Synthesis of Block Copolymers via Redox Polymerization Process: A Critical Review

Temel Ozturk and Ismail Cakmak*

Department of Chemistry, Kafkas University, 36200, Kars, Turkey

A B S T R A C T

The present review gives a comprehensive account on the synthesis of block copolymers via redox initiating systems. Redox polymerization systems for the synthesis of block copolymers have been evaluated. The mechanism of initiation by a redox process is a method which is used to obtain block copolymers by various transition metals, such as Ce(IV), Mn(IIII), Cu(II), and Fe(III). Redox polymerization has found wide applications in initiating polymerization reactions and has been specifically of industrial importance. As it follows from the 'contents', in addition to the above mentioned metals, other redox polymerization systems such as hydrogen peroxide and vanadium are described as well.

CONTENTS
- Introduction
- Redox Polymerization Systems
  - Ceric Ion Redox Polymerization Systems
  - Manganese Ion Redox Polymerization Systems
  - Cupper Ion Redox Polymerization Systems
  - Hydrogen Peroxide Redox Polymerization Systems
  - Iron Ion Redox Polymerization Systems
  - Vanadium Ion Redox Polymerization Systems
  - Other Redox Polymerization Systems
- Conclusion
- References

(*) To whom correspondence to be addressed:
E-mail: ismailcakmak@gmail.com

INTRODUCTION

Polymerizations initiated by a reaction between an oxidizing and a reducing agent are called redox polymerizations. The essence of redox initiation is a reduction-oxidation process. In this process an oxidant, i.e., Ce(IV) or Mn(III) forms initially a complex by reacting simply with organic molecules which then decomposes unimolecularly to produce free radicals that initiate polymerization. Commonly used oxidants include peroxides, persulphates, peroxydiphosphate,

and the salts of transition metals. These oxidants form effective redox systems with various reducing agents like alcohols, aldehydes, amines, thiols for the aqueous polymerization of vinyl monomers. The essential features of components constituting a redox pair for aqueous polymerization are their solubility in water and fairly fast and steady liberation of active radicals [1]. Apart from the fact that low temperatures can be employed with redox systems, the reaction rate is easy to control by varying the concentration of metal ion or peroxide [2].

There are many reports in the literature on the block copolymer synthesis. Initiation by a redox process is only a method to obtain these types of polymers [3-6]. However, initiation by a polymer having functional end groups attached to the chains, resulting from redox polymerization has not been investigated widely in the literature [7,8].

The synthesis of block copolymers by redox systems exerts a number of technical and theoretical advantages over other methods. Because of the applicability at low temperatures, side reactions are minimized [9]. This method has found wide applications in initiating various polymerization reactions [10,11] and with industrial importance, e.g. low-temperature emulsion polymerizations [12,13].

Redox polymerization of vinyl monomers initiated by transition metal ions in their higher oxidation states in an aqueous medium can provide valuable information regarding the mechanistic details of the elementary steps [14]. Besides the very short induction period (almost negligible), a lower energy of activation (40-80 kJ/mol) allows the redox polymerization to be carried out under milder conditions than thermal polymerization. This lowers the possibility of side chain reactions giving high molecular weight polymers with a high yield [13].

Redox polymerization has drawn the attention of scientists for many years. Ananthanarayanan and Santappa [15] studied the kinetics of vinyl polymerization initiated by ceric ion in aqueous acidic solution. Takahashi [16] observed the redox polymerization of acrylamide initiated by ceric ammonium nitrate. Saha and Chaudhuri [17] followed the influence of the nature of the amine used as reducing agent on the polymerization of acrylonitrile in aqueous solution. Fernandez [19] followed the kinetics of ceric ion–isopropyl alcohol initiated aqueous polymerization of methyl methacrylate.

Sarac et al. [20] generated electrolytically the redox-initiating system Ce(IV)/organic acid for acrylamide polymerization. Sarac et al. [21] also made potentiometric determination of the molecular weight of polymers obtained by redox polymerization. Redox initiation has already been widely studied, mainly for polymerizations carried out in aqueous media [22,23]. Tunca [24] performed the polymerization of acrylamide using the redox reaction of Ce(IV) with $HO-CH_2-$ group containing thermo- or photosensitive azo compounds.

There are still some problems with this redox system, namely a poor solubility of such inorganic salts in organic medium (acrylic resin), the formation of slightly colored products and an expected short pot-life due to the fact that polymerization may occur already at ambient temperature [18].

REDOX POLYMERIZATION SYSTEMS

Various redox systems, such as ceric, manganese, copper, iron, vanadium ion, and hydrogen peroxide, have been used as catalysts for synthesis block copolymers via redox polymerization. Ceric-based catalysts seem to be the most versatile. The redox systems including various catalysts have also been investigated.

Ceric Ion Redox Polymerization Systems
Ceric ions in acidic media are well-known oxidizing agents for various organic substrates [25]. Also, these ions, either by themselves or in combination with reducing agents function as initiators for vinyl polymerization [26-33]. A first attempt to initiate polymerization by Ce(IV) in organic solvents was performed in 1979 by Singh et al. [34] who observed that the solvent (toluene) inhibits the redox initiating process for the polymerization of acrylonitrile. The suitable reducing agents reported in the literature are alcohols [35], polyoils [36], ketones [37], acids [38], amines [17], thiols [39], and thiourea [40]. Based on the experimental results, the following kinetic reaction schema are proposed by Nagarajan et al. [3] for vinyl radical polymerization.
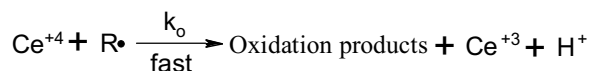
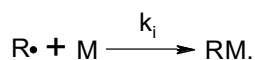I.   (a) Reaction of ceric ion with reducing agent:

$$Ce^{+4} + R \longrightarrow R\bullet + Ce^{+3} + H^+$$
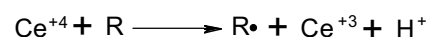
Where, R is reducing agent and R• is the organic free

radical formed from the reducing agent.

(b) Reaction of the radical with Ce^{+4} to give the oxidation products:
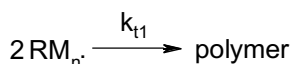
$$Ce^{+4} + R\bullet \xrightarrow[\text{fast}]{k_o} \text{Oxidation products} + Ce^{+3} + H^+$$

II. Initiation of polymerization by reaction of the free radical with monomer:

$$R\bullet + M \xrightarrow{k_i} RM\bullet$$

III. Propagation:

$$RM\bullet + M \xrightarrow{k_p} RM_2\bullet$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$
$$RM_{n-1}\bullet + M \xrightarrow{k_p} RM_n\bullet$$
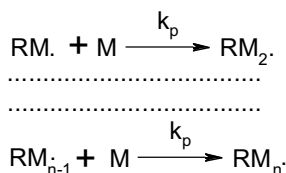
IV.   (a) Mutual termination:

$$2\,RM_n\bullet \xrightarrow{k_{t1}} \text{polymer}$$

(b) Linear termination by Ce^{+4} :

$$RM_n\bullet + Ce^{+4} \xrightarrow{k_{t2}} \text{polymer} + Ce^{+3} + H^+$$
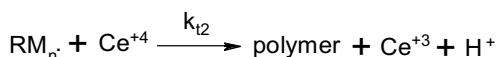
Katai et al. [41] have studied the polymerization of acrylonitrile with ceric ion-ethylene glycol redox system and proposed a mechanism for the formation of free radicals. The reaction mechanism is shown in Scheme I.

In the case of poly(ethylene glycol) (PEG) no such cleavage of the main chain could occur since, there are no 1,2-glycol units. Hence a block copolymer could be prepared by the polymerization of a vinyl monomer. The first attempt to synthesise the block copolymer was carried out by Novitskaya [42] using poly(propylene oxide)-ceric ion redox system for the polymerization of acrylonitrile. The reaction was conducted in aqueous medium at $0^{\circ}C$. Furthermore, Novitskaya and Konkin [43] have prepared the block copolymers of acrylonitrile with ethylene oxide in the presence of a redox initiating
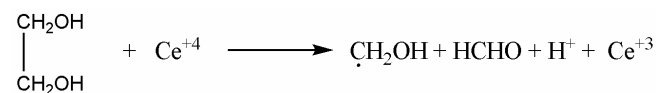
system comprising Ce^{4+} where the hydroxyl end groups of ethylene oxide units are the reducing agent.

Konkin [44] and Novitskaya [45] have obtained poly(acrylonitrile-*block*-ethylene oxide) block copolymers using Ce^{+4} salts as oxidizing agents for hydroxyl groups in the poly(ethylene oxide) prepolymer. Bi-, tri- or multi-segments block copolymers can be formed depending on the number of OH functional groups taking part in redox reactions.

Block copolymers of ethyl oxide and methyl methacrylate were prepared by redox polymerization with poly(ethyle oxide), a ceric ion as initiator, and 1,4-dioxane as solvent [46]. The copolymerization reaction gave two different products, one precipitated in methanol immediately after the reaction and the other was soluble in methanol but insoluble in water. The water-precipitated product was supposed to be the block copolymer of poly(ethylene oxide-*b*-methyl methacrylate). The GPC analysis showed that the high intensity peak had a retention time lower than that of poly(ethyle oxide) and higher than the precipitation time by methanol . Hence, it could be concluded that the molecular weight of the water-insoluble product was higher than 4,000.

Coutinho et al. [47] prepared poly(ethylene oxide-*b*-methyl methacrylate) block copolymers using dodecyl poly(ethylene oxide)-ceric ion redox system via emulsion polymerization. In these systems, dodecyl poly (ethylene oxide) have also played the role of emulsifying agent. The polymerization has been characterized by a pronounced gel effect and shown deviations from Smith–Ewart theory.
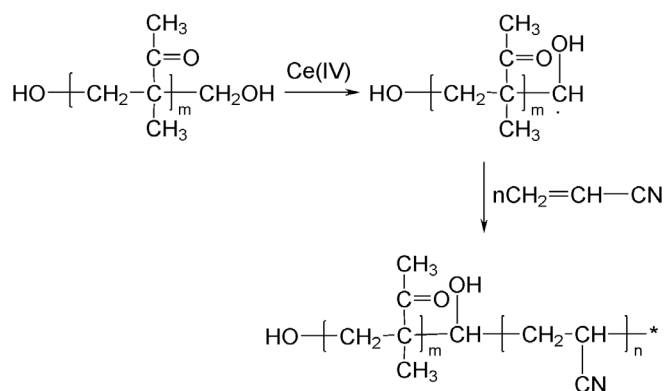
Scheme II. Copolymerization of acrylonitrile in the presence of Ce(IV) salts and ketonic resin.

Scheme I. Oxidation of ethylene glycol with Ce(IV).
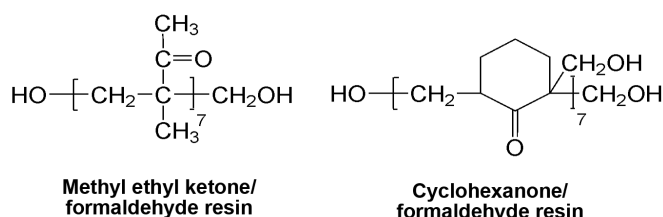
Scheme III. The structures of methyl ethyl ketone/formaldehyde and cyclohexanone/formaldehyde resins.

The copolymerization of acrylonitrile in the presence of Ce(IV) salts and ketonic resin such as methyl ethyl ketone/formaldehyde and cyclohexanone/formaldehyde resin is investigated by Akar et al. [48]. Formation of copolymer of methyl ethyl ketone/formaldehyde resin-polyacrylonitrile is proposed to proceed via free radical generation followed by vinyl polymerization of acrylonitrile, as shown in Scheme II. Ketonic resins used have the same structure as the Scheme III. The effects of temperature, time, catalyst, and monomer concentration are also investigated by Coutinho et al. [47].

Guilbault and Brooks [49] have reported the preparation of block copolymer by the reaction of hydroxyl-terminated poly(vinyl pyrrolidone) with methyl methacrylate in the presence of ceric ammonium nitrate. A patent is also issued by Guilbaut [50] for similar polymerization reactions utilizing water soluble monomers.

Since ceric ion participates readily in redox reactions with hydroxyl-containing substrates to generate free radicals [51], the hydroxyl end group on poly(vinyl pyrolidone) is considered to be the site of polymerization and thus deemed essential for block copolymer formation.

