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Redox polymerization

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Abstract

Virtually all free-radical chain reactions require a separate initiation step in which a radical species is generated in the reaction mixture. Some types of chain reactions are initiated by adding a stable free radical, one that shows little or no tendency for self-combination, directly to the reactants, but a separate initiation step is still involved because these stable radicals are most often inorganic ions or metals.

A very effective method of generating free radicals under mild conditions is by one-electron transfer reactions, the most effective of which is redox initiation.

This method has found wide application for initiating polymerization reactions and has industrial importance, e.g. in low-temperature emulsion polymerizations.

In this review, in addition to the classical examples of redox pairs, recently employed metal-ion–organic-compound redox systems, electrochemical regeneration of reduced metal ions, redox initiation in nonaqueous media and transition metal organic halide initiators and metal chelate initiators are all reviewed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Free-radical chain reactions; Redox initiation; Redox pairs; Electroinduced polymerization; Vinyl polymerization; Metal ion oxidation

Contents

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1. Introduction

Virtually all free-radical chain reactions require a separate initiation step in which a radical species is generated in the reaction mixture. Some types of chain reactions are initiated by adding a stable free radical, one that shows little or no tendency for self-combination, directly to the reactants, but a separate initiation step is still involved because these stable radicals are most often inorganic ions or metals.

Radical initiation reactions, therefore, can be divided into two general types according to the manner in which the first radical species is formed; these are: (1) homolytic decomposition of covalent bonds by energy absorption; or (2) electron transfer from ions or atoms containing unpaired electrons followed by bond dissociation in the acceptor molecule.

A very effective method of generating free radicals under mild conditions is by one-electron transfer reactions, the most effective of which is redox initiation.

This method has found wide application for initiating polymerization reactions [1,2] and has industrial importance, e.g. in low-temperature emulsion polymerizations [3].

For the homolytic cleavage of covalent bonds of most practical thermal initiators, the bond dissociation energy required is in the range of 125–160 kJ mol^{-1}, and compounds with values above or below this range give either too slow or too rapid a rate of generation of radicals at the polymerization temperatures generally used.

This narrow range of dissociation energies limits the types of useful compounds to those containing fairly specific types of covalent bonds, for example, oxygen–oxygen, oxygen–nitrogen and sulfur–sulfur bonds.

Besides the very short induction period (almost negligible), a lower energy of activation (40–80 kJ mol^{-1}) 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.

In this review, in addition to the classical examples of redox pairs, recently employed metal-ion–organic-compound redox systems, electrochemical regeneration of reduced metal ions, redox initiation in nonaqeous media and transition metal organic halide initiators and metal chelate initiators are all reviewed.

2. Redox initiation in aqueous media

2.1. Peroxide

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 [4]. A mechanism for the reaction between hydrogen peroxide and ferrous ion involves a one-electron transfer from the ferrous ion to the peroxide with the dissociation of the oxygen–oxygen bond and the generation of one hydroxyl radical and one hydroxyl ion [5]:

$$Fe^{2+} + H_2O_2 \rightarrow [HO\dot{-}OH]Fe^{3+} \rightarrow Fe^{3+} + OH^- + \cdot OH \tag{1}$$

In the presence of sufficient monomer, all of the $\cdot OH$ radicals generated can initiate polymerization. Polymerization of several vinyl monomers, in aqueous media initiated by the H_2O_2–Fe^{2+} redox system, have been studied [6–8].

Ferrous ions will promote the decomposition of a number of compounds, including alkyl and acyl peroxides. For diperoxides and hydroperoxides, the primary step (Eq. (2)) is followed by further reduction of $RO\cdot$ (Eq. (3)), but when monomer is present the $RO\cdot$ radicals are intercepted by the initiation of polymerization:

$$Fe^{2+} + ROOR \rightarrow Fe^{3+} + RO^- + RO^{\cdot} \tag{2}$$

$$Fe^{2+} + RO^{\cdot} \rightarrow Fe^{3+} + RO^- \tag{3}$$

where R is alkyl or H.

2.2. Persulfate

With disulphides (Eq. (4)), persulfates and elemental halogens, analogous reactions occur [9–13].

$$RS–SR + Fe^{2+} \rightarrow Fe^{3+} + RS\cdot + RS^- \tag{4}$$

$$^-O_3S–O–O–SO_3^- + Fe^{2+} \rightarrow Fe^{3+} + {}^-O_3SO^{\cdot} + SO_4^{2-} \tag{5}$$

$$^-O_3SO^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \tag{6}$$

$$Br_2 + Fe^{2+} \rightarrow Fe^{3+} + Br\cdot + Br^- \tag{7}$$

Besides the Fe^{2+}–$S_2O_8^{2-}$ redox pair, Ag^+ can be used to replace ferrous ion for the same purpose [14–16]:

from H_2O

$$Ag^+ + S_2O_8{}^{2-} \rightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\cdot -} \tag{8}$$

$$Ag^{2+} + S_2O_8{}^{2-} \rightarrow Ag^{3+} + SO_4^{2-} + SO_4^{\cdot -} \tag{9}$$

$$Ag^{3+} + 2OH^- \rightarrow Ag^+ + 2\dot{O}H \tag{10}$$

With persulfate initiator, several monomers (acrylonitrile, methacrylic acid, methacrylamide, methyl methacrylate and ethyl acrylate) have been grafted onto wool fibres with the aid of cysteine present in wool [17,18]:

$$R\text{–}SH \rightarrow RS^- + H^+ \tag{11}$$

$$RS^- + S_2O_8{}^{2-} \rightarrow \dot{R}S + SO_4^{\cdot -} + SO_4^{2-} \tag{12}$$

or

$$RS\text{–}SR \rightarrow \dot{R}S + \dot{S}R \tag{13}$$

$$\dot{R}S + S_2O_8^{2-} \rightarrow RSOSO_3^- + SO_4^{\cdot -} \tag{14}$$

$$SO_4^{\cdot -} + HOH \rightarrow H\dot{O} + HSO_4^- \tag{15}$$

Initiation of polymerization can result from $\dot{O}H$, $\dot{R}S$ or $SO_4^{\cdot -}$ depending on the reaction conditions, radicals and monomer reactivities.

The oxyacids of sulfur such as sulfite, bisulfite, bisulfate, thiosulfate, metabisulfite and dithionate form efficient redox systems in conjuction with persulfates [19,20]. The initiation reaction of these systems may be represented as:

$$S_2O_8^{2-} + S_xO_y^{n-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + \dot{S}_xO_y^{(n-1)-} \tag{16}$$

$$SO_4^{\cdot -} + HOH \rightarrow H\dot{O} + HSO_4^- \tag{17}$$

Both $SO_4^{\cdot -}$, and $\dot{S}_xO_y^{(n-1)-}$ can initiate the polymerization. The absence of hydroxyl end groups in the polymers obtained with this class of redox pairs is probably due to the fact that the reducing sulfoxy compounds (or radicals derived from them) are good scavengers for $\dot{O}H$ radicals.

