar{P}_n$) versus [I]/[M] for styrene polymerization in bulk at 60°C initiated by ABME.

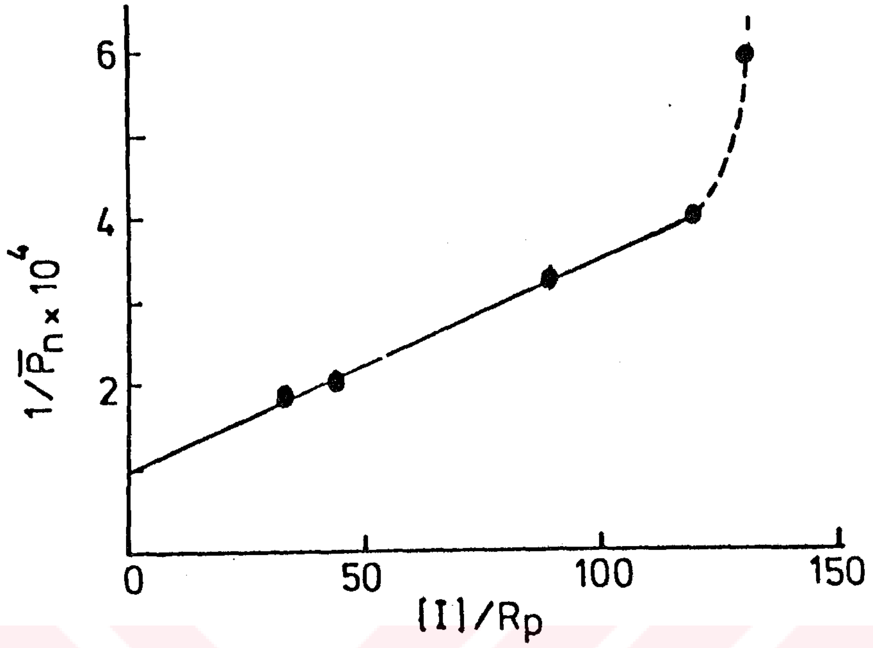


Figure 4.15. ($1/\bar{P}_n$) as a function of([I]/R_p) for the polymerization of styrene in bulk at 60°C initiated by ACPB

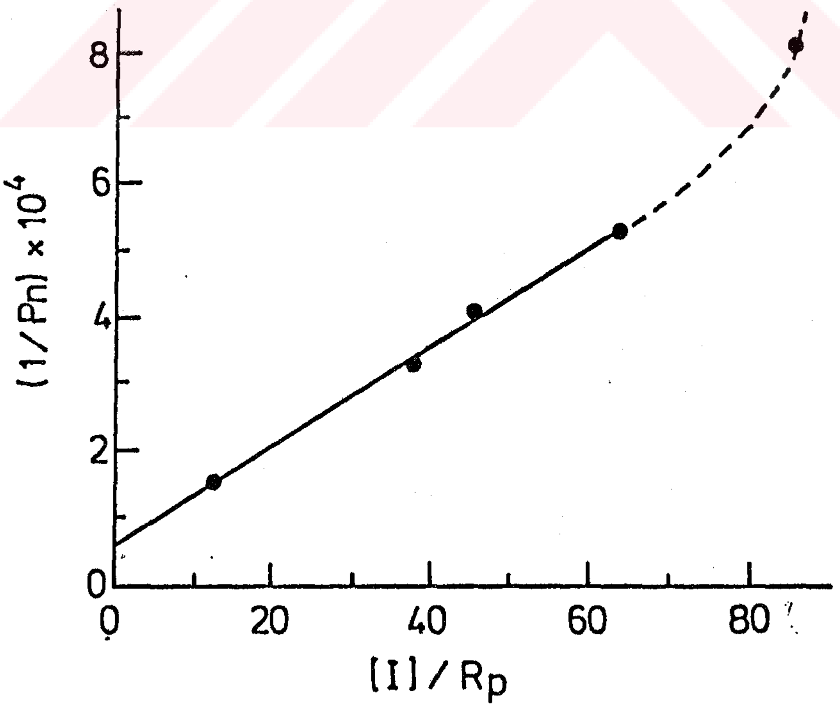
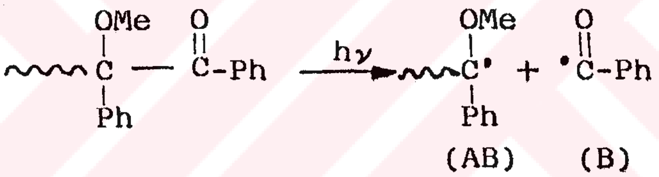