Tunca et al. [52] have used ceric ion Ce^{+4} with 4,4′-azo-bis(4-cyanapentanol) as a redox pair for the polymerization of acrylamide (AAm). The resulting polymer possesses central thermosensitive azo function which can be used for subsequent vinyl polymerization to yield block copolymers. The reaction pathways are presented as in Scheme IV.

A similar redox raction has been utilized for the preparation of acrylamide-ethyle glycol block copolymers (PAAm-PEG) containing azo groups in the main chain [7]. It is found that the azo groups retain their activity and the facile scission of these groups leads to the polymerization of vinyl monomers under suitable conditions with formation of multiblock copolymers. The reaction pathway is presented in Scheme V. The redox reaction in the presence of acrylamide yielded block copolymer with central azo groups which were decomposed on subjecting the polymer to thermolysis as shown in Scheme VI. Thermolysis in the presence of acrylamide or acrylonitrile give rise to multiphase polymer systems for which the overall structure depends on the termination mode of the second monomer polymerization.

Water-soluble polymers prepared with Ce(IV)–organic acid redox system containing amino, hydroxycarboxylic, and carboxylic acids end groups seem to be the potential source for the construction of the immunologically active controlled release drugs [13]. A Ce(IV) based redox system was shown to be a very efficient thermal initiator for acrylic polymerization [53] as shown in Scheme VII.

Redox reaction systems of Ce^{+4} salts and reducing
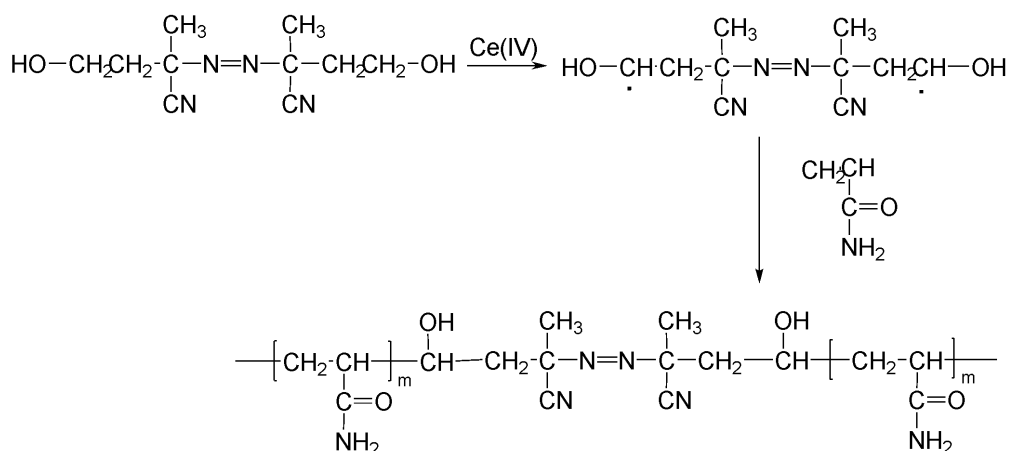
Scheme IV. Polymerization of acrylamide with 4,4'-azo-bis(4-cyanapentanol)/Ce^{+4} redox pair.

www.SID.ir
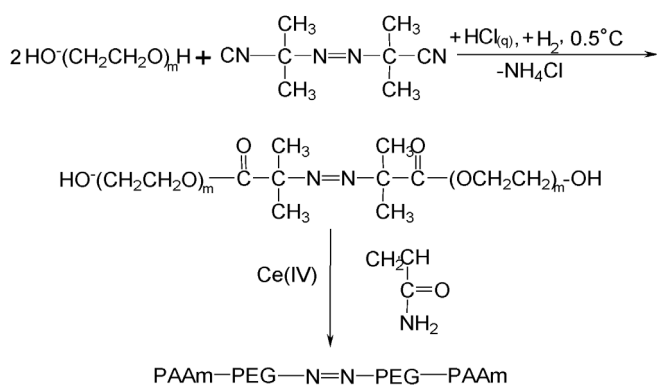
Scheme V. Polymerization of acrylamide with poly(ethylene glycol)azoester/Ce^{+4} redox system.

agents in aqueous solution are well-known initiators for vinyl polymerization. Öz and Akar [54] have used the redox initiator systems of ceric ammonium nitrate-aminomethylene phosphonic acids to initiate aqueous polymerization of vinyl monomers such as acrylonitrile, vinylacetate, acrylic acid, acrylamide and maleic anhydride. The polymerization mechanism involves complex formation between Ce^{+4} salts and reducing agent followed by the generation of free radicals which initiate the polymerization of vinyl monomers. Block copolymers are easily produced with this system.

Erbil [8] has carried out the synthesis of block copolymers of polyacrylonitrile-polyacrylamide with the use of polyacrylamide-malonic acid prepolymer which is a product of a redox polymerization initiated by the cerium sulphate-malonic acid redox pair. The effects of prepolymer concentration and daylight on the yield and molecular structure were interpreted by means of FTIR spectroscopy. Furthermore, this prepolymer along with ceric ammonium nitrate are also used to induce the radical polymerization of acrylamide which results in further chain extension. Both FTIR spectra and intrinsic viscosities of the samples have shown that the chain extension of PAAm-MA with AAm is influenced by temperature and prepolymer content.

Studer et al. [18] have cured a combination of isocyanate-acrylate and hydroxylated acrylate monomers by heating and UV-irradiation in the presence of a

Scheme VI. Thermal decomposition of PAAm-PEG-N=N-PEG-PAAm block copolymer.
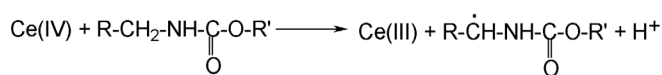

Scheme VII. Oxidation of aminomethylene phosphonic acids with Ce(IV).

Ce(IV) salt thermal initiator and an acylphosphine oxide photoinitiator.

Arslan and Hazer [55] have investigated the polymerization of methyl methacrylate (MMA) initiated by ceric ammonium nitrate in combination with polytetrahydrofuran diol (PTHF-diol) and polycaprolactone diol (PCL-diol) in aqueous nitric acid. Thus, PMMA-*b*-PTHF and PMMA-*b*-PCL block copolymers have been obtained. The polymerization reactions are presented in Scheme VIII. Also, block copolymer yield has been increased using tetrabutyl ammonium hydrogen sulphate as a surfactant. The effects of nitric acid, ceric ions, and diol concentration on the block copolymer yield have been investigated. According to their reports the block copolymers are characterized using GPC, 1H-NMR, FTIR, DSC, TGA, and fractional precipitation methods.

Hazer et al. [56] have carried out polymerization of methyl methacrylate initiated by ceric ammonium nitrate in combination with poly(glycidyl azide)-diol (PGA-diol) in aqueous nitric acid and obtained poly(methyl methacrylate)-*b*-poly(glycidyl azide) copolymer. The reaction mechanism is shown in Scheme IX.

The redox system of a ceric salt and α,ω-dihydroxy poly(dimethylsiloxane) is used by Öz and Akar to polymerize vinyl monomers such as acrylonitrile and styrene to produce block copolymers [57]. The concentration and type of α,ω-dihydroxy poly(dimethylsiloxane) has shown to affect the yield
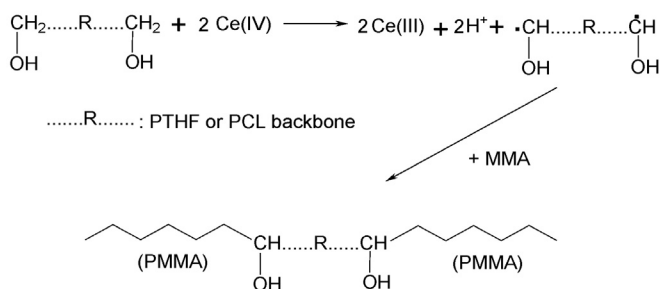
Scheme VIII. Synthesis of PMMA-*b*-PCL-*b*-PMMA block copolymer with PCL-diol/Ce(IV) redox systems.

www.SID.ir
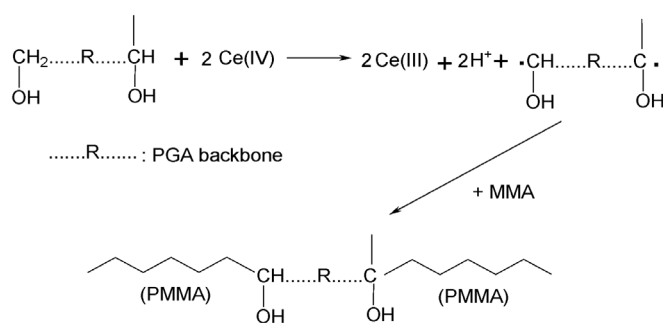
Scheme IX. Polymerization of methyl methacrylate initiated by ceric ammonium nitrate in combination with poly(glycidyl azide)-diol (PGA-diol).

and molecular weight of the copolymers. The copolymers obtained have lower glass-transition temperatures at about 208ºC and much higher contact angle values than those of the corresponding homopolymer of vinyl monomers, regarding the fact that the weight percentage of α,ω-dihydroxy poly(dimethylsiloxane) of the copolymers was in the range of 1-2%.

Asymmetric star-branched block copolymers based on polystyrene (PS), polytetrahydrofuran (PTHF), and poly(methyl methacrylate) (PMMA) were synthesized by the combination of cationic ring opening polymerization and redox polymerization methods in two steps by Arslan et al. [58]. In the first step, cationic ring opening polymerization of THF was initiated by using chain-end-multifunctionalized polystyrenes with 2, 4, and 8 benzyl bromide moieties as initiators in the presence of $AgSbF_6$ at 30ºC to obtain 3-, 5-, and 9-arms AB_2, AB_4, and AB_8 type asymmetric star-branched polymers consisting of PS (A) and PTHF-OH (B) segments. In the second step, redox polymerization of methyl methacrylate was initiated by using these asymmetric star-branched polymers as macroinitiators in the presence of Ce(IV) salt at 40ºC to obtain PS-*s*-(PTHF-b-PMMA)$_n$ (*n*= 2, 4, and 8) asymmetric star-branched block copolymers.

Thermal characterization of the polymers was done by using TGA and DSC techniques. TGA thermograms of AB_2, AB_4, and AB_8 types of PS-*s*-(PTHF-OH)$_x$ asymmetric star branched polymers have exhibited only one decomposition temperature (T_d) at 370ºC, while PTHF homopolymers have T_d at 230ºC and PS homopolymers have T_d around 400ºC. TGA

thermograms of PS-*s*-(PTHF-*b*-PMMA)$_x$ star-branched block copolymers exhibited two main decomposition temperatures (T_d's), the first at 240ºC and the second at 50ºC.

A poly[(R,S)-3-hydroxybutyrate] macroinitiator (PHB-MI) was obtained through the condensation reaction of poly[(R,S)-3-hydroxybutyrate] (PHB) oligomers containing dihydroxyl end functionalities with 4,4´-azo-bis(4-cyanopentanoyl chloride) by Arslan et al. [59]. The PHB-MI obtained in this way had hydroxyl groups at both ends of the polymer chain and an internal azo group. The synthesis of ABA-type PHB-*b*-PMMA block copolymers [where A is poly(methyl methacrylate) (PMMA) and B is PHB] via PHB-MI was accomplished in two steps. First, multiblock active copolymers with azo groups (PMMA-PHB-MI) were prepared through the redox free-radical polymerization of methyl methacrylate (MMA) with a PHB-MI/Ce(IV) redox system in aqueous nitric acid at 40ºC. Second, PMMA-PHB-MI was used in the thermal polymerization of MMA at 60ºC to obtain PHB-*b*-PMMA. When styrene (S) was used instead of MMA in the second step, ABCBA-type PMMA-*b*-PHB-*b*-PS multiblock copolymers [where C is polystyrene (PS)] were obtained. In addition, the direct thermal polymerization of the monomers (MMA or S) via PHB-MI provided AB-type diblocks copolymers with MMA and BCB-type triblock copolymers with S.

In 2002 Bajpai and Simon [60] carried out radical polymerization of styrene (S) with hydroxyl-terminated polybutadiene (HTPB) using Ce(IV) as an oxidant under nitrogen atmosphere. The variation in reaction parameters seems to have affected the yield of the product. The PS homopolymer formation under the reaction conditions used was ruled out. The cross-linking of polybutadiene chains through the styryl radical on growing block copolymer chains was suggested from viscosity and swelling measurements.