Polymerization initiated by the persulfate thiosulfate redox pair can be represented as

$$S_2O_8^{2-} \rightarrow SO_4{}^{\cdot -} + SO_4^{\cdot -} \tag{18}$$

$$S_2O_8^{2-} + S_2O_3^{2-} \rightarrow SO_4^{\cdot -} + S_2O_3^{-\cdot} + SO_4^{2-} \tag{19}$$

It has been suggested that these radicals react with each other giving anions. However at high concentrations of $S_2O_3^{-\cdot}$, polymerization probably initiates with $\dot{O}H$ according to the following reaction [21]:

$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^- + \dot{O}H \tag{20}$$

The polymerization of acrylamide, acrylonitrile, methacrylamide and methylmethacrylate with persulfate (peroxidisulfate) and several different reducing agents has also been reported [22–28].

From kinetic studies with ascorbic acid involving acrylonitrile monomer, the formation of charge transfer complexes between ascorbic acid and persulfate was suggested. This produces ascorbate radicals for the initiation of polymerization. $SO_4^{\cdot -}$ radicals produced via the thermal decomposition of $S_2O_8^{2-}$ is considered to be responsible for the acrylamide polymerization [24].

Mercaptans have been known as good redox pairs for vinyl polymerization, and recently α-mercaptocarboxylic acids have been used as redox systems [29–34].

Thiomalic acid is one example of acids used for the polymerization of acrylonitrile in the presence of peroxidisulfate and in a nitrogen atmosphere [23]. The rate of polymerization was found to depend on acrylonitrile concentration in first order, an order of 0.40 on the thiomalic acid concentration and 0.60–0.75 on $[S_2O_8{}^{2-}]$ depending on the monomer concentration.

The following reaction mechanism has been suggested for the formation of initiating species, and sulfhydryl radical derived from thiomalic acid is assumed to be the predominant initiating species:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -} \tag{21}$$

$$S_2O_8^{2-} + RSH \rightarrow SO_4^{\cdot -} + RS^{\cdot} + HSO_4^- \tag{22}$$

$$SO_4^{\cdot -} + RSH \rightarrow RS^{\cdot} + HSO_4^- \tag{23}$$

$$RS^{\cdot} + M \rightarrow RSM^{\cdot} \tag{24}$$

The polymerization of acrylonitrile initiated by an ascorbic-acid–peroxidisulfate redox system has been studied in an aqueous solution and in the presence of air at 35°C [22]. Molecular oxygen was found to have no effect on the polymerization reaction. Depending on the experimental conditions, oxygen may act as an initiator, inhibitor or retarder of polymerization.

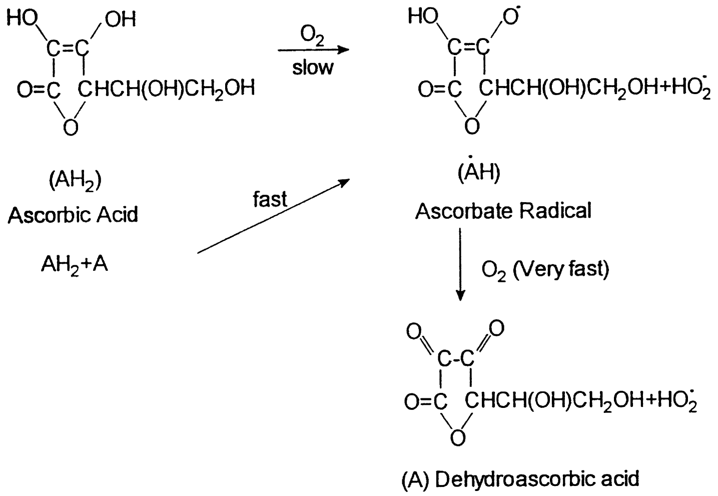
The rate of polymerization of acrylonitrile by ascorbic-acid–peroxidisulfate redox system was shown to be dependent on the square of the monomer concentration and a half order dependent on peroxidisulfate concentration. A first-order dependence on ascorbic acid concentrations at low concentrations was found.

The following reaction mechanism has been proposed for the polymerization of acrylonitrile in the presence of oxygen by $S_2O_8{}^{2-}$–ascorbic acid redox system, based on kinetic results:

$$M + AH^- \overset{K_1}{\rightleftharpoons} MAH^- \tag{25}$$

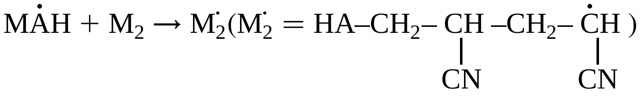
$$S_2O_8^{2-} + AH_2 \overset{K_2}{\rightleftharpoons} S_2O_8^{2-}\text{–}AH_2 \tag{26}$$

$$MAH^- + S_2O_8^{2-}\text{–}AH_2 \rightarrow M\dot{A}H + HSO_4^- + \dot{A}H + SO_4^{2-} \tag{27}$$



Scheme 1.

$$M + \dot{A}H + \longrightarrow M\dot{A}H \tag{28}$$



$$M\dot{A}H + M_2 \longrightarrow M_2^\bullet(M_2^\bullet = HA\text{–}CH_2\text{–}\underset{\underset{\displaystyle CN}{|}}{CH}\text{–}CH_2\text{–}\underset{\underset{\displaystyle CN}{|}}{\dot{C}H}\,) \tag{29}$$

$$M\dot{A}H + O_2 \longrightarrow M + A + HO_2^\bullet \tag{30}$$

$$M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet \tag{31}$$

$$2M_n^\bullet \longrightarrow \text{Polymer} \tag{32}$$

where $\dot{A}H$ may form by the autocatalytic oxidation of ascorbic acid.

The formation of complexes MAH^- and $S_2O_8^{2-}$–AH_2 was explained by the fact that both $S_2O_8^{2-}$ and acrylonitrile are electron-deficient species which form charge transfer complexes with ascorbic acid (Scheme 1).

The species $M\dot{A}H$ is susceptible to oxidation by O_2 since it can be considered as a resonance hybrid of $(A\dot{H}\text{–}M)$ and $(AH\text{–}\dot{M})$. But once the species $(\dot{M}_2\text{–}AH)$ is formed, further oxidation can be neglected and the only possible reactions considered are propagation and mutual termination.

The effect of pH on the rate of polymerization was related to the effect of pH on the equilibrium constants (K_1 and K_2) and increase on the concentration of complex ($S_2O_8^{2-}$–AH_2). The overall effect is the decrease in the production of $M\dot{A}H$ and $\dot{A}H$ at lower pH values with the resulting lower R_p values and higher induction periods.

Kinetic studies on the redox system organic-acid–peroxidisulfate indicates the formation of $SO_4^{\bullet -}$, $O\dot{H}$ and organic radical intermediates which initiate polymerization depending on the nature of the media. A similar redox system has also been applied for methacrylamide [35] and methylmethacrylate [36].