Figure 4.16. ($1/\bar{P}_n$) as a function of ([I]/R_p) for the polymerization of styrene in bulk at 60°C initiated by ABME

IV.4. SEQUENTIAL DECOMPOSITION OF AZO-BENZOIN INITIATORS

Azo-benzoin initiators have sequential bifunctional character due to the presence of both thermo-sensitive azo group and thermally stable but photosensitive benzoin groups in the structure. To test the sequential character of the azo-benzoin initiators ACPB was considered as a representative initiator and a series of two-stage polymerizations of styrene were carried out. As can be seen from the Table (4.5), the conversion increased significantly when the polymerization mixture was irradiated in the second stage. Notably, lower molecular weights and broader molecular weight distribution as compared to the one stage procedure has been obtained. This may due to the fact that benzoyl radical (B) being a better initiator than the alkoxy benzyl radical (AB) for styrene polymerization [65].



$$\sim\!\!\sim C(OMe)(Ph)-C(=O)-Ph \xrightarrow{h\nu} \sim\!\!\sim C^{\bullet}(OMe)(Ph) + {}^{\bullet}C(=O)-Ph \qquad (4.3.)$$

(AB) (B)

Table 4.5: Two Stage Polymerization of Styrene with ACPB

Run	Stage I Heating time at 60°C (h)	Stage II Photolysis time[a] at 25°C (h)	Conversion (%)	$M_n x 10^{-4}$	M_w/M_n
I	2	-	6.81	26.69	1.51
III[b]	2	-	8.66	33.12	1.43
III	2	24	39.73	4.54	4.47