In 2005 Motokawa et al. [61] focused on the self-assembly of poly(*N*-isopropylacrylamide)-*block*-poly(ethylene glycol) (PNIPA-*block*-PEG) in water. A quasi-living radical polymerization technique including a Ce(IV) ion redox system enabled the preparation of block copolymers with relatively narrow molecular weight distributions. Five regions in the phase diagram were distinguished: a transparent sol, opaque sol, transparent gel, opaque gel, and syneresis. By examining the

extent of changes in the spectroscopic properties of a fluorescence probe, pyrene, as a function of block polymer concentration and/or temperature, and the critical association concentration as well as the partition coefficient K were determined for pyrene. The PEG chains were more swollen in water than the PNIPA chains. Dynamic light scattering measurements have also indicated that the contraction of PNIPA blocks started around 18ºC, which was consistent with the results obtained by fluorescence measurements. Preparation of PNIPA-*b*-PEG is shown in Scheme X.

The kinetic and mechanistic features of tetravalent cerium-poly(ethylene glycol) (PEG, molecular weight 6000) redox couple initiated block copolymerization of methyl methacrylate (MMA) were investigated in aqueous acidic medium in the temperature range 30-50ºC by Nagarajan et al. [62]. The block copolymerization behaviour as a function of $[Ce^{4+}]$, [PEG], [MMA], $[H^+]$, $[NO_3^-]$, and temperature were studied. The overall rate of polymerization (R_p), the rate of disappearance of Ce^{4+} (R_{Ce}), and the number average molecular weight (M_n) were determined from gravimetry, cerimetry, and gel permeation chromatography, respectively. R_p was found to bear a square dependence on [MMA] and independent from both $[Ce^{4+}]$ and $[H^+]$. R_{Ce} was found to be directly proportional to $[Ce^{4+}]$ and $[H^+]$, and independent of [MMA]. Both R_p and R_{Ce} were found to be retarded by the addition of nitrate ions, while the increase in temperature accelerated the rates. The M_n of

the block copolymer was found to depend on $[Ce^{4+}]$, [PEG], [MMA], and $[H^+]$ as well as on temperature. It was concluded that by varying the temperature and concentration of the components of the redox system, it is possible to control the rate of polymerization and the molecular weight of the resulting block copolymer.

However, as early as in 1993 Nagarajan et al. [63] studied the polymerization of acrylonitrile initiated by a new redox couple, cerium (IV)-poly(ethylene glycol) [PEG, molecular weight 6000] in aqueous sulphuric acid medium at 50ºC.

Shimizu et al. [64] in 2004 synthesized thermosensitive block copolymers of poly(*N*-isopropylacrylamide) (PNIPAM) and poly (ethylene glycol) (PEG) by the redox reaction of the hydroxyl end group of PEG with a ceric ion. The effects of polymerization temperature and NIPAM concentration on the molecular weight of block copolymers were investigated. The molecular weight of the copolymer was found to increase in an exponential manner with the increase in NIPAM concentration when the polymerization was performed below the lower critical solution temperature (LCST) of PNIPAM. At the temperature above the LCST, on the other hand, few NIPAM monomers were polymerized regardless of NIPAM concentration, and the molecular weight of the block copolymers obtained was almost the same as that of the original PEG. These results indicate that above the LCST polymeric micelles are formed during polymerization reaction, which hardly proceeds within the
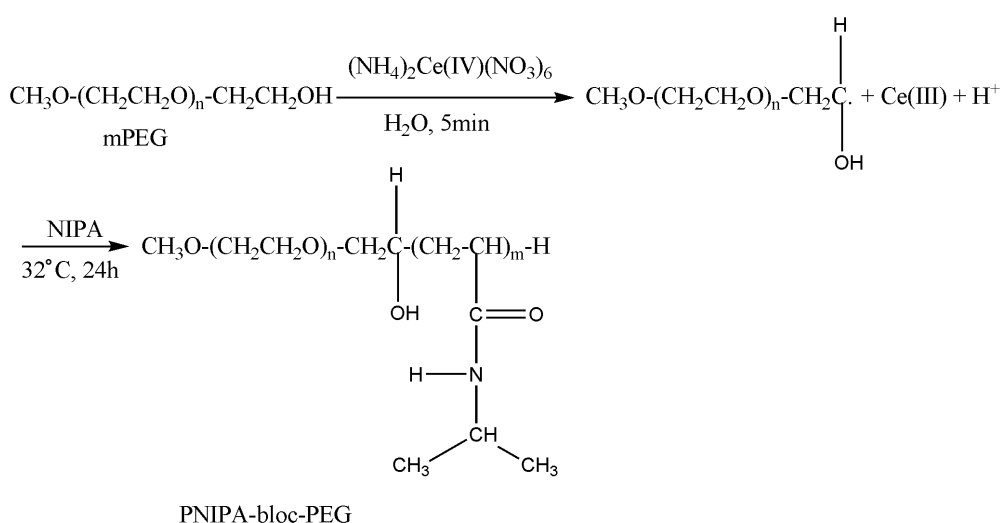
Scheme X. Synthesis of poly(*N*-isopropylacrylamide)-*block*-poly(ethylene glycol) block copolymer via poly(ethylene glycol)/Ce(IV) redox pair.

hydrophobic cores of the polymeric micelles.

Sui and Gu [65] in 2003 had conducted the synthesis of polyacrylonitrile-*b*-poly(ethylene oxide) (PAN-*b*-PEO) diblock copolymers by sequential initiation and Ce(IV) redox polymerization using amino-alcohol as the parent compound. In the first step, amino-alcohol potassium with a protected amine group initiated the polymerization of ethylene oxide (EO) to yield poly(ethylene oxide) (PEO) with an amine end group (PEO-NH$_2$) which was used to synthesize a PAN-*b*-PEO diblock copolymer with Ce(IV) that takes place in the redox initiation system. A PAN-poly(ethylene glycol)-PAN (PAN-PEG-PAN) triblock copolymer was prepared by the same redox system consisting of ceric ions and PEG in an aqueous medium. The propagation of the PAN chains was found to be dependent on the molecular weight and concentration of the PEO prepolymer. The PEO and PAN blocks was shown to have influence on crystallization in the presence of the other one, and the crystallinity of the PEO chain segments in the PAN-*b*-PEO diblock copolymer being higher than the PAN-PEG-PAN triblock copolymer with the same PEO content. It has been concluded that the PEO segments have secondary crystallization phenomena that are dependent on the PEO content in the block copolymer. The mechanism is shown in Scheme XI.

Acrylamide polymerization initiated with a redox initiation system consisting of ceric ion and ethyl *N*, *N*-diethyldithiocarbamyl acetate (EDCA) was studied ear-

lier by Xu and Qiu in 1997 [66]. It had been found that the polymerization rate equation was in good agreement with that of a redox initiated polymerization, and the overall activation energy of the polymerization was determined to be 25.2 kJ.mol^{-1}. Accordingly, the system belonging to a redox initiator, it was revealed that the *N,N*-diethyldithiocarbamyl radicals produced from the redox reaction of EDCA with ceric ion could initiate acrylonitrile (AN) polymerization and form the end group on PAN. The resulting PAN was then photopolymerized with butyl acrylate (BE) to form PAN-*b*-PBA block copolymer.

The polyacrylonitrile-poly (ethylene glycol)-polyacrylonitrile (PAN-PEG-PAN) block copolymers have been synthesized in 2007 by polymerization of PAN triggered by the help of redox reaction of the ceric ion system [67].

An acrylic block copolymer resin emulsion comprised of the reaction of a water-soluble polyol (polyethylene glycol) with a hydrophobic or hydrophilic acrylic vinyl monomer or their combination using Ce (IV) redox initiator in an acidic medium at pH 3-4 at 30-40ºC over 2-3 h in dark and inert atmosphere has been reported to be conducted by a known iodometric titration for completion of polymerization. The resin emulsion is used in leather finishing, paints, and sizings [68].

Kizilcan et al. [69] have produced block copolymers of α,ω-diamine polydimethylsiloxane (DA-PDMS) and polypyrrole by the polymerization of pyrrole with the
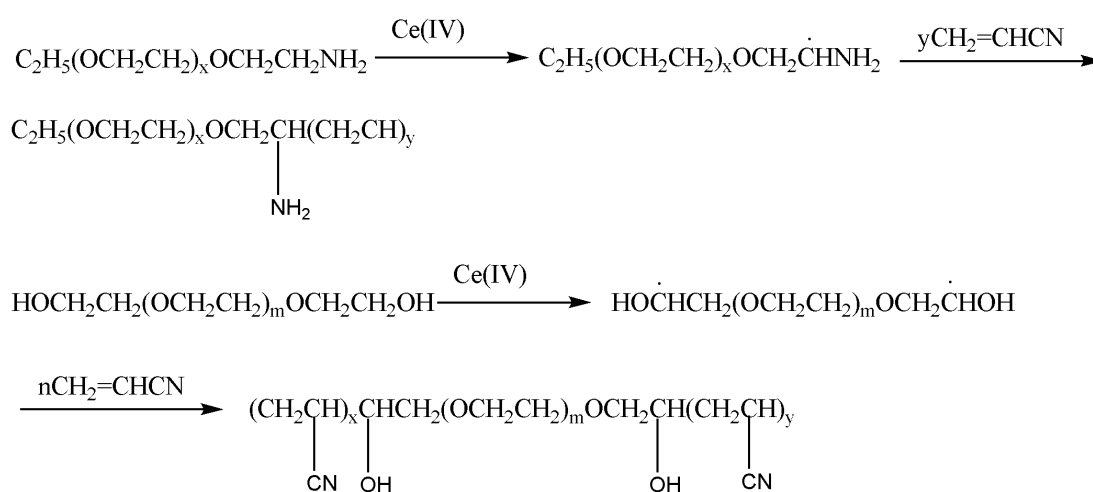
Scheme XI. Synthesis of poly(acrylonitrile)-*block*-poly(ethylene glycol) block copolymer via poly (ethylene glycol)/Ce(IV) redox pair.

redox system of ceric salt/DA-PDMS. The properties of the copolymers may be regulated by the ratio of DA-PDMS/pyrrole/$Ce_4(NH_4)_2(NO_3)_6$.

Yagci et al. [70] have carried out the redox initiated free-radical polymerization of methyl methacrylate (MMA) with allyl alcohol 1,2-butoxylate-*b*-ethoxylate (AABE) using cerium(IV) ammonium nitrate/nitric acid (HNO_3) redox system to yield AABE-*b*-PMMA copolymers.

The ceric ion redox method and the atom transfer radical polymerization (ATRP) have also been applied to synthesize novel thermally sensitive ABA block copolymers of poly(*N*-isopropylacrylamide) (PNIPAAm) and polypropylene glycol (PPG) by using PPG with molecular weight of 2000 g/mol as a precursor [71].

Poly(ethylene oxide) macromonomer containing amine end group (PEO-NH_2) has been obtained by anion polymerization using alkali amine as parent compound. The diblock copolymer of polyacrylonitrile-poly(ethylene oxide) (PAN-b-PEO) is prepared using Ce(IV)/PEO-NH_2 as redox initiation system in the aqueous solutions [72].

Arslan et al. [73] in 2002 obtained poly [(R,S)-3-hydroxybutyrate] oligomers containing dihydroxyl (PHB-diol), dicarboxylic acid (PHB-diacid) and hydroxyl-carboxylic acid (a-PHB) end functionalities by an anionic polymerization of β-butyrolactone (β-BL). The ring-opening anionic polymerization of β-BL was initiated by a complex of 18-crown-6 with γ-hydroxybutyric acid sodium salts (for PHB-diol and a-PHB) or succinic acid disodium salt (for PHB-diacid). Dihydroxyl functionalization was formed by the termination of polymerization with bromoethanol or bromodecanol while the others were conducted by protonation. Hydroxyl and/or carboxylic acid functionalized PHB oligomers with ceric salts were used to initiate the polymerization of methyl methacrylate (MMA). PHB-*b*-PMMA block copolymers obtained by this way were purified by fractional precipitation. The block copolymers can be used as compatibilizers in PMMA and PHB blends.

Polymerization and copolymerization of vinyl monomers, such as acrylamide, acrylonitrile, vinyl acetate, and acrylic acid, in a redox system of Ce(IV) and organic reducing agents containing hydroxy groups were studied by Atici et al. [74]. The reducing compounds were PEG, Ixol B251, and depolymerized

PET and block copolymers were produced with them. Physical properties, such as solubility, water absorption, UV resistance and viscosity were reported. The yield of acrylamide polymerization and the molecular weight of the copolymer increased considerably when about 4% vinyl acetate was added into the acrylamide monomer. However, the molecular weight of the copolymer was reported to be decreased when 4% vinyl acetate was added into the acrylonitrile monomer.