2.3. Peroxomonosulfate

Peroxomonosulfate (PMS, HSO_5^-) as a water-soluble initiator for vinyl polymerization in the presence of different types of reductants has been studied [37]. One system with Co(II) was used for acrylonitrile polymerization. The catalytic decomposition of peroxomonosulfate by metal ions in acidic and weakly basic media [38,39], Ag^{2+}–$S_2O_8^{2-}$ dual systems [40] and ketones [41] has been reported.

The Co(II)-catalyzed decomposition of peroxomonosulfate in aqeous phosphate buffer and the formation of $SO_4^{\cdot -}$ by a one electron reduction of PMS [44] were also reported.

In principle, it is possible to produce reactive metal ion-intermediates like Co(III) and Ag(II) from Co(II) and Ag(I) by peroxo compounds, and the higher valent metal ions can directly react with monomer to initiate polymerization:

$$HSO_5^- + Co(II) \rightarrow Co(III) + SO_4^{\cdot -} + OH^- \tag{33}$$

$$M + Co(III) \rightarrow Co(II) + M^{\cdot +} \tag{34}$$

where M is monomer. In such redox systems, there is also a possibility that the metal ion component of the redox pair functions not only as the reducing agent but also as a catalyst, since the metal ion is regenerated in the initiation reaction or in subsequent reactions. The oxidation potential of peroxomonosulfate (1.82 V) is slightly higher than that of Co(III), and the former can oxidize Co(II) to Co(III). In this redox system, Co(III) is highly reactive and oxidizes water itself [45], giving another initiating species, viz. the hydroxyl radical.

A mechanism was proposed and several conclusions were made after obtaining kinetic data for the polymerization of arcylonitrile (AN) by the redox pair, peroxomonosulfate–Co(II). The kinetic orders were: $[AN]^{1.5}$, $[PMS]^{1.0}$ and $[Co(II)]^{0.5}$, (at pH = 2.2–2.5).

It was proposed that:

(a) the radical producing reactions do not involve both components of the redox pair;
(b) either PMS or Co(II) alone is involved in complexation with the monomer.

$$HSO_4^- + Co(II) \leftrightharpoons \underset{(C_1)}{HSO_5^- - Co(II)} \tag{35}$$

$$M + HSO_4{}^- \leftrightharpoons \underset{(C_2)}{M - HSO_3^-} \tag{36}$$

$$C_1 + C_2 \rightarrow M^{\cdot} + Co(III) + SO_4^{\cdot -} + HSO_4^- \tag{37}$$

$$M + SO_4 \rightarrow M^{\cdot} \tag{38}$$

$$M + Co(III) \rightarrow M^{\cdot} + Co(II) \tag{39}$$

$$M + M_n^{\cdot} \rightarrow M_{n+1}^{\cdot} \tag{40}$$

$$M_n^{\cdot} + M_n^{\cdot} \rightarrow \text{Polymer} \tag{41}$$

There is also a possibility of the production of hydroxyl radicals, which does not alter the kinetic order and was not involved in the main reaction scheme.

$$\mathrm{Co(III)} + \mathrm{H_2O} \rightarrow \mathrm{Co(II)} + \mathrm{H}^+ + \dot{\mathrm{O}}\mathrm{H} \qquad (42)$$

$$\mathrm{SO_4^{\cdot -}} + \mathrm{H_2O} \rightarrow \mathrm{HSO_4^-} + \dot{\mathrm{O}}\mathrm{H} \qquad (43)$$

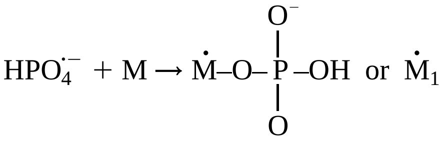
$$\mathrm{M} + \dot{\mathrm{O}}\mathrm{H} \rightarrow \mathrm{M}^{\cdot} \qquad (44)$$

2.4. Peroxidiphosphate

In the presence of Ag^+ [46], Co^{2+} [48], V^{5+} [42,47] and acid [43] peroxidiphosphate forms an efficient redox system in aqueous media for the polymerization of acrylonitrile. The initiating species were considered to be $\dot{O}H$ and $HPO_4^{\cdot -}$ and the termination was assumed to be mutual, for peroxidiphosphate–$AgNO_3$ redox system:

$$\mathrm{H_2P_2O_8^{2-}} + \mathrm{Ag}^+ \rightarrow \mathrm{HPO_4^{\cdot -}} + \mathrm{HPO_4^{2-}} + \mathrm{Ag}^{2+} \qquad (45)$$

$$\mathrm{Ag}^+ + \mathrm{HOH} \rightarrow \dot{\mathrm{O}}\mathrm{H} + \mathrm{H}^+ + \mathrm{Ag}^{2+} \qquad (46)$$



$$\mathrm{HPO_4^{\cdot -}} + \mathrm{M} \rightarrow \dot{\mathrm{M}}\text{–O–}\underset{\underset{\displaystyle \mathrm{O}}{|}}{\overset{\overset{\displaystyle \mathrm{O^-}}{|}}{\mathrm{P}}}\text{–OH} \;\text{ or }\; \dot{\mathrm{M}}_1 \qquad (47)$$

$$\dot{\mathrm{O}}\mathrm{H} + \mathrm{M} \rightarrow \dot{\mathrm{M}}\text{–OH} \;\text{ or }\; \dot{\mathrm{M}}_1 \qquad (48)$$

$$\dot{\mathrm{M}}_1 + \mathrm{M} \rightarrow \dot{\mathrm{M}}_2 \qquad (49)$$

$$\dot{\mathrm{M}}_n + \dot{\mathrm{M}}_m \rightarrow \mathrm{M}_{n+m} \qquad (50)$$

Peroxidiphosphate–Ag^+ redox system was also recently used for the polymerization of *N*,*N*′-methylenebisacrylamide (*N*,*N*′-MBA) [164] and *N*-vinylpyrolidone [210].