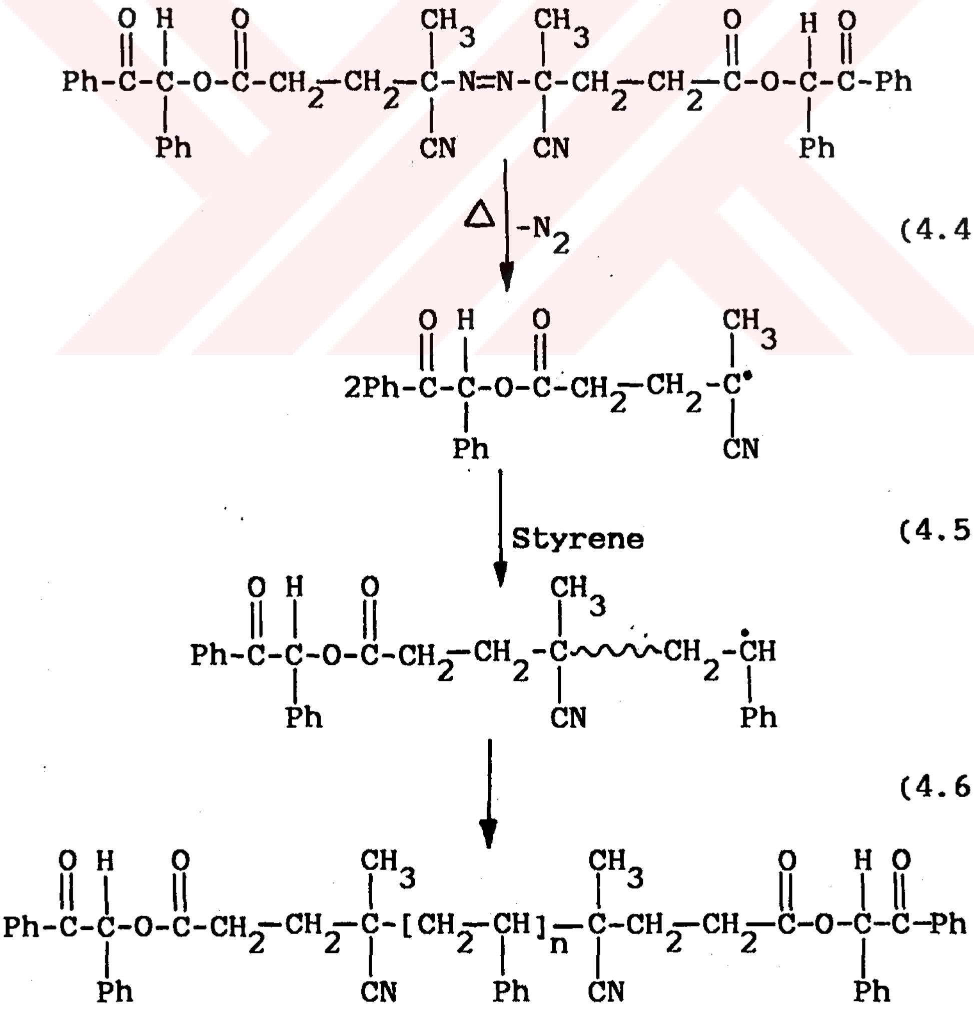
[a] λ = 350 nm

[b] Kept at 25°C for 24 hours.

IV.5. ATTACHMENT OF BENZOIN CHROMOPHORES TO THE POLYMER CHAINS

The initiation of polymerization by means of azo-benzoin initiators yields polymers with one or two benzoin end groups according to the termination mode of the polymerization of particular monomer involved.

In order to use in block copolymerization experiments polystyrenes (PSt) with various molecular weight, possessing benzoin and benzoin methyl ether end groups, were prepared according to the following sequences of reactions.



(4.4)

(4.5)

(4.6)

Figure (4.17) shows the absorption spectra of ACPB and ABME together with the absorption spectra of polystyrenes obtained by initiation with these initiators. It can be seen that both spectra contain an absorption band characteristic of the precursor benzoin group.