By using the redox reaction between Ce(IV) and terminal -CH_2OH groups of polyethylene oxide, block copolymers with the composition of poly(*N*-isopropylacrylamide) (PNIPAAm) and poly(ethylene oxide) was prepared by Lee et al. [75]. The aqueous solution of the block copolymers exhibited thermal phase transition higher than the PNIPAAm homopolymer.

Topp et al. [76] in 1997 obtained thermosensitive micelles with dimensions of 60-120 nm and a narrow size distribution from aqueous solutions of block-copolymers of poly(ethylene glycol) (PEG, M_n=5.0-12.0 $\times$ 10^3) and poly(*N*-isopropylacrylamide) (PNIPAAm, M_n = 0.7-3.8 $\times$ 10^3) after heating the solution above the LCST of the copolymer (29-31°C). The block copolymers were synthesized in an aqueous environment at 50°C, using a ceric ion redox system to initiate the radical polymerization of NIPAAm at the end-groups of PEG. Because the LCST of PNIPAAm is already lower than 50°C during the initial stage of the polymerization micelles were formed. Propagation proceeded via an emulsion type polymerization in which NIPAAm diffused from the solution into the core of the micelles. This led to block copolymers with a narrow molecular weight distribution (M_m/M_n=1.04-1.15). These micellar systems had a good potential to be used in drug delivery.

In the same year Nagarajan and Srinivasan [77] prepared a series of block copolymers of polyethylene glycol (PEG) with methyl methacrylate (MMA) using a redox system consisting of ceric ion and PEG of various molecular weights in aqueous medium. The block copolymerization was carried out under conditions with no homopolymerization of MMA by Ce^{4+}. The triblock nature of the block copolymers was ascertained through the cleavage of the ether linkage of the PEG segment.

Prior to the above publication Nagarajan and Srinivasan [78] reported the synthesis of novel block copolymers of poly(ethylene glycol) (PEG) with acrylamide (AAm) and methacrylic acid (MAA) using a

redox system consisting of ceric ions and PEG in aqua acidic medium. The molecular weight of PEG in the redox system was varied to obtain a series of block copolymers with differing molecular weights of PEG segments. The polymerization proceeded via macroradical generation. This macroradical acted as a redox macroinitiator for the block copolymerization of the vinyl monomers.

Tauer [79] in 1996 prepared poly (ethylene oxide)-*b*-poly(styrene) block copolymers with the redox initiation system poly(ethylene glycol)/Ce^{4+}.

Tunca [80] also used hydroxyl functional azo compounds as reducing agents in redox polymerization of methyl methacrylate (MMA) in conjunction with ceric ammonium nitrate. Kinetic measurements were followed by gravimetric method, at lower conversions, not exceeding 10% conversion. The homopolymers which contain thermo- and photolabile azo groups were utilized with different comonomers to give block or graft copolymers depending on termination mechanism of homopolymerization.

Hazer et al. [81] carried out the redox polymerization of methyl methacrylate in 1992 using Ce(IV) with poly(oxyethylene) having azo and hydroxy functions to yield methyl methacrylate-oxirane block copolymers with labile azo linkages in the main chain. The kinetics of the redox polymerization was detected. These prepolymers were being used then to initiate the radical polymerization of styrene through the thermal decomposition of the azo group resulting in the formation of multiblock copolymers.

Some years later Wang et al. [82] prepared PEO-*b*-PBA [PEO: poly (ethylene oxide); PBA: poly(butyl acrylate)], an amphiphilic block copolymer by redox radical polymerization. The result revealed the existence of PEO and PBA segments in purified block copolymer. With the introduction of PBA non-crystalline segments, the crystallinity of PEO was decreased. It was found that the emulsifying volume and type were dependent on the amount of block copolymer and the PEO content in block copolymer. Under a certain range the emulsifying volume increases with an increase in the PEO content. It was found that the higher the PEO content in block copolymer, the stronger was the water absorptivity.

Chen et al. [83] in 2005 reported the preparation of PNIPAAm-*b*-PPG-*b*-PNIPAAm [poly(*N*-isopropylacrylamide)-*block*-polypropylene glycol-*block*-poly(N-iso-

propylacrylamide)] triblock copolymers by redox polymerization. The results have shown that the LCST of the copolymers is 32°C which is consistent with that of the pure PNIPAAm. The copolymers can form a vesicular structure in an aqueous solution by self-assembly. The hollow structure of the PNIPAAm-*b*-PPG-b-PNIPAAm vesicles combined with the temperature-sensitive property might enable many potential applications of the vesicles.

Manganese Ion Redox Polymerization Systems

Mn(III) in the form of pyrophosphate [84], sulphate [84], perchlorate [86] and acetate [87] has received attention as an oxidant in the presence of a number of organic substrates such as malonic acid, isobutyric acid, cyanoacetic acid, glycerol [88], and ethylene glycol [89] for the polymerization of various monomers in aqueous media, Mn(III) reacts with simple organic molecules to form a complex that decomposes unimolecularly to produce a free radical that initiates polymerization [9].

According to a report by Cakmak [9] in 1993 a redox polymerization of acrylonitrile with poly(ethylene glycol) using Mn(III) as catalyst was carried out to yield poly(ethylene glycol-*b*-acrylonitrile). The polymerization was then suggested to proceed according to the following Scheme XII.
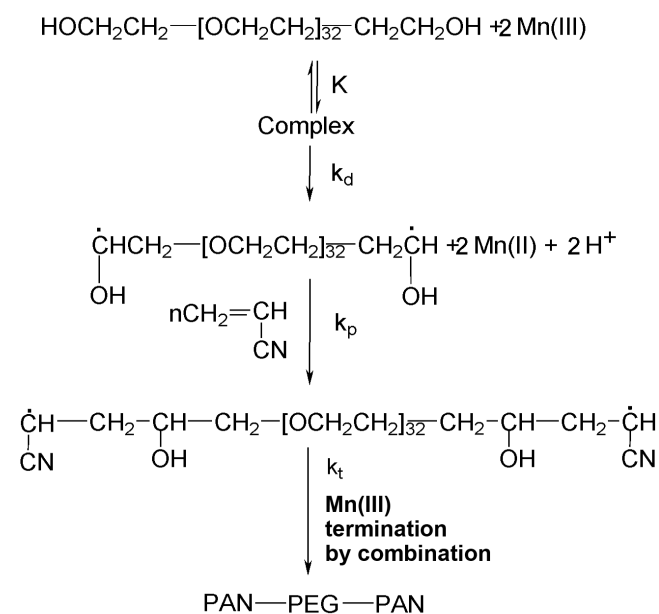
Scheme XII. Synthesis of poly(acrylonitrile)-*block*-poly(ethylene glycol) block copolymer via poly(ethylene glycol)/Mn(III) redox couple.

It was shown that in the first step, Mn (II)/methylol reaction occurs and free radicals are generated. These free radicals initiate the polymerization of acrylonitrile, Both the termination of growing chains by Mn (III) (linear termination) or by combination (mutual termination) could be possible depending on the Mn(III) concentration.

ABA type triblock copolymers comprising poly(ethylene oxide) as the A component and the poly(acrylonitrile), poly(acrylamide), or poly(methyl methacrylate) as the B component were prepared via redox initiation [9]. In aqueous polymerization, these block copolymers were obtained by initiating the polymerization of AN, AAm or MMA with poly(ethylene glycol) in the presence of Mn(III) ions. CH_3COOH and H_2SO_4 were added to the reaction medium to increase the stability of the Mn(III) ions [1].

Cakmak [90] reported in 1994 the redox polymerization of AN using Mn(III) with PAAm having terminal carboxyl groups to yield block copolymers of PAN and PAAm. The polymerization mechanism which was then suggested to proceed is shown in Scheme XIII.

Some years later Rai et al. [14] studied the polymerization of acrylonitrile, initiated by the free radicals formed in situ in the Mn (III)-glycine redox system, in aqueous sulphuric acid medium in the temperature range of 40-55ºC.

Nagarajan et al. [91, 92] in 1998 reported the synthesis of novel block copolymers of polyethylene glycol (PEG) with various vinyl monomers namely acrylonitrile, acrylamide, methyl methacrylate and methacrylic acid using Mn^{3+}-PEG redox system in aqueous acidic medium. They postulated that the polymerization proceeded via a macroradical generation, which acted as a redox macroinitiator for the block copolymerization of vinyl monomers. The triblock nature of the block copolymers was established through the cleavage of the ether linkage of the PEG segments.

Redox polymerization of methyl methacrylate using Mn(III) with polyethylene glycol having azo and hydroxy functions was carried out to yield ethylene glycol-methyl methacrylate block copolymers with labile azo linkages in the main chain by Cakmak [93]. These prepolymers were used to initiate free-radical polymerization of styrene through thermal decomposition of the azo groups, resulting in the formation of multiblock copolymers. Successful blocking has been confirmed by
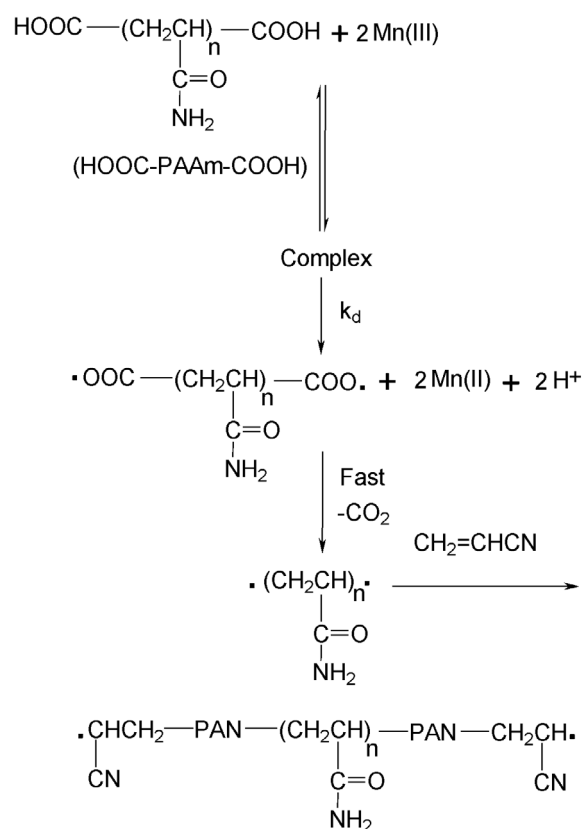
Scheme XIII. Synthesis of poly(acrylamide)-*b*-poly(acrylonitrile) block copolymer via Mn(III) / poly(acrylamide) possessing carboxyl groups.

fractional precipitation, a strong change in the molecular weight, and spectral measurements.

Redox-initiated free-radical polymerization of methyl methacrylate (MMA) and acrylamide (AAm) with poly(ethylene glycol) (PEG) using Mn(III) as reduction agent was carried out by Cakmak [94] to yield PMMA-*block*-PEG-*block*-PMMA and AAm-*block*-PEG-*block*-AAm triblock copolymers.