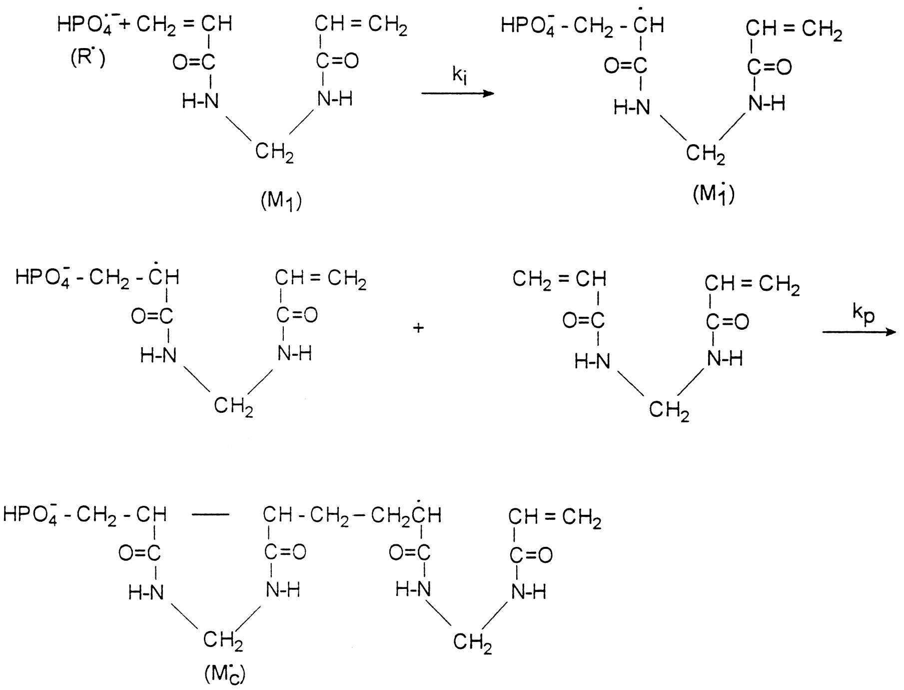
In the case of *N*,*N*′-methylenebisacrylamide, an intramolecular cyclization prior to propagation was proposed to explain the kinetic data which the rate of polymerization was found to be proportional to *N*,*N*′-MBA and square root dependent to the concentration of Ag^+ and peroxidiphosphate. Gel formation was observed at higher concentrations of the monomer by comparing with other conventional redox systems used in the vinyl polymerization process.

Since linear, isotactic poly(*N*,*N*′-MBA) is water soluble, it was possible to subject it to spectral and end group analysis.

The IR spectrum of poly(*N*,*N*′-MBA) showed a prominent peak corresponding to the –P–O– group, which supported the idea of initiation of the monomer takes place via phosphate ion radicals. The

Initiation:

Propagation:



$$M_c^{\cdot} + M \xrightarrow{k_p} M_{c+1}^{\cdot}$$

$$M_{c_{n-1}}^{\cdot} + M \xrightarrow{k_p} M_{c_n}^{\cdot}$$

Termination:

$$M_{c_n}^{\cdot} + M_{c_m} \longrightarrow M_{c_{n+m}}$$

Scheme 2.

negative dye partition test for the OH end group precluded initiation through OH radicals in this system. On the basis of experimental findings, the following scheme was proposed.

Radical formation:

$$H_2P_2O_8^{2-} + Ag^+ \overset{K}{\leftrightharpoons} AgH_2P_2O_8^- \tag{51}$$

$$AgH_2P_2O_8^- \xrightarrow{k_1} HPO_4^{\cdot-} + Ag^{2+} + H_2PO_4^{2-} + \dot{O}H \tag{52}$$

The seven-membered ring formed in the cyclization step is assumed to be stable due to the presence of the two carbonyl groups in the ring which reduce the ring strain (Scheme 2). The observed high reactivity of *N*,*N*′-MBA in comparison with acrylamide and related vinyl monomers further suggests that cyclization of the pendant bulky group might be the reason for its high reactivity in comparison with acrylamide and methacrylamide which contain bulky pendant groups like $-NH_2$ and $-CH_3$.

These groups cannot be cyclized, and their steric hindrance in the propagation steps of the polymerization process ultimately slows down the rate of polymerization.

In this intra-intermolecular mechanism, a primary free radical is first formed by the interaction of free radicals. Then propagation takes place through intramolecular cyclization and intermolecular addition of the next monomer. A radical which is formed at the end of the added monomer which remains uncyclized until further interaction occurs with the next monomeric unit. This mode of propagation was proposed to be responsible for the generation of a linear, gel-free, soluble polymer from *N*,*N*′-MBA, found to be predominant in the presence of peroxidiphosphate as an oxidant.

Free radical polymerization of *N*-vinylpyrrolidone (*N*-VP) is important because of extensive use of polyvinylpyrrolidone in the pharmaceutical and cosmetics industries, and cationic polymerization of *N*-vinylpyrrolidone leads to the formation of oligomers.

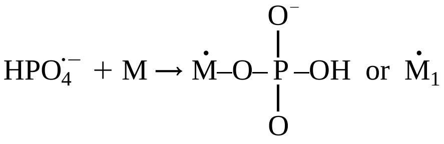
The kinetics of polymerization of *N*-VP in the presence of the azobisisobutyronitrile (AIBN) and persulfate initiators have been reported [48,49].

The polymers formed in the organic solvent using peroxides as initiators were found to be of low molecular weight due to fascile chain transfer reactions to the solvents. Peroxidiphosphate alone does not initiate the polymerization of *N*-VP at the ambient temperature, but in the presence of the Ag^+ ions the reaction occurred at a faster rate even at low temperatures. (Mechanism is given in Section 5.6.)

In the case of peroxidiphosphate–Co^{2+} initiated [50] polymerization of same monomer a different mechanism was proposed:

$$H_2P_2O_8{}^{2-} + Co^{2+} \longrightarrow H_2PO_4^- + HPO_4^{\cdot -} + Co^{3+} \tag{53}$$

$$Co^{3+} + HOH \longrightarrow \dot{O}H + H^+ + Co^{2+} \tag{54}$$



$$HPO_4^{\cdot -} + M \longrightarrow \dot{M}\text{–O–}\underset{\displaystyle O}{\overset{\displaystyle O^-}{\overset{|}{\underset{|}{P}}}}\text{–OH} \text{ or } \dot{M}_1 \tag{55}$$

$$Co^{3+} + M \longrightarrow M_1^{\cdot} + Co^{2+} \tag{56}$$

$$\dot{O}H + M \longrightarrow \dot{M}\text{–OH} \text{ or } \dot{M}_1 \tag{57}$$

$$\dot{M}_1 + M \longrightarrow \dot{M}_2 \tag{58}$$

$$\dot{M}_2 + nM \longrightarrow M_{n+2} \tag{59}$$

$$\dot{M}_n + \dot{M}_m \longrightarrow M_{n+m} \tag{60}$$

Linear termination of polymer by metal ion (Co^{2+} or Co^{3+}) was not proposed. Mutual termination has been proposed for $P_2O_8^{4-}$ whereas degredative chain transfer involving the initiator has been invoked in $S_2O_8^{2-}$–Co^{2+} redox system [51].

Fe^{2+} can also be used as a reducing agent which gives single initiating species, $HPO_4^{\bullet -}$ (1)

$$H_2P_2O_8{}^{2-} + Fe^{2+} \rightarrow HPO_4^{\bullet -} + HPO_4^{2-} + Fe^{3+} \tag{61}$$

3. Metal ion oxidants in redox initiation

Numerous reducing agents like alcohols, thiols, ketones, aldehydes, acids, amines and amides have been used in combination with oxidizing metal ions to participate in general single-electron transfer reactions for free radical polymerization. Metal ions used mainly for this purpose are Mn(III) (and Mn(VII)), Ce(IV), V(V), Co(III), Cr(VI) and Fe(III).