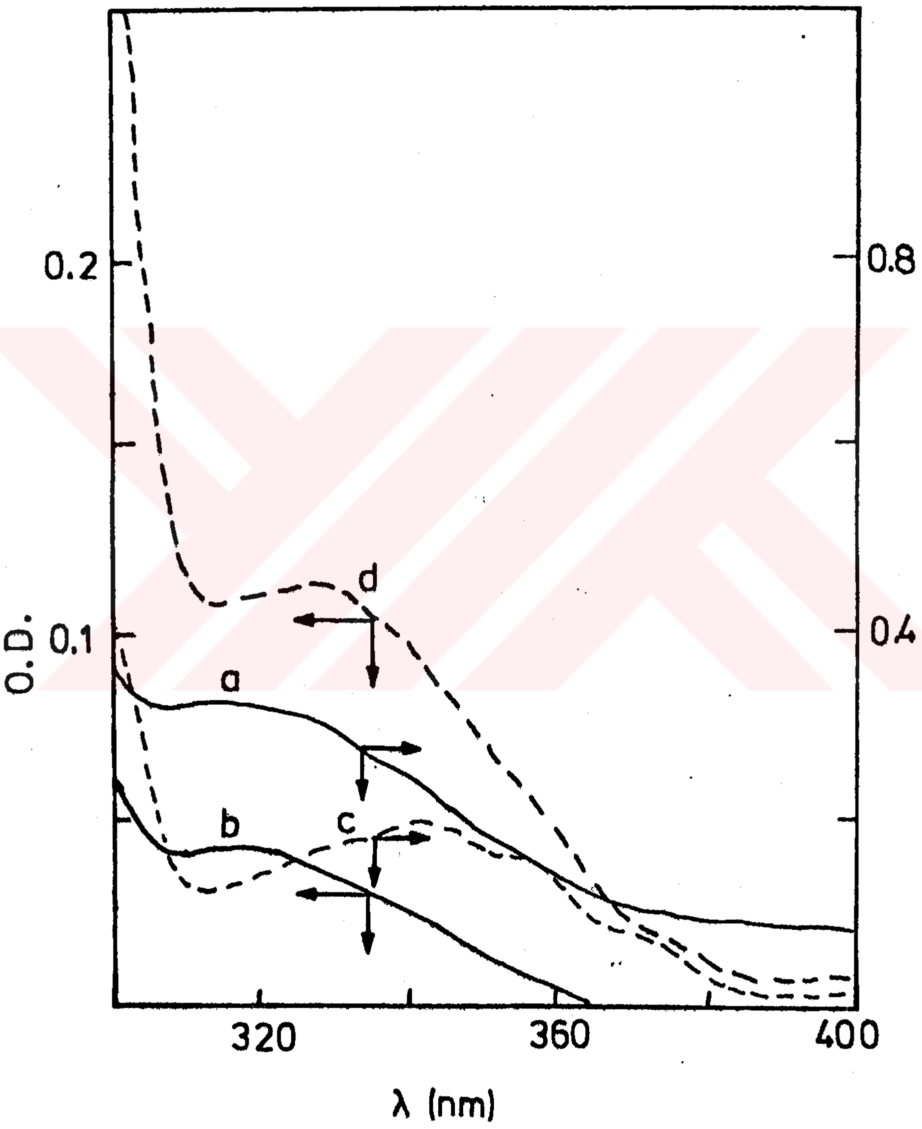
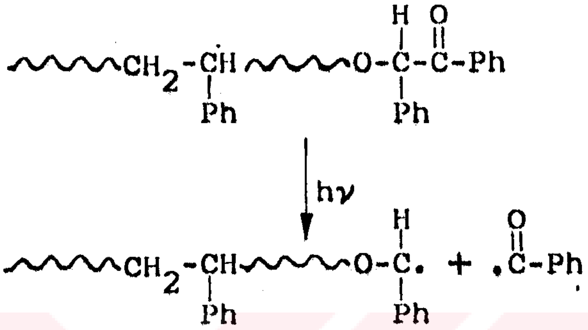


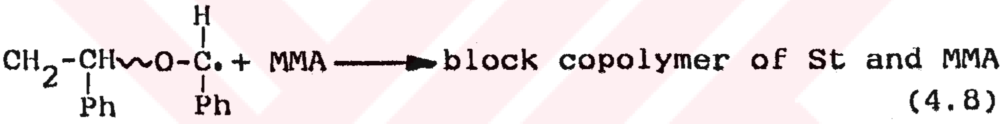
Figure 4.17. UV absorption spectra of THF solutions containing;
a) ACPB (2.98×10^{-4} mol/l)
b) polystyrene (2.18 g/l) initiated with ACPB
c) ABME (4.41×10^{-4} mol/l)
d) polystyrene (8.04 g/l) initiated with ABME

IV.6. BLOCK COPOLYMERIZATION

Polystyrenes possessing benzoin or benzoin methyl ether end groups were used as initiator in the polymerization of methyl methacrylate (MMA). UV irradiation of the prepolymers causes an α-scission and yielded benzoyl radicals and polymer-bound radical according to the reaction (4.7).