Cupper Ion Redox Polymerization Systems
Narita et al. [95] have obtained poly(styrene-*b*-methyl methacrylate) using Cu(II) ions as oxidizing agents for imino groups in the 2,2′-azo-bis[(2-imidazolin-2-yl)propane]dihydrochloride. The reaction scheme is shown in Scheme XIV. Polysiloxanes with terminal or pendent aldehyde functionality were used as components of copper salt-based redox initiation systems by Kim et al. [96] to prepare block, graft, and cross-linked copolymers containing poly(4-vinylpyridine) and polysiloxane segments. The block and graft copolymers
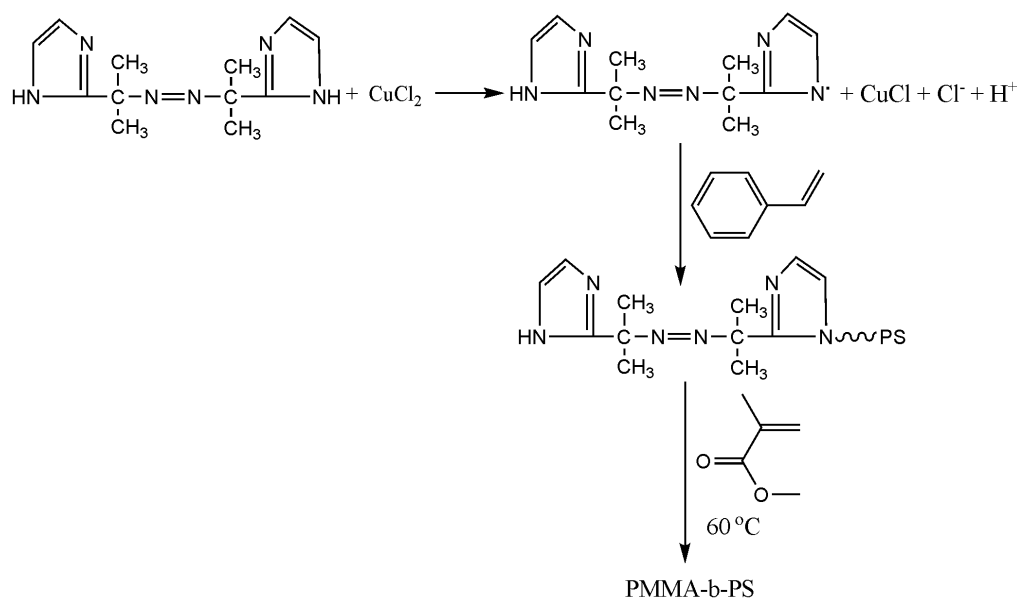
Scheme XIV. Synthesis of poly(styrene-*b*-methyl methacrylate) block copolymer using Cu(II)/ 2,2'-azo-bis[(2-imidazolin-2yl)propane] dihydrochloride redox couple.

form very viscous solutions in dilute HCl and have useful anti-foam activity.

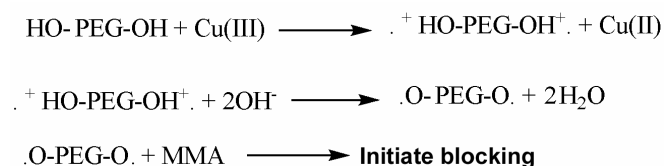Silicone segments containing alkene side chains or end-groups were prepared in the usual way by polycondensation using an acid or base catalyst. The double bonds of the alkene groups are oxidized to carbonyls which are then used to initiate vinyl monomer polymerization and link the siloxane with the vinyl segments. This initiation step was based on a redox system of copper (II) salts which generates free radicals on the alpha carbons next to the carbonyl groups. This copolymerization process was reported to be relatively fast to give high yields [97].

Acrylonitrile-methacrylic acid block copolymer and acrylamide-acrylonitrile block copolymer were prepared and reported in 1981 by Jiang et al. [98] using 4,4′-diphenyltetraazonium fluoroborates and Cu^{2+} as initiators. Similarly, the synthesis of acrylamide-methyl acrylate block copolymer was reported as well.

Block copolymers of methyl acrylate (MA) and poly(ethylene glycol) (PEG) have been obtained by Liu et al. [99] using a novel redox system-potassium diperiodatocuprate(III)[DPC]/PEG system in alkaline aqueous medium. Block copolymers with a high percentage of blocking were obtained, which indicated that the DPC/PEG redox system was an efficient initiator for this blocking. The effects of different factors on the

blocking parameters were examined. The overall activation energy of this blocking was calculated to be 55.12 kJ/mol. The initiation mechanism was proposed as in Scheme XV.

A redox system of potassium diperiodatocuprate (III) (DPC)/poly(diethylene glycol phthalic anhydride) (PPAG) was employed to initiate block copolymers of methyl acrylate (MA) and PPAG in alkaline medium by Bai et al. [100]. Block copolymers with high total conversion were obtained, which indicated that potassium diperiodatocuprate (III)/poly(diethylene glycol phthalic anhydride) redox pair is an efficient initiator for this blocking. The kinetics of block copolymerization and total conversion at different conditions (concentration of reactants, temperature, concentration of potassium diperiodatocuprate (III), and reaction time) were investigated. The results have indicated that the best reaction conditions were as follows: reaction time= 40 min, reac-

$$HO\text{-}PEG\text{-}OH + Cu(III) \longrightarrow {}^{\cdot +}HO\text{-}PEG\text{-}OH^{\cdot}. + Cu(II)$$

$${}^{\cdot +}HO\text{-}PEG\text{-}OH^{\cdot}. + 2OH^{-} \longrightarrow {}^{\cdot}O\text{-}PEG\text{-}O. + 2H_2O$$

$${}^{\cdot}O\text{-}PEG\text{-}O. + MMA \longrightarrow \textbf{Initiate blocking}$$

Scheme XV. Block copolymerization of methyl acrylate (MA) and poly(ethylene glycol) (PEG) using potassium diperiodatocuprate(III)[DPC]/PEG redox system.

tion temperature= 35ºC, concentration of potassium diperiodatocuprate (III)= 3.12×10^{-3} mol/L, and the reactants concentration=2.45 mol/L. The equation of the polymerization rate (R_p) was as follows: R_p= k[methyl acrylate](1.63)[potassium diperiodatocuprate (III)/poly (diethylene glycol phthalic anhydride)](0.67), that the overall activation energy of block polymerization was 44.57 kJ/mol.

Block copolymers of methyl acrylate (MA), methyl methacrylate(MMA) and poly(diethylene glycol phthalic anhydride)(PPAG) were synthesized by Bai et al. [101] and reported in 2005 using a novel redox system-potassium diperiodatocuprate(III)[DPC]/PPAG in alkali medium. The block copolymers with high total conversion were obtained which indicated that DPC/PPAG redox system is an efficient initiator for this blocking. The overall activation energy of this blocking is 44.57 kJ/mol. The block copolymer was used as the compatibilizer in blends of PMMA and nylon 6.

Hydrogen Peroxide Redox Polymerization Systems
The potassium or sodium salt of PEO xanthate with H_2O_2 were used in AN [102,103] and MMA [104] polymerization in sulphuric acid media. The synthesis of block copolymers was carried out in aqueous medium in the presence of H_2SO_4 using PEO-xanthate as reducing agent and H_2O_2 as oxidizer. The oxidation of xanthate ions results in the formation of active centers on sulphur atoms, which then they undergo isomerization and bring about active centres on carbon atoms [102,105]. Wodka [102,106] has obtained polyacrylonitrile (PAN)-PEO block copolymers using PEO containing xanthate groups and H_2O_2 redox system.

Wodka et al. [107] also prepared acrylonitrile-polyethylene glycol block copolymer fibres with low surface charge using H_2O_2-polyethylene glycol xanthate redox systems. The effects of molecular weight and xanthate concentration of H_2O_2-polyethylene glycol xanthate on the compound of acrylonitrile-polyethylene glycol block copolymer were detected. Acrylonitrile-polyethylene glycol block copolymer of similar chemical compound was formed in the presence of H_2O_2-polyethylene glycol xanthate containing 2 xanthate groups at equal xanthate concentration independent of the molecular weight. Increasing the molecular weight of H_2O_2-polyethylene glycol xanthate increased the polyacrylonitrile segment length and decreased the acrylonitrile-

$$Fe^{2+} + H_2O_2 \longrightarrow [HO \cdot OH]Fe^{3+} \longrightarrow Fe^{3+} + OH^- + \cdot OH$$
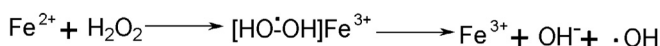
Scheme XVI. Mechanism of the reaction between hydrogen peroxide and ferrous ion.

polyethylene glycol block copolymer yield. The average length of these segments in acrylonitrile-polyethylene glycol block copolymer prepared with H_2O_2-polyethylene glycol xanthate containing only 1 xanthate group was higher than with bifunctional H_2O_2-polyethylene glycol xanthate.

Fenton's reagent, the combination of H_2O_2 and ferrous salt has been applied to the oxidation of many organic compounds including alcohols, glycols, aldehydes, ethers, esters, and amines [108]. As shown in Scheme XVI, a mechanism for the reaction between hydrogen peroxide and ferrous ion involves single-electron transfer from the ferrous ion to the peroxide with the dissociation of oxygen–oxygen bond and generation of a hydroxyl radical and a hydroxyl ion [109,13]. In the presence of sufficient monomer, all the generated OH radicals can initiate polymerization [13].

Iron Ion Redox Polymerization Systems
Polymers containing hydroperoxy groups at chain ends with Fe^{+2} were used as redox macro initiators for the block copolymerization of vinyl monomers [110-116]. Catula et al. [117,118] in mid seventies prepared the hydroperoxide terminated poly (styrene) by a reaction sequence as shown below. Reacting polymeric hydroperoxide with ferrous sulphate in the presence of a second monomer afforded block copolymers as in Scheme XVII.

The redox system ferric salt/acyl hydrazide had been used to obtain a poly(aminotriazole-*block*-acrylonitrile) block copolymer in 1962 [119]. The formation of free radicals by the reaction of terminal acyl hydrazide groups of poly(aminotriazole) $RCONHNH_2$ and Fe(III) are demonstrated in Scheme XVIII.

At the same time Iwakura et al. [120] obtained block copolymers of PAN and polyaminotriazole, using Fe(III) ions as oxidizing agents, while the amino groups of polyaminotriazole prepolymer were reductors.

In 2007 Liu et al. [121] have reported the interfacial-initiated polymerization of styrene in inversed emulsion with cumene hydroperoxide (CHPO) and ferrous sul-
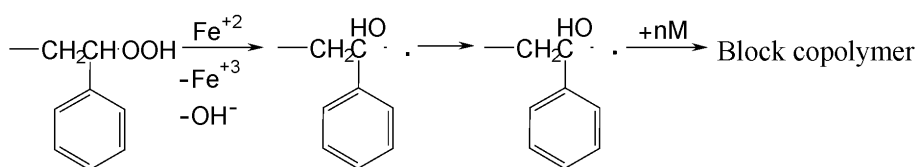
Scheme XVII. Synthesis of block copolymers via Fe^{+2}/hydroperoxy containing polymers.

phate (FeSO$_4$)/disodium ethylenediaminetetraacetate (NaEDTA)/sodium formaldehyde sulphoxylate (SFS) as the redox initiation system. The water-soluble Fe^{2+}-NaEDTA-SFS acted as the reducing component and the oil-soluble CHPO as the oxidant component of the redox initiation system.

Bera and Saha [122] in 1998 studied the aqueous polymerization of acrylamide by Fe(III)-thiourea redox couple in homogeneous conditions as well as by loading Fe(III) ions in the interlayer spaces of montmorillonite. A dramatic effect was observed in the latter case, resulting in a very high degree of polymerization. The yielding polymers having high intrinsic viscosity were considered due to imposed constraint on linear termination process. The technique, in general, demonstrates a promising method of achieving high molecular weight polymers by redox initiators.

Paik et al. have combined ATRP with a redox initiated system [123]. Vinyl acetate (VAc) was polymerized in the presence of CCl$_4$/Fe(OAc)$_2$/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) to yield pVAc with trichloromethyl end groups (M$_n$=3600; M$_w$/M$_n$=1.81). The polymer obtained was dissolved in styrene and block copolymerized by ATRP to form polyVAc-*b*-polyS (M$_n$=24,300; M$_w$/M$_n$=1.42).

Nabekura and Shimizu [124] have prepared block copolymers by redox polymerization vinyl chloride, optionally comonomers and ferrous sulphate in the presence of the peroxides HO$_2$CR$_1$R$_2$O$_2$R$_3$R$_4$CO$_2$H (R$_{1-4}$ = H or alkyl groups) to give peroxides having terminal vinyl chloride polymers and block polymerization with comonomers by thermal decomposition of the peroxides.