3.1. Manganese(III) and manganese(VII)

3.1.1. Manganese(III)

The general mechanism for almost all cases of vinyl polymerization initiation of Mn(III)–reducing agent system, is a formation of a complex between Mn(III) and the reducing agent which decomposes to give initiating free radicals [52–54]:

$$\text{Mn(III)} + \text{reducing agent} \leftrightharpoons \text{Complex} \tag{62}$$

$$\text{Complex} \rightarrow \dot{R} + \text{Mn(II)} + H^+ \tag{63}$$

$$\dot{R} + \text{Mn(III)} \rightarrow \text{Mn(II)} + H^+ \tag{64}$$

$$\dot{R} + M \rightarrow RM_1^{\bullet} \tag{65}$$

$$RM_n^{\bullet} + RM_m^{\bullet} \rightarrow R(M)_{n+m}\text{–}R \tag{66}$$

and/or

$$R\text{–}M_n^{\bullet} + \text{Mn(III)} \rightarrow RM_n + \text{Mn(II)} + H^+ \tag{67}$$

The order of reactivity of organic acids in Mn(III)–organic-acid redox system for the polymerization of acrylonitrile is in the following order [55]: citric > tartaric > ascorbic > oxalic > succinic > glutaric > adipic.

In the polymerization of methyl methacrylate initiated with Mn(III)–alcohol redox system, the order of the reactivity of alcohols was found to be in the following order [56]: 1-propanol > glycerol > ethyleneglycol > iso-butyl alcohol > 1-butanol > 1,2-propanediol > cycloheptanol > cyclohexanol > cyclopentanol. In the Mn(III)–$(CH_3)_2SO$ redox initiated polymerization [57–59] of acrylonitrile [AN] in H_2SO_4 and $HClO_4$, the radical ion produced after complexation between reactants which is followed by a reversible electron-transfer step:

$$\text{Mn(III)} + (CH_3)_2SO \rightarrow \text{Complex} \rightarrow (CH_3)_2S^+\text{–}\dot{O} + \text{Mn(II)} \tag{68}$$

$$(CH_3)_2S^+\text{–}\dot{O} + HOH \rightarrow (CH_3)_2SO + \dot{O}H + H^+ \tag{69}$$

The rate of polymerization was dependent on $[(CH_3)_2SO]$ and $[AN]^2$ and independent of oxidant concentration.

Polymerization of methylmethacrylate with Mn(III) and reducing agents, i.e. $(CH_3)_2SO$, diacetone alcohol and malonic acid was also proceeded through complex formation but varying stability with Mn(III) which decomposed slowly to produce initiating species.

In the polymerization of acrylonitrile and methylmethacrylate with Mn(III)–cyclohexanone redox system in H_2SO_4 and $HClO_4$ [60], it was also found that the rate of polymerization in H_2SO_4 was varied with [cyclohexanone] and $[AN]^2$, but not effected with changes in acidity, ionic strength or initially added Mn(II).

In perchloric acid the rate of polymerization was found to be dependent on [cyclohexanone] and [AN] complex formation constants of Mn(III) with cyclohexanone were found to be larger for sulfuric acid than in perchloric acid due to the difference of complex formation of $SO_4^{=}$ and ClO_4^{-} ligands in Mn(III).

In the polymerization of acrylamide initiated with Mn(III)–pinacol system [61], The free radical formation was explained after complexation between the oxidant and glycol after protonation or without protonation of glycol.

$$\underset{\text{(Complex)}}{\text{Pinacol–H}^{+}\text{–Mn(III)}} \rightarrow (CH_3)_2C{=}O + \text{Mn(II)} + H^{+} + (CH_3)_2\dot{C}(OH) \tag{70}$$

or

$$\text{Pinacol–H}^{+}\text{–Mn(III)} \rightarrow \text{Pinacol–Mn(III)} + H^{+} \tag{71}$$

$$\text{Pinacol–Mn(III)} \rightarrow (CH_3)_2C{=}O + \text{Mn(II)} + (CH_3)_2\dot{C}(OH) \tag{72}$$

The rate was found to be first-order dependent on [Mn(III)] and unaffected by added [Mn(III)].

The decrease in the rates of oxidation with increasing hydrogen ion concentration was attributed to the reactivity of Mn(III)_{aq} and Mn(OH)^{2+} as well as protonation of glycol which inhibits complexation.

Mn(III) was proposed to be the most predominant species in sulfuric acid, as $MnSO_4^{+}$.

In the investigation of kinetics of polymerization of acrylamide initiated with Mn(III)–ethoxyacetic acid (EAA) redox system in aqueous sulfuric acid [62], direct electron transfer from reducing agent to metal ion was proposed, probably due to a small complex formation constant of Mn(III)–EAA under experimental conditions.

Production of primary radical:

$$C_2H_5\text{–O–}CH_2COOH + \text{Mn(III)} \rightarrow \underset{(\dot{R})}{C_2H_5\text{–O–}\dot{C}H_2} + CO_2 + H^{+} + \text{Mn(II)} \tag{73}$$

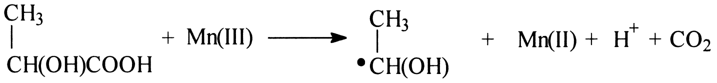
The rate of polymerization was found to be depend on monomer [M] with an order of unity, but the order with respect to [Mn(III)] and [EAA] was found to be 0.5. According to these findings, termination was suggested as the mutual combination of growing polymer radicals.

No significant change was observed on the rate of polymerization by the increase in $[H^{+}]$ at constant ionic strength or by the increase in ionic strength at constant $[H^{+}]$.

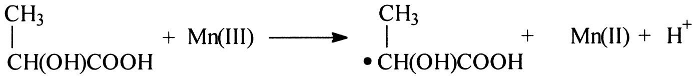
3.1.2. Manganese(VII)

In the polymerization of acrylamide, acrylonitrile, methacrylamide, methylmethacrylate and vinyl acetate, the manganese dioxide produced by the reaction between monomer and permanganate reacts with reducing agent to yield highly reactive Mn(III) ions. These Mn(III) ions then generate active free radicals with reducing agent.

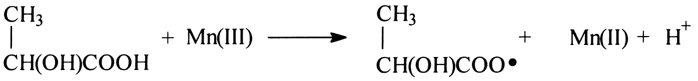
Some hydroxy carboxylic acids were used for the polymerization of acrylamide along with permanganate in aqueous medium. These acids are malic [63], tartaric [64], citric [65] and lactic acids [66]. Free radical formation of the mechanism of lactic-acid–$KMnO_4$ redox system was proposed as following:



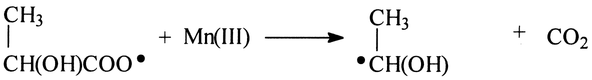
$$\begin{array}{l}CH_3\\|\\CH(OH)COOH\end{array} + Mn(III) \longrightarrow \begin{array}{l}CH_3\\|\\{\bullet}CH(OH)\end{array} + Mn(II) + H^+ + CO_2 \quad (74)$$



$$\begin{array}{l}CH_3\\|\\CH(OH)COOH\end{array} + Mn(III) \longrightarrow \begin{array}{l}CH_3\\|\\{\bullet}CH(OH)COOH\end{array} + Mn(II) + H^+ \quad (75)$$



$$\begin{array}{l}CH_3\\|\\CH(OH)COOH\end{array} + Mn(III) \longrightarrow \begin{array}{l}CH_3\\|\\CH(OH)COO{\bullet}\end{array} + Mn(II) + H^+ \quad (76)$$

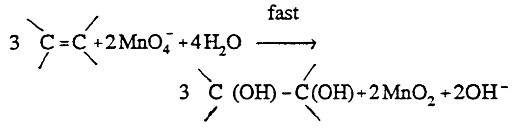


$$\begin{array}{l}CH_3\\|\\CH(OH)COO{\bullet}\end{array} + Mn(III) \longrightarrow \begin{array}{l}CH_3\\|\\{\bullet}CH(OH)\end{array} + CO_2 \quad (77)$$

In hydroxycarboxylic acid reducing agent systems, the rate of polymerization was found to be independent of the hydroxy acid concentration and vary linearly with the monomer concentration within the studied range.