$$\sim\sim\sim CH_2-\underset{Ph}{\dot{C}H}\sim\sim\sim O-\underset{Ph}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{h\nu} \sim\sim\sim CH_2-\underset{Ph}{CH}\sim\sim\sim O-\underset{Ph}{\overset{H}{C}}\cdot + \cdot\overset{O}{\overset{\|}{C}}-Ph \qquad (4.7)$$



$$CH_2-\underset{Ph}{CH}\sim O-\underset{Ph}{\overset{H}{C}}\cdot + MMA \longrightarrow \text{block copolymer of St and MMA} \qquad (4.8)$$

$$Ph-\overset{O}{\overset{\|}{C}}\cdot + MMA \longrightarrow poly(MMA) \qquad (4.9)$$

Either or both of these radicals may then initiate polymerization of the second monomer according to the polymerization conditions. In this connection it is suitable to refer the work of Pappas [66] who demonstrated that both radicals are equally effective as initiators in the polymerization of methylacrylate and MMA. In our case it would appear necessary for the polymer-bound alkoxy-benzyl radical to initiate polymerization for successful block copolymerization (reaction 4.8). Typical results concerning block copolymerization of St and MMA using photoactive polystyrenes obtained from ACPB and ABME are presented in Tables (4.6), (4.7), (4.8) and (4.9). Homopolystyrene formation in all cases may be due to the primary radical combination of polymeric alkoxy benzyl radicals. PSt molecules which for any reason fail to acquire benzoin end groups during the synthetic procedure

Table 4.6. Block copolymerization[a] of the PSt initiator, obtained by the thermolysis of ACPB, with MMA in benzene depending on the molecular weight of the PSt initiator.

$M_n \times 10^{-4}$ (prePSt)	Conversion[b] (%)	Composition of the reaction mixture PSt (%)	PMMA (%)	PSt-b-PMMA (%)
22.44	30.71	2	70	28
27.10	31.48	4	71	25
32.09	14.90	9	62	29
43.01	20.00	18	59	23

[a] λ= 350 nm, [M]= 7.5 mol/l, [I]= 1.4×10^{-4} mol/l, Photolysis time= 3h, Temperature= 25°C

[b] Overall MMA conversion

Table 4.7. Block copolymerization[a] of the PSt initiator, obtained by the thermolysis of ACPB, with MMA at different PSt/MMA ratios.

PSt $\times 10^{-4}$ (mol/l)	PSt/MMA $\times 10^{-4}$ (mol/mol)	Conversion[b] (%)	Composition of the reaction mixture PSt (%)	PMMA (%)	PSt-b-PMMA (%)
1.2	15.9	18.08	1	81	18
2.4	31.9	13.94	4	66	30
3.6	47.8	14.73	8	57	35
4.8	63.8	9.61	9	30	61

[a] λ = 350 nm, [M]= 7.5 mol/l, Photolysis time= 3h. Temperature= 25°C, $\bar{M}_n$ of PSt initiator= 1.61×10^{5} g/mol

[b] Overall MMA conversion

Table 4.8. Block copolymerization[a] of the PSt initiator, obtained by the thermolysis of ABME, with MMA in benzene depending on the molecular weight of the PSt initiator.

M_nx10^{-4}	Conversion[b]	Composition of the reaction mixture		
(prePSt)	(%)	PSt	PMMA	PSt-b-PMMA
	(%)	(%)	(%)	(%)
10.46	23.34	1	81	18
19.52	34.99	3	73	24
26.23	13.00	7	63	30

[a] λ= 350 nm, [M]= 7.5 mol/l, [I]= 1.8x10^{-4}mol/l
Photolysis time= 3 h, Temperature= 25°C.

[b] Overall MMA conversion

Table 4.9. Block copolymerization[a] of the PSt initiator, obtained by the thermolysis of ABME, with MMA at different PSt/MMA ratios.