Jiang et al. [98] have prepared acrylonitrile-methacrylic acid block copolymer and acrylamide-acrylonitrile block copolymer by using 4,4′-diphenylte-

RCONHNH$_2$ + Fe(III) $\longrightarrow$ RCO$\dot{N}$NH$_2$ + Fe(II) + H$^+$

Scheme XVIII. Ferric salt/acyl hydrazide redox system.

traazonium fluoroborates, Fe^{2+} as initiators. Similarly, acrylamide-methyl acrylate block copolymer was prepared.
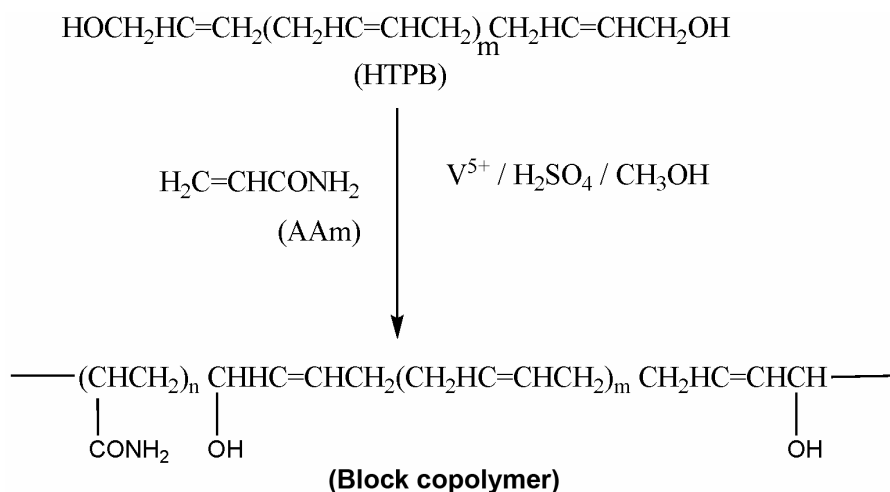
Living polymers of styrene or dimethylstyrene were treated with azobisisobutyronitrile to give polymers having reactive end azo or OH groups, respectively, which act as radical initiators in block copolymerization. The block copolymerization of the hydroxy polymer was also facilitated by the presence of iron(III) acetylacetonate redox catalyst. The block copolymers prepared were polystyrene-methyl acrylate block copolymer, polystyrene-methyl methacrylate block copolymer, polystyrene-vinyl acetate block copolymer, and poly(dimethylstyrene)-butyl acrylate block copolymer [125].

Vanadium Ion Redox Polymerization Systems
Skaria et al. [126] in 1997 synthesized macro reticular glycidyl methacrylate-ethylene glycol dimethacrylate (GMA-EGDM) copolymers of controlled particle size by suspension polymerization. Vanadium ion was chelated on the modified copolymers. The vanadium chelated copolymers were used in combination with cyclohexanone as redox reagent for the free radical polymerization of acrylamide at 30ºC. In the presence of cyclohexanone the polymeric vanadium complex initiates the polymerization of acrylamide.

Bajpai et al. [127] in 2004 used pentavalent vanadium and hydrophobic hydroxy-terminated polybutadiene (HTPB) as a macroredox initiator for polymerization of styrene in methanolic sulphuric acid medium at 35ºC. The product was fractionated with petroleum ether and benzene. The homopolystyrene formation was not observed. Cross-linking through growing polystyrene chains was inferred.

Later Bajpai and Dixit [128] synthesized block copolymers of butadiene and acrylamide (AAm) by radical initiation using the hydroxy terminated polybutadiene (HTPB) and ammonium meta vanadate (AMV) macro redox initiator pair in heterogeneous medium in

Archive of SID

Ozturk T. et al.   Synthesis of Block Copolymers via Redox ...

$$HOCH_2HC=CH_2(CH_2HC=CHCH_2)_m CH_2HC=CHCH_2OH$$

(HTPB)

$$H_2C=CHCONH_2$$

(AAm)

$$V^{5+} / H_2SO_4 / CH_3OH$$

———(CHCH_2)_n CHHC=CHCH_2(CH_2HC=CHCH_2)_m CH_2HC=CHCH———
          | | |
        CONH_2   OH   OH

(Block copolymer)

Scheme XIX. Synthesis of block copolymers of butadiene and acrylamide by radical initiation using the hydroxy terminated polybutadiene and ammonium meta vanadate macroredox initiator pair.

the presence of sulphuric acid/methanol at 35ºC in air and under nitrogen atmosphere. The homopolymer of AAm was not formed under these reaction conditions. The yield of block copolymer decreased on dilution with methanol. No copolymerization was observed in other solvents, namely DMF, DMSO, CHCl_3, and toluene. Self-assembly of amphiphilic block copolymers was evidenced by swelling, solubility, and viscosity measurements. The reaction pathway is shown in Scheme XIX.
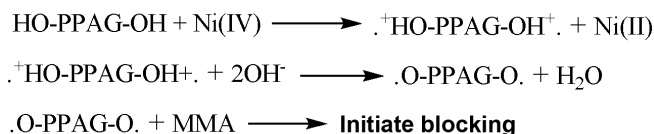
Other Redox Polymerization Systems
Liu et al. have synthesized the block copolymers of methyl methacrylate (MMA) and poly(diethylene glycol phthalic anhydride) (PPAG) by using a novel redox system-potassium diperiodatonickelate(IV) [DPN]/PPAG system in an alkaline medium [129]. The mechanism is presented in Scheme XX.

Block copolymers with high percentage of blocking are obtained, which indicate that DPN/PPAG redox system is an efficient initiator for this blocking. The overall activation energy of this blocking is calculated to be 55.12 kJ/mol.

Redox reaction between the thiol group at one end of poly(vinyl alcohol) (PVA) and potassium bromate has initiated polymerization of several monomers in water, yielding block copolymers having the roly(vinyl alcohol) as one component. The block copolymers thus obtained showed behaviour obviously different from the blend systems of PVA and corre-

sponding homopolymers. The block copolymer show slow phase separation in aqueous solution and gives transparent films compared with the homopolymer blend that does not give films due to fast phase separation. Although PVA is not compatible with starch, the block copolymer of PVA with PAAm which is compatible with starch has shown considerable improvement in compatibility of PVA with starch. The blend of starch with the block copolymer has given more transparent and tougher films than the blend of starch with PVA [130].

Okaya et al. [131] have investigated the aqueous polymerization of acrylamide initiated by a redox system of cysteine containing a thiol group and ammonium persulphate. This is a model of a redox initiator system composed of poly(vinyl alcohol) having a thiol group at one end and ammonium persulphate which polymerized many monomers yielding various block copolymers. The activation energy of over-all rate of polymerization is 4 kcal.mol^{-1} which indicates a typical redox initiator

$$HO-PPAG-OH + Ni(IV) \longrightarrow .^+HO-PPAG-OH^+. + Ni(II)$$

$$.^+HO-PPAG-OH+. + 2OH^- \longrightarrow .O-PPAG-O. + H_2O$$

$$.O-PPAG-O. + MMA \longrightarrow \text{Initiate blocking}$$

Scheme XX. Synthesis of block copolymers of methyl methacrylate and poly(diethylene glycol phthalic anhydride) using potassium diperiodatonickelate(IV) [DPN]/PPAG redox system.

for the system. The rate constant of the redox decomposition reaction, k, is detected as 1.7 L.mol^{-1}.s^{-1}. The chain transfer constant of polyacrylamide radical to ammonium persulphate is calculated to be 0.65.

The successful use of the combination of benzoyl peroxide (BPO) and *N,N*-dimethylaniline (DMA) as a low-temperature redox initiating system for the radical dispersion polymerization of methyl methacrylate in liquid CO_2 was demonstrated in 1996 by Dessipri et al. [132]. Polymerizations were run at room temperature and 76 bar pressure using a variety of polymeric stabilizers.

Poly(vinyl alcohol) and poly(vinyl acetate) having a thiol group at one end were synthesized by free-radical polymerization of vinyl acetate in the presence of thioacetic acid as a chain transfer agent followed by treatment with NaOH/MeOH and NH_3, respectively. The block copolymers containing the poly(vinyl alcohol) sequence as one constituent were obtained by the redox-initiated polymerization of acrylic acid and acrylamide, using poly(vinyl alcohol) having a thiol end group as reductant and an oxidant such as potassium bromate and potassium persulphate [133].

CONCLUSION

The synthesis of block copolymers by redox systems exerts a number of technical and theoretical advantages over the other methods. Because of applicability at low temperatures the side reactions which lead to formation of homopolymers are minimized.

Water-soluble polymers prepared with Ce(IV)–organic acid redox system containing amino, hydroxycarboxylic, and carboxylic acids end groups seems to be potential source for the construction of immunologically active controlled release drugs.

There are still some problems with this redox system, namely the poor solubilities of such inorganic salts in the organic medium (acrylic resin), the formation of slightly coloured products, and an expected short pot-life due to the fact that polymerization may occur already at ambient temperature.

REFERENCES

1. Cakmak I., Synthesis of block copolymers by redox macro initiators, *Macromol. Rep.*, **A32**, 197-206, 1995.
2. Stewens P.M., *Polymer Chemistry An Introduction*, 3rd ed., Oxford University, New York, 550, 1999.
3. Nagarajan S., Srinivason K.S.V., Redox polymerization process: An efficient tool for the synthesis of block copolymers, *Eur. Polym. J.,* **30**, 113-119, 1994.
4. Nagarajan S., Srinivasan K.S.V., Redox polymerization process: An efficient tool for the synthesis of block copolymers, *J. Polym. Sci. Pol. Chem.,* **33**, 2925-2933, 1995.
5. Wodka T.J., Studies on the synthesis of block copolymers of acrylonitrile and ethylene oxide, *Appl. Polym. Sci.,* **47**, 407-416, 1993.
6. Nagarajan S., Sudhakar S., Srinivasan K.S.V., Block copolymerization initiated by Mn(III)-poly(ethylene glycol) redox system - general features and kinetics, *Colloid Polym. Sci.,* **272**, 777-783. 1994.
7. Cakmak I., Hazer B., Yagci Y., Polymerization of acrylamide by the redox system cerium(IV) with poly(ethylene glycol) with azo groups, *Eur. Polym. J.,* **27**, 101-103, 1991.
8. Erbil C., Block copolymerization and chain extension by using PAAm prepolymer initiated with Ce (IV)-malonic acid, *Eur. Polym. J.,* **35**, 1747-1754, 1999.
9. Cakmak I., Preparation of multiphase block copolymers by redox polymerization process. 2: Polymerization of acrylonitrile by the manganese(III)-poly(ethylene glycol) redox system, *Die Angew. Macromol. Chem.,* **211**, 53-60, 1993.
10. Misra G.S., Bajpai V.D.N., Redoks polymerization, *Prog. Polym. Sci.,* **8**, 61-131, 1982.
11. Misra G.S., Dubey G.P., Aqueous polymerization of acrylamide initiated by Ce(IV)-thiomalic acid redox system, *Polym. Bull.,* **1**, 671-678, 1979.
12. Vanderhoft J.W., In: *Vinyl Polymerization*, G.E. Ham (Ed.), Marcel Dekker, New York, 988, 1969.
13. Sarac A.S., Redox polymerization, *Prog. Polym. Sci.,* **24**, 1149-1204, 1999.
14. Rai S.K., Shivakumar K., Sherigara B.S., Polymerization of acrylonitrile initiated by the manganese (III)-glycine redox system: A kinetic study, *Eur. Polym. J.,* **36**, 1339-1346, 2000.
15. Ananthanarayanan V.S., Santappa M., Kinetics of vinyl polymerization initiated by ceric ion in aque-

ous solution, *J. Appl. Polym. Sci.,* **9**, 2437-2449, 1965.

16. Takahashi T., Hori Y., Sato I., Coordinated radical polymerization and redox polymerization of acrylamide by ceric ammonium nitrate, *J. Polym. Sci. A-1*, **6**, 20911968.

17. Saha S.K., Chaudhuri A.K., Effect of amines on ceric ion-initiated polymerization of vinyl monomers. 2: Polymerization of acrylonitrile by ceric ion in presence of various substituted amines, *J. Polym. Sci.,* **10**, 797-799, 1972.

18. Studer K., Decker C., Beck E., Schwalm R., Gruber N., Redox and photoinitiated crosslinking polymerization. I: Dual-cure isocyanate-acrylate system, *Prog. Org. Coat.,* **53**, 126-133, 2005.

19. Fernandez M.D., Fernandez T., Fernandez M.J., Guzman G.M., Polymerization of methyl-methacrlate initiated by a ceric ion isopropyl-alcohol redox system, *J. Polym. Sci. Pol. Chem.,* **22**, 2729-2732, 1984.

20. Sarac A.S., Basak H., Soydan A.B., Akar A., Polymerization of acrylamide by electrolytically generated Ce(IV)-organic acid redox systems, *Angew. Makromol. Chem.,* **198**, 191-198, 1992.

21. Sarac A.S., Ustamehmetoglu B., Erbil C., Potentiometric determination of the molecular-weight of polymers, *Polym. Bull.,* **32**, 91-95, 1994.

22. Nayak P.L., Lenka S., Redox polymerization initiated by metal-ions, *J. Macromol. Sci. Rev. Macromol. Chem.,* **1**(C19), 83-134, 1980.