In the aqueous polymerization of acrylamide initiated by the permanganate–glyceric acid redox system, it was reported that the permanganate first reacts with acrylamide and produces the hydrated manganese dioxide, which interacts with the glyceric acid to produce free radicals ($CH_2OHCHOHCOO$) and highly reactive Mn(III) [54].

These Mn(III) species are supposed to be more reactive to produce the free radical ($CH_2OHCHOH$), which is capable of initiating the polymerization of acrylamide:



(78)

$$Mn(IV) + CH_2OHCHOHCOOH \xrightarrow{k_1} Mn(III) + \underset{(A^{\bullet})}{CH_2OHCHOHCO\dot{O}} + H^+ \quad (79)$$

$$CH_2OHCHOHCOO \xrightarrow{\text{fast}} \underset{(B^{\bullet})}{CH_2OH\dot{C}HOH} + CO_2 \quad (80)$$

$$Mn(III) + CH_2OHCHOHCOOH \xrightarrow{k_2} Mn(II) + \underset{(B^{\bullet})}{CH_2OH\dot{C}HOH} + CO_2 + H^+ \quad (81)$$

Initiation

$$M + \dot{B} \rightarrow M_1^{\cdot} \tag{82}$$

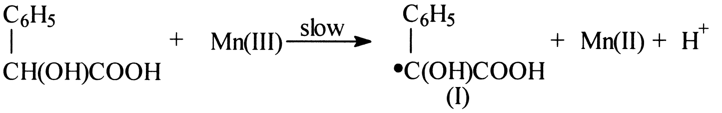
The rate of polymerization was found to be maximum at an optimum concentration of reducing agent (glyceric acid) but directly proportional to the concentration of monomer. The order with respect to permanganate was found to be 0.5, indicating the bimolecular mode of termination. At high concentration of the reducing agent, decrease in the rate was attributed to prevention of free radicals due to the direct reduction of Mn(IV) into Mn(II) as shown in the following equation:

$$2MnO_2 + 4H^+ \rightarrow 2H_2O + 2Mn(II) + O_2 \tag{83}$$

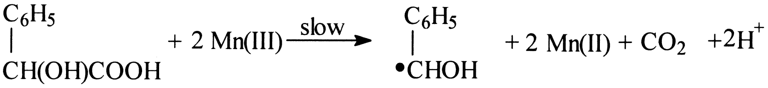
The addition of manganeous sulfate shows an increase on the initial rate of polymerization as well as maximum conversion. This behavior is related to the fact that Mn(II) reacts with Mn(IV) and produces the highly reactive Mn(III) species or ions, therefore producing primary free radicals (B) which in turn enhances the rate of polymerization and maximum conversion.

In the polymerization of acrylamide by the $KMnO_4$–mandelic acid redox system, as in the $KMnO_4$–glyceric acid system, the manganese dioxide produced by the reaction between acrylamide and permanganate reacts with mandelic acid to yield Mn(III) ions or species [53].

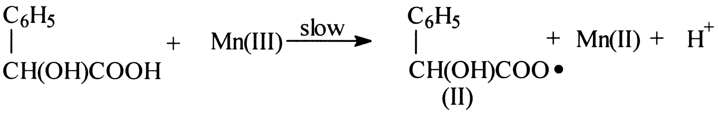
For this system, the following reaction mechanism was proposed:



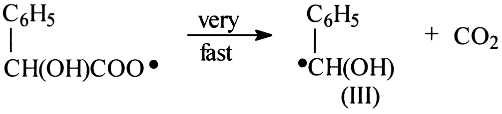
$$\underset{\text{CH(OH)COOH}}{\overset{C_6H_5}{|}} + \text{Mn(III)} \xrightarrow{\text{slow}} \underset{\substack{\bullet\text{C(OH)COOH}\\ \text{(I)}}}{\overset{C_6H_5}{|}} + \text{Mn(II)} + H^+ \tag{84}$$



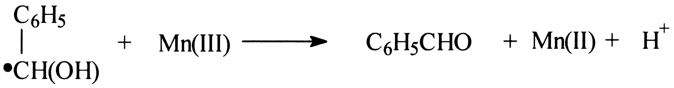
$$\underset{\text{CH(OH)COOH}}{\overset{C_6H_5}{|}} + 2\,\text{Mn(III)} \xrightarrow{\text{slow}} \underset{\bullet\text{CHOH}}{\overset{C_6H_5}{|}} + 2\,\text{Mn(II)} + CO_2 + 2H^+ \tag{85}$$



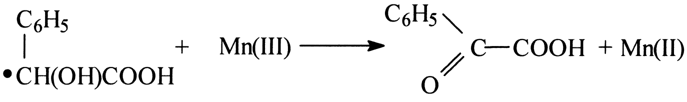
$$\underset{\text{CH(OH)COOH}}{\overset{C_6H_5}{|}} + \text{Mn(III)} \xrightarrow{\text{slow}} \underset{\substack{\text{CH(OH)COO}\bullet\\ \text{(II)}}}{\overset{C_6H_5}{|}} + \text{Mn(II)} + H^+ \tag{86}$$



$$\underset{\text{CH(OH)COO}\bullet}{\overset{C_6H_5}{|}} \xrightarrow[\text{fast}]{\text{very}} \underset{\substack{\bullet\text{CH(OH)}\\ \text{(III)}}}{\overset{C_6H_5}{|}} + CO_2 \tag{87}$$



$$\underset{\bullet\text{CH(OH)}}{\overset{C_6H_5}{|}} + \text{Mn(III)} \longrightarrow C_6H_5CHO + \text{Mn(II)} + H^+ \tag{88}$$



$$\underset{\bullet\text{CH(OH)COOH}}{\overset{C_6H_5}{|}} + \text{Mn(III)} \longrightarrow C_6H_5\text{—}\underset{\|}{\overset{}{C}}\text{—COOH} + \text{Mn(II)} \tag{89}$$

$$C_6H_5CHO + \text{Mn(III)} \rightarrow C_6H_5COOH + \text{Mn(II)} \tag{90}$$

Free radicals I, II and III (R·) may initiate polymerization or lead to formation of products. Benzaldehyde might also cause the termination of the growing microradical chain in addition to mutual termination.