PSt x10^{-4}	PSt/MMA x10^{-4}	Conversion[b]	Composition of the reaction mixture		
			PSt	PMMA	PSt-b-MMA
(mol/l)	(mol/mol)	(%)	(%)	(%)	(%)
1.6	21.2	17.58	1	87	12
3.4	45.2	14.10	15	59	26
5.2	69.1	14,33	18	54	28
7.0	93.0	14.57	19	50	31

[a] λ= 350 nm, [M]= 7.5 mol/l, Photolysis time= 3 h.
Temperature= 25°C, $\overline{M}_n$ of PSt initiator= 1.13x10^5g/mol.

[b] Overall MMA conversion

in the first step are also automatically included in non-blocked PSt component. The molecular weight and concentration of the PSt initiator influence the yield and the block copolymer ratio in the mixture. The highest amount of block copolymer formation was observed by using benzoin attached PSt with lowest molecular weight and at the highest concentration (Table 4.7).

G.P.C. analysis clearly evidences the formation of block copolymer as shown in Figure (4.18) where GPC chromatogram recorded with the prepolymer, mixture and extraction products. The new peak at higher molecular weight region is ascribed to the block copolymer. Furthermore, dual detection by RI and UV recording allowed a clear assigment of this peak to block copolymer as homo poly(methyl methacrylate) is transparent at wavelength (254 nm) of the UV detector. The block copolymer structure was also evidenced by means of IR and NMR spectral measurements. The IR spectra of purified block copolymers (Figure 4.19) show the charecteristic band of PMMA at 1720 cm^{-1} in addition to that of PSt at 690, 810,2940 and 3040 cm^{-1}. The NMR spectrum of a typical block copolymer (Figure 4.20) displays signals at; 0.8-1.1 ppm (CH_3), 1.4-2.0 ppm (CH_2), 3.6 ppm ($O-CH_3$) and 6.55-7.05 ppm (C_6H_5).

A different sequence of the same procedure may also be used to prepare block copolymers. For this purpose MMA (9.4 g/mol) was polymerized by utilizing ABME as an initiator at the concentration of 10^{-5} mol/l at 60 °C for 3 h. The resulting polymer was presumed to contain only one benzoin methyl ether moiety per macromolecular chain since propagating MMA radicals terminate mainly by disproportionation. Terminally photoactive PMMA (M_n=13.4x10^4 g/mol) was used to attempt photoinitiated block copolymerization of St (5.76 mol/l) in benzene. St containing PMMA at a concentration of 3x10^{-4} mol/l was irradiated for 3 h at 25 °C. It is interesting to note that the resulting polymer mixture gave 90 % of block copolymer