23. Yashoda M. P., Sherigara B.S., Venkateswaran G., Electroinitiated polymerisation of methyl methacrylate mediated by titanium(III)-hydroxylamine redox system: a kinetic study, *Polymer*, **41**, 7381-7389, 2000.

24. Tunca U., Aqueous polymerization of acrylamide initiated by redox pair - Ce(IV)-azo compounds with methylol functional-groups, *Eur. Polym. J.,* **31**,785-789, 1995.

25. Trahanovsky W.S., Young L.B., Brown, G.L., Oxidation of organic compounds with cerium(IV). 4: Oxidation of benzyl and related alcohols, *J. Org. Chem.,* **32**, 3865, 1967.

26. Leza M.L., Guzman G.M., Ceric salt initiated polymerization of 4-vinylpyridine, *Eur. Polym. J.,* **27**, 445-447, 1999.

27. Saldick J., Thermal initiation of vinyl polymeriza-

28. Venkatakrishnan S., Santappa M., Thermal polymerization of methyl acrylate initiated by ceric ion in aqueous solution, *Makromol. Chem.*, 27, 51-60, 1958.

29. Ananthanarayanan V.S., Santappa M., Kinetics of vinyl polymerization initiated by ceric ion in aqueous solution, *J. Polym. Sci.* **9**, 2437-2448, 1965.

30. Mino G., Kaizerman S., A new method for the preparation of graft copolymers: Polymerization initiated by ceric ion redox systems, *J. Polym. Sci.*, **31**, 242-243, 1958.

31. Misra G.S., Arya B.D., Aquaus polymerization of methacrylic-acid initiated by Ce^{+4}-glycolic acid redox pair, *J. Polym. Sci.*, **22**, 3563-3569, 1984.

32. Fernandez M.D., Guzman G.M., Aquaus polymerization of methyl-methacrylate initiated by Ce^{+4}-alcohol redox system-effect of acid concentration and additives, *J. Polym. Sci. Pol. Chem.,* **27**, 2427-2433, 1989.

33. Sudhakar D., Srinivasan K.S.V., Joseph K.T., Santappa M., Grafting of methyl-methacrylate to nitrocellulose by ceric ions, *J. Appl. Polym. Sci.,* **23**, 2923-2928, 1979.

34. Singh B.C., Misra B.K., Rout A., Mallick N., Rout M.K., Kinetics of inhibited or retarted polymerization-investigation on the cerium(IV)-toluene-acrylonitrile system, *Makromol. Chem.,* **180**, 953-1968, 1979.

35. Mino G., Koizerman S., Rasmussen B., The polymerization of acrylamide initiated by ceric nitrate-3-chloro-1-propanol redox systems, *J. Polym. Sci.*, **38**, 393-401, 1959.

36. Mohanty M., Pradkan B., Mohanta M.C., Vinyl polymerization of acrylonitrile by the cerium(IV)-propane-1,2-diol system, *Eur. Polym. J.,* **15**, 743-746, 1979.

37. Subramanian S.V., Santappa M., Ceric ion-reducing agent redox initiated vinyl polymerisation, *Makramol. Chem.*, **112**, 1, 1968.

38. Subramanian S.V., Santappa M., Vinyl polymerization initiated by ceric ion reducing agent systems in sulfuric acid medium, *J. Polym. Sci.*, **6**, 493, 1968.

39. Chakrabarty N.K., Chaudhuri A.K., Polymerization of acrylonitrile with ceric ion-2-propanethiol as initiator system, *J. Macromol. Sci. Chem.,* **A22**, 1961-1709, 1985.

40. Pramanick D., Chalterjee A.K., Sarkar S.K., Ceric salt thiourea redox initiator system for vinyl polymerization, *Makromol. Chem.,* **180**, 1085-1088, 1979.

41. Katai A.A., Kulshrestha V.K., Machessault R.H., Polymerization of acrylonitrile by ceric ion-ethylene glycol redox system, *J. Polym. Sci.,* **C2**, 403-407, 1963.

42. Novitskaya M.A., Carbochain Fibres, (Russian), *Tr. Sib. Teknol. Inst.*, **38**, 303-309, 1966.

43. Novitskaya M. A., Konkin A. A., Production of fibers from block-copolymers of polyacrylonitrile and poly(oxyethylene), (Russian), *Karbots. Volokna*, 173-181, 1966.

44. Konkin A.A., Methods of polyakrylonitrile fibre modification, (Russian), *Prezemysl Chem.,* **45**, 233, 1966.

45. Novitskaya M. A., Konkin A. A., Methods of polyakrylonitrile fibre modification, (Russian), *Vyskomol. Soedin.*, **7**, 1966-1969, 1965.

46. Gomes A.S., Coutinho F.M.B., Block copolymerization.1: Synthesis of block copolymers of poly(ethylene oxide-b-methyl methacrylate) by the ceric ion method using 1,4-dioxane as solvent, *J. Polym. Sci. Pol. Lett.,* **25**, 237-241, 1987.

47. Coutinho F.M.B., Furtado G.R.G., The emulsion polymerization of methyl-methacrylate initiated by Ce(IV)/dodecyl poly(ethylene oxide) redox system, *Eur. Polym. J.,* **28**, 1111-1114, 1992. 48. Akar A., Gaŭođlu O., Göçmen A., Copolymer of ketonic resin-polyacrylonitrile, *J. Appl. Polym. Sci.,* **39**, 1657-1663, 1990.

49. Guilbault L.J., Brooks T.W., Grafting to vinylpyrollidone polymers and copolymers by ceric ion method, *J. Macromol. Sci.,* **A7**, 1581-1590, 1973.

50. Guilbault L.J., Water-soluble vinyl-pyrrolidone-acrylamide block copolymers, *US Patent 3, 907,927*, 1975.

51. Mino G., Kaizerman S., A new method for the preparation of graft copolymers: Polymerization initiated by ceric ion redox systems, *J. Polym. Sci.,* **21**, 242-243, 1958.

52. Tunca U., Serhatli I.E., Yagci Y., Polymerization of acrylamide initiated by the redox system Ce(IV)-4,4-azo-bis (4-cyano pentanol), *Polym. Bull.*, **22**, 483-488, 1989.

53. Studer K., Decker C., Babe C., Beck E., Schwalm R., Gruber N., Redox and photoinitiated crosslinking polymerization. I: Dual-cure isocyanate-acrylate system, *Prog. Org. Coat.*, **53**, 126-133, 2005.

54. Öz N., Akar A., Aminomethylene phosphonic acid-ceric ion redox systems for aqueous polymerization of vinyl monomers, *Eur. Polym. J.,* **36**, 193-199, 2000.

55. Arslan H., Hazer B., Ceric ion initiation of methyl methacrylate using polytetrahydrofuran diol and polycaprolactone diol, *Eur. Polym. J.,* **35**, 1451-1455, 1999.

56. Arslan H., Eroðlu M.S., Hazer B., Ceric ion initiation of methyl methacrylate from poly(glycidyl azide)-diol, *Eur. Polym. J.,* **37**, 581-585, 2001. 57. Öz N., Akar A., Redox initiation system of ceric salt and dihydroxy poly(dimethylsiloxane)s for vinyl polymerization, *J. Appl. Polym. Sci.,* **102**, 2112-2116, 2006.

58. Arslan H., Hazer B., Higashihara T., Hirao A., Synthesis of asymmetric star-branched block copolymers based on PS, PTHF, and PMMA by combination of cationic ring opening polymerization and redox polymerization methods, *J. Appl. Polym. Sci.,* **102**, 516-522, 2006.

59. Arslan H., Mentes A., Hazer B., Synthesis and characterization of diblock, triblock, and multiblock copolymers containing poly(3-hydroxy butyrate) units, *J. Appl. Polym. Sci.,* **94**, 1789-1796, 2004.

60. Bajpai A., Simon J., Redox initiation of copolymerization of styrene with hydroxyl terminated polybutadiene using Ce(IV) as an oxidant, *J. Appl. Polym. Sci.* **85**, 244-256, 2002.

61. Motokawa R., Morishita K., Koizumi S., Nakahira T., Annaka M., Thermosensitive diblock copolymer of poly(*N*-isopropylacrylamide) and poly(ethylene glycol) in water: polymer preparation and solution behavior, *Macromolecules*, **38**, 5748-5760, 2005.

62. Nagarajan S., Kumari S.S.S., Srinivasan K.S.V., Kinetic and mechanistic studies on the block copolymerization of methyl methacrylate initiated by Ce^{4+}-poly(ethylene glycol) redox system, *J. Appl. Polym. Sci.,* **63**, 565-571, 1997.

63. Nagarajan S., Srinivasan K.S.V., Synthesis and characterization of poly(acrylonitrile)-block-poly(ethylene glycol)-block-poly(acrylonitrile)-block-copolymer, *J. Macromol. Sci. Pure Appl. Chem.* **A30**, 397-405, 1993.

64. Shimizu H., Yokohara T., Wada R., Okabe M., Influence of preparation conditions of poly (ethylene glycol)/poly (*N*-isopropylacrylamide) block copolymers on their properties, (Japaneese) *Kob. Ronbun Shu,* **61**, 640-642, 2004.

65. Sui K.Y., Gu L.X., Preparation and characterization of amphiphilic block copolymer of polyacrylonitrile-block-poly(ethylene oxide), *J. Appl. Polym. Sci.*, **89**, 1753-1759, 2003.

66. Xu S.J., Qiu K.Y., Vinyl radical polymerization initiated with ceric ion and ethyl N,N-diethyldithiocarbamyl acetate system, *Chin. J. Polym. Sci.*, **15**, 254-261, 1997.

67. Yu L.-Y., Zhao Q., Qian J.-W., An Q.-F., Preparation and separation performance of modified polyacrylonitrile microporous membrane, (Chinese), *J. Chem. Eng. Chin.Uni.,* **21**, 211-215, 2007.

68. Nagarajan S., Srinivasan K.S.V., Preparation of an acrylic block copolymer resin emulsion, *US Patent 194803, A1,* 2004.

69. Kizilcan N., Oz N.K., Ustamehmetoglu B., Akar A., High conductive copolymers of polypyrrole-á,ù - diamine polydimethylsiloxane, *Eur. Polym. J.,* **42**, 2361-2368, 2006.

70. Yagci C., Yildiz U., Redox polymerization of methyl methacrylate with allyl alcohol 1,2-butoxylate-block-ethoxylate initiated by Ce(IV)/HNO$_3$ redox system, *Eur. Polym. J.,* **41**, 177-184, 2005.

71. Hasan E., Zhang M., Mueller A., Tsvetanov C.B., Thermoassociative block copolymers of poly(*N*-Isopropylacrylamide) and poly(propylene oxide), *Pure Appl. Chem.,* **A41**, 467-486, 2004.

72. Sui K.-Y., Gu L.-X., Studies on polyacrylonitrile-poly(ethylene oxide) block copolymer by Ce(IV)/PEO-NH$_2$ redox system, (Chinese), *Qing. Da. Xueb.Kexueban*, **15**, 10-17, 2002.

73. Arslan H., Hazer B., Kowalczuk M., Synthesis and characterization of poly[(R,S)-3-hydroxybutyrate] telechelics and their use in the synthesis of poly(methyl methacrylate)-*b*-poly(3-hydroxybutyrate) block copolymers, *J. Appl. Polym. Sci.,* **85**, 965-973, 2002.

74. Atici O.G., Akar A., Ayar Y., Mecit O., Synthesis of block copolymers via redox polymerization, *J. Appl. Polym. Sci.,* **71**, 1385-1395.

75. Lee K.K., Jung J.C., Jhon, M.S., The synthesis and thermal phase transition behavior of poly(N-iso-propylacrylamide)-b-poly(ethylene oxide), *Polym. Bull.,* **40**, 455-460, 1998.

76. Topp M.D.C., Dijkstra P.J., Talsma H., Feijen J., Forming block copolymers of poly(ethylene glycol) and poly(*N*-isopropylacrylamide), *Macromolecules*, **30**, 8518-8520, 1997.

77. Nagarajan S., Srinivasan K.S.V., Block copolymerization of poly(ethylene glycol) with methyl methacrylate using redox macroinitiators, *Angew. Makromol. Chem.*, **245**, 9-22, 1997.

78. Nagarajan S., Srinivasan K.S.V., Synthesis of polyethylene glycol block copolymers by a redox process and their spectral characterization, *Macromol. Rap. Commun.*, **17**, 261-267, 1996.