The mechanism proposed predicts the formation of free radicals which are resonance-stabilized. (The overall energy of activation was found to be 3.45 kcal/mol, which resonance stabilized free radicals are known to have low E_{act}.)

The least stable radical initiates polymerization while others lead to formation of benzaldehyde, a known chain transfer agent. Chain transfer to benzaldehyde may also not be ruled out.

The growing polymer chain may attack the benzaldehyde molecule, which leads to termination.

Initiation:

$$R^{\cdot} + M \xrightarrow{k_i} RM^{\cdot} \tag{91}$$

Propagation:

$$RM^{\cdot} + M \xrightarrow{k_p} RMM^{\cdot} \tag{92}$$

$$RM^{\cdot}_{n-1} + M \xrightarrow{k_p} RM^{\cdot}_{n} \tag{93}$$

Termination:

$$RM^{\cdot}_{n} \xrightarrow{k_t} \text{Polymer} \tag{94}$$

or

$$RM^{\cdot} + C_6H_5CHO \xrightarrow{k_t} RM_nH + C_6H_5\text{–}CO^{\cdot} \tag{95}$$

Chain transfer to benzaldehyde brings about retardation in the rate, as radicals produced by chain transfer have lower activity. The primary radicals are more efficiently initiate polymerization than radicals formed by chain transfer. In the presence of a chain transfer agent, whether retardation or complete inhibition takes place, depending on the relative proportions and activities of these two types of radicals.

The order of dependence of concentration of Mn(III) was found to be about 2.0 and mandelic acid as unity.

Addition of aliphatic alcohols and DMF (S%v/v) into this system caused an increase in induction period and a decrease in rate of polymerization in the order of Ethanol > Methanol > DMF > Isopropylalcohol. Conclusions about the effect of solvents are given in Section 5.2.

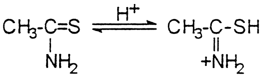
Addition of retarders/chain transfer agents (methylamine) to $KMnO_4$–mandelic acid system showed a complete inhibition, carbon tetrachloride and benzene caused a decrease in polymerization yield due to increased chain transfer. Molecular weight of the polymer was about 60,000; but on the other hand by the addition of 1 ml benzene to the reaction mixture reduced the molecular weight to about 600.

Mercaptans are also used as chain transfer agents for controlling molecular weight, in addition polymerization, exert activating influences on metal and nonmetal ions. Investigations on the activating influence of mercaptans for initiation of free radical polymerization were also carried out [108]. The coupling of these compounds with transition-metal ions in higher valence states, i.e. V(V), Co(III), Cr(VI), Ce(IV), Mn(IV), Mn(III), to generate free radicals seems to be facile. The kinetics of vinyl polymerization with V(V), Ce(IV), Mn(III) and Cr(VI) using thiourea, thioacetamide, thioglycolic acid and ethanethiol were studied [108].

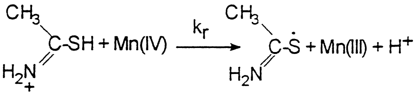
Polymerization of acrylonitrile in aqueous media initiated by an acidic permanganate: thioacetamide redox system indicated the characteristic features of heterogeneous polymerization, due to insolubility of the polymer in the aqueous phase [108].

Rate of polymerization was found to be second order dependent on the concentration of monomer and acrylonitrile. The initial rate and maximum conversion were found to be depressed in the presence of organic solvents (i.e. methanol, ethanol, formic and acetic acids).

From kinetic results following mechanism was proposed involving initiation of organic free radicals produced by the interaction of Mn(IV) with thioacetamide. Formation of MnO_2 was resulted from the reaction of HCl with $KMnO_4$ and linear termination step by Mn(III) was proposed.



$$CH_3\text{-}C(NH_2)\text{=}S \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3\text{-}C(\text{=}{}^+NH_2)\text{-}SH \quad (96)$$



(97)

$$R^{\bullet} + Mn(III) \xrightarrow{k_o} Product + Mn(II) \quad (98)$$

The symmetrical nonconjugated divinyl monomer (*N*,*N*′-MBA) polymerized by acidic permanganate–thiourea redox systems [67], the primary reactions suggested have been also proposed for the polymerization mechanism initiated by permanganate–$H_2C_2O_4$ [68], Thioglycollic acid [69] and ethylene glycol [69] systems.

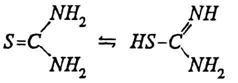
Primary reactions:

$$Mn(VII) + \underset{(Monomer)}{(M)} \overset{fast}{\longrightarrow} Mn(III) + Oxidation\ Products \quad (99)$$

$$2Mn(III) \overset{K_1}{\leftrightharpoons} Mn(IV) + Mn(II) \quad (100)$$

$$Mn(III) + H_2O \overset{K_2}{\leftrightharpoons} Mn(OH)^{2+} + H^+ \quad (101)$$

$$Mn(OH)^{2+} + M \leftrightharpoons [Mn(OH)^{2+}\text{–}M] \quad (102)$$

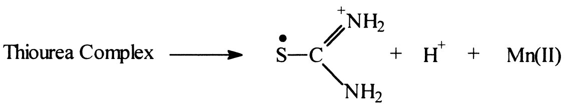


(TU) (ITU)

(103)

$$ITU + H^+ \overset{K_4}{\leftrightharpoons} ITUH^+ \quad (104)$$

$$Mn(OH)^{2+}TU \leftrightharpoons \underset{Thiourea\ \ complex}{[Mn(OH)^{2+}\text{–}TU]} \quad (105)$$

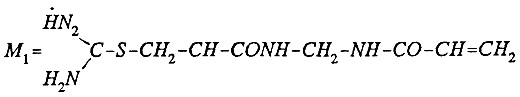


(106)

(i) initiation

$$M + R^\bullet \xrightarrow{k_1} M_1^\bullet \tag{107}$$

where



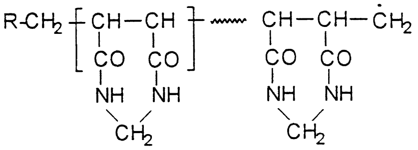
$$M_1 = (\dot{H}N_2)(H_2N)C\text{-}S\text{-}CH_2\text{-}CH\text{-}CONH\text{-}CH_2\text{-}NH\text{-}CO\text{-}CH{=}CH_2$$

(ii) propagation

$$M_1^\bullet \rightarrow M_2^\bullet \tag{108}$$

$$M_2^\bullet + M \rightarrow M_1^\bullet \tag{109}$$

where $M_2^\bullet$



Complex formation between $Mn(OH)^{2+}$ and protonated thiourea was less favored because of the like charges present on both. The resulting radical $M_1^\bullet$ from the decomposition of the complex, may cyclize itself [67–69], to yield $M_2^\bullet$ radical can add another monomer to yield $M_1^\bullet$, which can cyclize itself to repeat the cyclo polymerization sequence.