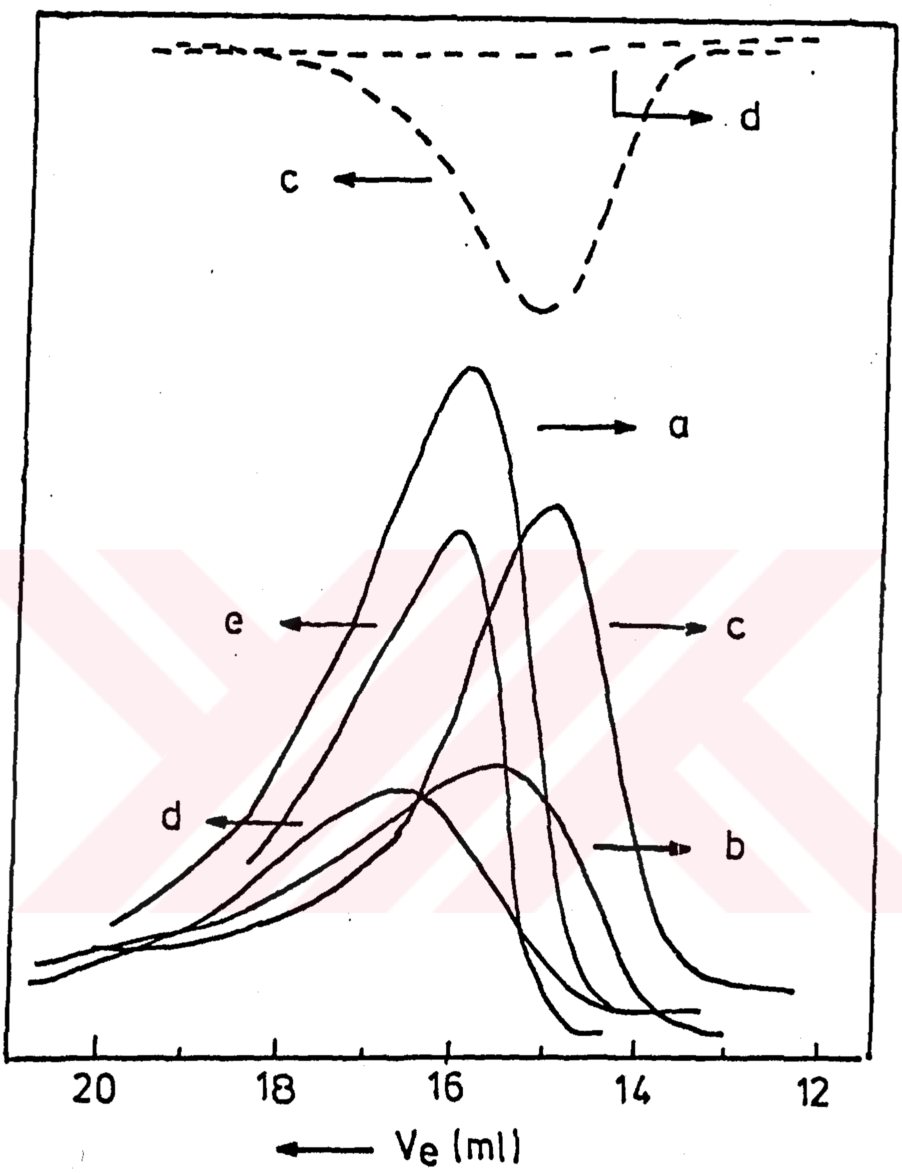


Figure 4.18. Gel permeation chromatograms recorded with the products formed on block copolymerization.

a) Prepolystyrene

b) Crude block copolymer

c) Pure block copolymer after extraction with boiling cyclohexane and acetonitrile.

d) Homopoly(methyl methacrylate) (acetonitrile soluble part)

e) Homopoly(styrene) (cyclohexane soluble part

(———) RI detection; (----) UV detection.

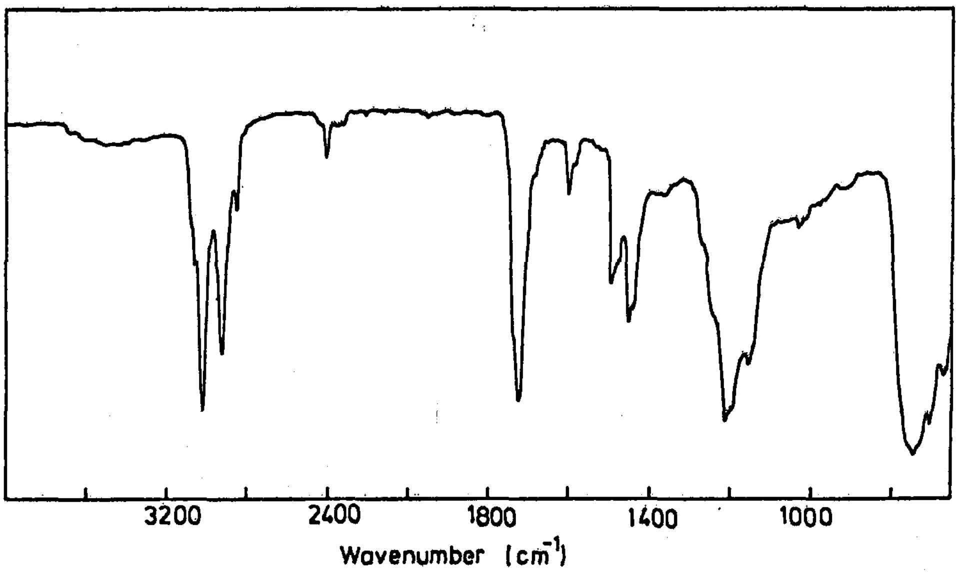


Figure 4.19. IR spectra of block copolymer.