79. Tauer K., Block copolymers prepared by emulsion polymerization with poly(ethylene oxide)-azo-initiators, *Polym. Adv. Technol.*, **6**, 435-440, 1996.

80. Tunca U., Aqueous polymerization of methyl methacrylate initiated by redox pair: Ce(IV)-Azo compounds with methylol functional groups and synthesis of copolymers, *J. Appl. Polym. Sci.,* **54**, 1491-1497, 1994.

81. Hazer B., Cakmak I., Denizligil S., Yagci Y., Preparation of multiphase block copolymers by redox polymerization process, *Angew. Makromol. Chem.*, **195**, 121-127, 1992.

82. Wang C.Q., Zhang G., Zhang Z.H., Chen X.F., Tang X.Y., Tan H.M., Characterization and properties of amphiphilic block polymer based on poly(ethylene oxide) and poly(butyl acrylate, *J. Appl. Polym. Sci.,* **89**, 3432-3436, 2003.

83. Chen X., Ding X., Zheng Z., Peng Y., Thermosensitive polymeric vesicles self-assembled by PNIPAAm-b-PPG-b-PNIPAAm triblock copolymers, *Coll. Poly. Sci.,* **283**, 452-455, 2005.

84. Drummond A.Y., Waters W.A., Stages in oxidations of organic compounds by potassium permanganate. 6: Oxidations of ketones and of pyruvic acid, *J. Chem. Soc.*, **2**, 497-504, 1955.

85. Devi N.G., Mahadevan V., Vinyl polymerization initiated by redox systems based on trivalent manganese, *J. Chem. Soc.,* **D 79**, 1970.

86. Wells C.F., Barnes C., Kinetics of oxidation of 2,3-dimettjylbutane-2,3-diol (pinacol) by aquamanganese(III) ions in aqueous perchlorate media, *J. Chem. Soc. A*, 1405-1408, 1971.

87. Andrulis P.J., Dewar M.J.S., Aromatic oxidation by

electron tansfer. 3: Oxidation of 1- and 2-methoxy-naphthalene by manganic acetate, *J. Am. Chem. Soc.,* **88**, 5483-5484, 1966.

88. Nayak P.L., Samal R.K., Baral N., Aqueous polymerization of methyl-methacrlate initiated by Mn(III)-fructose redox system, *J. Macromol. Sci. Chem.*, **A11**, 1071-1080, 1977.

89. Samal N.C., Senapati M., Mishra R., Sahu S.S., Rout S.P., Patnaik L.N., Polymerization of methyl methacrylate by a Mn(III)- acetate /ethylene glycol redox system in acetic-sulfuric acids mixture, *J. Macromol. Sci. Chem.* **A19**, 97-102, 1983.

90. Cakmak I., Polymerization of acrylonitrile by the redox system Mn(III) with poly(acrylamide) possessing terminal carboxyl groups, *Macromol. Rep.*, **A31**, 85-93, 1994.

91. Nagarajan S., Sudhakar S., Srinivasan K.S.V., Polyethylene glycol block copolymers by redox process: Kinetics, synthesis and characterization, *Pure Appl. Chem.*, **70**, 1245-1248, 1998.

92. Nagarajan S., Sudhakar S., Srinivasan K.S.V., Proceedings of the IUPAC International Symposium on Advances in Polymer Science and Technology, Chennai, India, Jan. 5-9, 1998, 1, 164-168.

93. Cakmak I., Preparation of multiphase block copolymers by redox polymerization process. 4. Polymerization of methyl methacrylate by the redox system Mn(III)-polyethylene glycol containing azo groups, *Angew. Makromol. Chem.*, **224,** 49-54, 1995.

94. Cakmak I., Preparation of multiphase block copolymers by redox polymerization process. 3. Polymerization of methyl methacrylate and acrylamide by the Mn(III)-polyethylene glycol redox system, *Angew. Makromol. Chem.*, **224**, 1-8, 1995.

95. Narita H., Kinoshita H., Araki T., Radical block copolymerization by a novel bifunctional redox and azo compound, *J. Polym. Sci. Pol. Chem.*, **30**, 333-335, 1992.

96. Kim Y., Graiver D., Decker G.T., Hamilton F.J., Harwood H.J., Block and graft copolymers containing poly(dimethylsiloxane) and poly(4-vinylpyridine) segments by free radical polymerization, *ACS Symposium Series*, **838**, 296-305, 2003.

97. Graiver D., Decker G.T., Kim Y., Hamilton F.J., Harwood H.J., Graft and block copolymers with polysiloxane and vinyl polymer segments, *Silicon*

Chem., **1**, 107-120, 2002.

98. Jiang C.-J., Zhang Q.-H., Jiang S.-Z., Studies on redox initiations of aromatic diazonium salts. IV: Block copolymerization using 4,4'-diphenyltetraazonium fluoroborates as initiator, (Chinese), *Gao.Tong.*, **1**, 11-17, 1981.

99. Liu Y., Bai L., Zhang R., Li Y., Liu Y., Deng K., Block copolymerization of poly(ethylene glycol) and methyl acrylate using potassium diperiodatocuprate(III), *J. Appl. Polym. Sci.*, **96**, 2139-2145, 2005.

100. Bai L.B., Liu Y.H., Run M.T., Deng K.L., A kinetic study of block copolymerization of poly (diethylene glycol phthalic anhydride) and methyl acrylate, *Iran. Polym. J.,* **15**, 577-581, 2006.

101. Bai L., Liu Y., Liu Y., Deng K., Block copolymerization of poly(diethylene glycol phthalic anhydride) and acrylate initiated by potassium diperiodatocuprate(III), *Macromolecules (Rajkot, India)*, **1**, 1-7, 2005.

102. Wodka T., Studies on the synthesis of fiber-forming block copolymers of polyacrylonitrile and poly(ethylene oxide), *J. Appl. Polym. Sci.,* **37**, 581-594, 1989.

103. Kwiatwkowski R., Wlochowicz A., Wodka T., X-ray-scattering investigated of acrylonitrile-ethylene oxide block copolymers, *Die Angew. Makromol. Chem.,* **180**, 145-157, 1990.

104. Cakmak I., Polymerization of methyl methacrylate initiated by the redox system H_2O_2-poly(ethylene oxide) with xanthate groups, *Eur. Polym. J.,* **31**, 1015-1018, 1995.

105. Dimov K., Pavlov P., Grafting with acrylonitrile with redox system cellulose xanthogenate-hydrogen peroxide, *J. Polym. Sci. Pol. Chem.,* **A1**, 2775, 1969.

106. Wodka T., Preparation of block copolymers of polyacrylonitrile and poly(ethylene oxide), (Polish), *Polimery (Warsaw, Poland),* **32**, 48-51, 1987.

107. Wodka T., Gabrielyan G.A., Rogovin Z.A., Synthesis of fiber-forming block copolymers of polyacrylonitrile and polyethylene oxide using xanthates of ethylene oxide oligomers, (Russian), *Vysokomol. Soedin. Ser.*, **22**, 6-9, 1980.

108. Jellinek H.H.G., *Degradation of Vinyl Polymers*, Academic, New York, 320, 1955.

109. Jellinek H.H.G., Polymer morphology and random chain scission, *Pure Appl. Chem.,* **4**, 419, 1962.

110. Hicks J.A., Melville H.W., The synthesis of block copolymers in a flow systems, *J. Polym. Sci.,* **12**, 461-468, 1954.

111. Molyneux P., *Water-Soluble Synthetic Polymers: Properties and Behavior*, Vol. I, CRC, Boca Raton, 1984.

112. Burnelt G.M., Paton C., Meares P., Styrene + methyl methacrylate block copolymers. 1: Preparation and fractionation styrene, *Trans. Faraday. Soc.,* **58**, 723-736, 1962.

113. Orr R.J., Williams H.L., The synthesis and identification of block polymers of butadiene and styrene, *J. Am. Chem. Soc.,* **79**, 3137-3141, 1957.

114. Urwin J.R., The preparation of block copolymer of styrene and methyl methacrylate, *J. Polym. Sci.*, **27**, 580-581, 1958.

115. Molyneux P., Block copolymers from a dihydroperoxide .2. the emulsion polymerization stage, *Makromol. Chem.,* **43**, 31-60, 1961.

116. Kobayashi S., Ide F., Nakasuka K., Synthesis of block copolymers via hydroproxy macroinitiators, *Chem. High. Polymers (Japan),* **24**, 17, 1967.

117. Reeb R., Vinchon Y., Riess G., Catula J.M., Borassas J., Peroxidation of dicarbanium ion of 1,1-diphenylethylene-dimer-synthesis of 1,1,4,4-tetraphenyl-1,4-dihydroperoxobutane, *J. Bull. Soc. Chim. France,* **11-12**, 2717-2721, 1975.

118. Catala J.M., Riess G., Borassas J., Synthesis of omega-hydroperoxy polymers, *Makromol. Chem.,* **178**, 1249-1258, 1977.

119. Iwakura J., Kakajima M., Kitani E., Synthesis of poly(aminotriazole-b-acrylonitrilo) block copolymers acyl hydrazide/ ferri redox system, *Chem. High. Polymers (Japan)*, **19**, 161, 1962.

120. Iwakura J., Nakayama M., Kitani E., Copolycondensation of episilon-caprolactam and polyaminotriazole or polytriazole, (Japanese), *Kob. Kagaku,* **19**, 1611, 1962.

121. Liu W.-J., Zhang Z.-C., He W.-D., Ge X.-W., Liu H.-R., Wang M.-Z., Chang, Z.-Q., Novel one-step route for synthesizing sub-micrometer PSt hollow spheres via redox interfacial-initiated method in inversed emulsion, *Mater. Lett.*, **61**, 2818-2821, 2007.

122. Bera P., Saha S.K., Redox polymerization of acrylamide on aqueous montmorillonite surface: Kinetics and mechanism of enhanced chain growth,

Polymer, **39**, 1461-1469, 1998.

123. Paik H. J., Teodorescu M., Xia J. H., Matyjaszewski K., Block copolymerizations of vinyl acetate by combination of conventional and atom transfer radical polymerization, *Macromolecules,* **32**, 7023-7031, 1999.

124. Nabekura H., Shimizu T., Vinyl chloride block copolymers, *Japanese Patent JP 02129212*, 1990.

125. Shimomura T., Kudo K., Block copolymers, *German Patent DE 2009066*, 1970.

126. Skaria S., Rajan C.R., Ponrathnam S., Redox polymerization of acrylamide by polymer supported vanadium (V) ion, *Polymer*, **38**, 1699-1704, 1997.

127. Bajpai A., Simon J., Tiwari S., Dixit N., Macroredox polymerization of styrene on the hydrophobic substrate, hydroxy-terminated polybutadiene using V(V) as an oxidant, *J. Macromol. Sci. Pure Appl. Chem.,* **A41**, 669-684, 2004.

128. Bajpai A., Dixit N., Synthesis of amphiphilic block copolymer of butadiene and acrylamide using telechelic polybutadiene and V(V) as redox system, *J. Macromol. Sci. Pure Appl. Chem.,* **A42**, 993-1012, 2005.

129. Liu Y., Bai L., Zhou W., Liu Y., Li Y., Deng, K., Block copolymerization of poly(diethylene glycol phthalic anhydride) and methyl methacrylate initiated by potassium diperiodatonickelate(IV), *J. Appl. Polym. Sci.*, **100**, 1312-1317, 2006.

130. Terada K., Sato T., Maruyama H., Yamauchi J., Okaya T., Syntheses and properties of block copolymers having poly(vinyl alcohol) as one component, (Japanese), *Kob. Ronbun Shu,* **42**, 885-891, 1992.

131. Okaya T., Kikuchi K., Morii Y., Polymerization of acrylamide in aqueous medium initiated with a redox system of cysteine and ammonium persulfate, *Polym. J.*, **29**, 545-549, 1997.

132. Dessipri E., Hsiao Y.-L., Mathes A.C.J., Shaffer K.A., DeSimone J.M., Free radical dispersion polymerizations in liquid carbon dioxide using a redox initiator, *Polym. Mater. Sci. Eng.*, **74**, 433-434, 1996.

133. Sato T., Terada K., Yamauchi J., Okaya, T., Synthesis of poly(vinyl alcohol) having a thiol group at one end and new block copolymers containing poly(vinyl alcohol) as one constituent, *Makromol. Chem.*, **194**, 175-185, 1993.

www.SID.ir