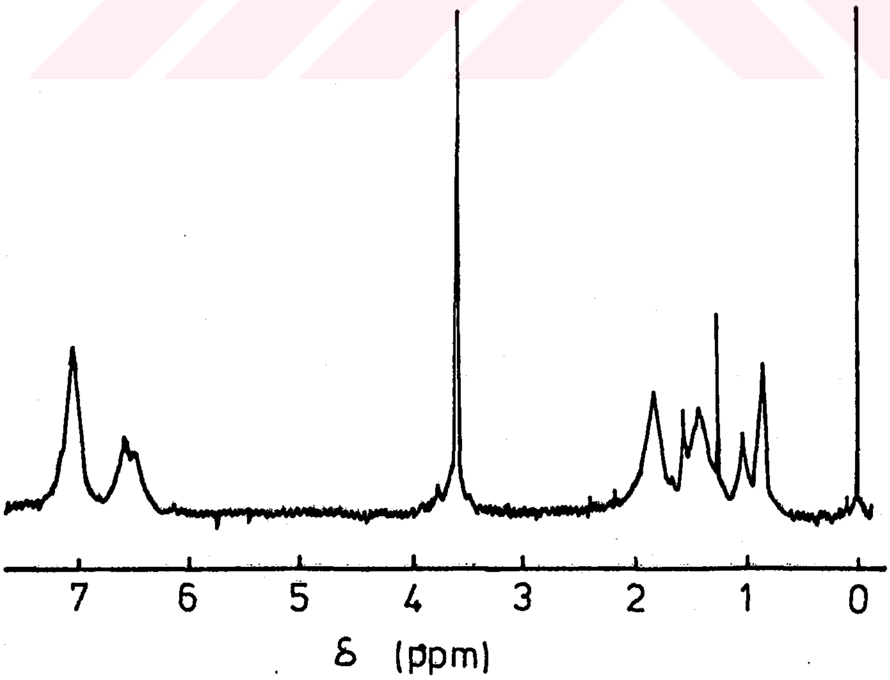


Figure 4.20. ^{1}H-NMR spectrum of block copolymer.

after extraction of homopolymers with 3 % overall St conversion. High yield of block copolymer is entirely consistent with the usual assumption that the termination reaction in styrene polymerization occurs by combination. In this way, less reactive PMMA bound alkoxybenzyl radicals also contribute to the formation of block copolymer by coupling with the propagating styryl radical derived from either benzoyl or alkoxy-benzyl radical[67].

CHAPTER V. CONCLUSIONS

It is obvious that bifunctional initiators can be synthesized by simple condensation of azo containing acid chloride with benzoin or benzoin methyl ether. Kinetic studies showed that azo-benzoin initiators exhibit initiator properties similar to that of common azo initiators except their participation in transfer reactions.

Presence of two different chromophores in the structure makes it possible to utilize these initiators for multi purposes. For instance high molecular weight photoinitiators, obtained by the decomposition of azo group in the presence of monomer, have several advantages in UV curing systems due to the less toxic properties.

In conclusion, block copolymerization via azo-benzoin initiators provides a versatile two stage method applicable to vinyl monomers. Both radicals, benzoyl and alkoxy-benzyl, although at different rates, are effective in initiating polymerization. It is clear that the efficiency of the block copolymerization greatly depends on the kinetic behavior of free radical polymerizable monomer involved in the photochemical step.

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