A complex formation between $Mn(OH)^{2+}$, which is suggested to be an active manganic species, and the unprotonated thiourea form. The thiocarbamido free radical (R) yielded by the decomposition of the complex, is capable of initiating the polymerization.

Cyclization of M_1 to M_2 and addition of M_2 to another monomer yielding M_1, which can cyclize itself to repeat the cyclopolymerization sequence.

The most preferred termination path was proposed as

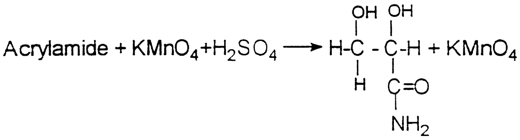
$$M_2^\bullet + M_2^\bullet \rightarrow \text{Polymer} \tag{110}$$

based on Gibb’s free energy.

3.1.3. Electrolytically generated Mn(III)

At low concentrations of Mn(III) (or $KMnO_4$) electrolytically generated Mn(III) has shown an advantage over the nonelectrolytic method for which polymerization did not occur under these conditions [70]. Aqueous polymerization of acrylamide was carried out by using potassium permanganate–malonic, tartaric and citric acid under electrolytic and nonelectrolytic conditions. The reaction between potassium permanganate and organic reducing agents (tartaric and citric acids) and polymerization of acrylamide

(AM) was proposed to be following. For malonic acid case reaction proceeded with only secondary radicals.



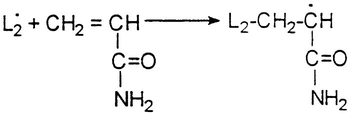
$$\text{Acrylamide} + KMnO_4 + H_2SO_4 \longrightarrow \text{H-}\underset{\text{H}}{\overset{\text{OH}}{\text{C}}}\text{-}\underset{\underset{NH_2}{C=O}}{\overset{\text{OH}}{\text{C}}}\text{-H} + KMnO_4 \quad (111)$$

$$\text{Mn(IV)} + \text{Organic Reducing Agent} \longrightarrow \underset{\text{Complex}}{[\text{Mn(III)–Reducing Agent}]} \longrightarrow \quad (112)$$

$$\text{Mn(III)} + \underset{(L_1^{\bullet})}{R\dot{C}H(OH)} + H^+ + CO_2$$

$$\text{Mn(III)} + RCH(OH)COOH \longrightarrow \text{Mn(II)} + \underset{(L_2\,\bullet)}{R\dot{C}(OH)COOH} + H^+ \quad (113)$$

Initiation



$$L_2^{\bullet} + CH_2=\underset{\underset{NH_2}{C=O}}{CH} \longrightarrow L_2\text{-}CH_2\text{-}\underset{\underset{NH_2}{C=O}}{\dot{C}H} \quad (114)$$

Propagation

$$\text{L–AM} + n\text{AM} \longrightarrow \text{L–(AM)}_n\text{–AM} \quad (115)$$

Termination

$$\text{(a)} \quad \text{L–(AM)}_n\text{AM} + \text{L–(AM)}_m\text{–(AM)} \longrightarrow \text{L–(AM)}_{n+1}\text{–(AM)}_{m+1}\text{–L} \quad (116)$$

$$\text{(b)} \quad \text{L–(AM)}_n\text{–AM} + \text{Mn(III)} \longrightarrow \text{L–(AM)}_n\text{–AM–Mn(II)} + H^+ \quad (117)$$

Regeneration of Mn(III) species electrolytically;

$$\text{Mn(II)} \xrightarrow{e^-} \text{Mn(III)} \quad (118)$$

Beside the termination by combination, the possibility of termination by metal ion was shown according to atomic absorption measurements.

Blank experiments indicated that there was no polymerization under experimental conditions with and without electrolysis, either in the absence of reducing agents (malonic, citric and tartaric acids) or potassium permanganate.

FT-IR results comparatively with H_2O_2–$KMnO_4$ system were also shown the presence of characteristic peaks of carboxylic groups: indicating the initiation by mentioned reducing agents molecular weights of polymer was lower than chemical method probably partly due to anodic termination of polymer radical.

3.2. Cerium(IV) and electroinduced polymerization

3.2.1. Cerium(IV)

Cerium(IV) ion has been used for the oxidation of many organic compounds, in the form of cerium(IV) ammonium nitrate (CAN), cerium(IV) ammonium sulfate (CAS), cerium(IV) sulfate (CS) and ceric perchlorate and the mechanism of such reactions has been well established.

Reducing agents combined with cerium(IV) are, alcohols, aldehydes, acids and amines. Earlier investigations revealed the fact that the rates of vinyl monomers were in the order of: ceric perchlorate $>$ ceric nitrate $>$ ceric sulfate which is in the order of oxidation power of mentioned species (1.7, 1.6 and 1.4 V, respectively)

Ceric ion forms complexes with anions such as sulfate, nitrate and hydroxyl in aqueous solution whose relative concentrations have been found to be function of hydrogen ion, respective anion concentration and ionic strength.

Increase of ligand concentration, $X = SO_4^{2-}$ and NO_3^- depress the rate of polymerization due to formation of less reactive cerium(IV) species, CeX_n than Ce^{4+} and $Ce(OH)_n$.

The mechanism and kinetics of polymerization involving ceric ion alone [71] and also in combination with reducing substrates such as alcohols [72–78], diols [79–81] polyols (glycols, sorbitol, mannitol) [82], aldehydes [83] and ketones [84], and amines [85] etc. with different monomers, acrylamide, acrylonitrile and methylmethacrylate etc.

Some of these studies have been reviewed in Ref. [1]. On the line of previous studies, it was generally suggested that for the ceric salts initiated vinyl polymerization, both ceric ions and primary free radicals participate in the initiation process while the termination occurs exclusively by the interaction of propogating chain radicals and ceric ions, or mutual combination of growing chain radicals.

On the cerium(IV)–2-chloroethanol redox pair initiated polymerization of acrylamide under nitrogen [75], it was reported that ceric ion was not able to initiate the acrylamide polymerization under the experimental conditions of the study which was reported by other workers too [86–92].

In this study, it was proposed that cerium(IV) ion forms a complex with 2-chloroethanol which on decomposition produces free radicals via single-electron transfer process. It was found that the rate of polymerization is directly proportional to the concentration of 2-chloroethanol, dependent on the square of monomer concentration at lower concentration and inversely proportional to the concentration of cerium(IV) ion.

The rate of ceric ion disappearance was found to be independent of monomer concentration and directly proportional to the concentration of ceric ion and 2-chloroethanol.

Following reaction steps were proposed by making a conclusion that ceric ion do not participate directly in the initiation process and termination occurs exclusively through the oxidative termination of ceric ion only.

The square dependence on monomer concentration also rules out the possibility of mutual termination of growing chain radicals,

$$\mathrm{Ce(IV)} + \mathrm{ClCH_2CH_2OH} \leftrightharpoons \underset{\mathrm{Complex(C)}}{[\mathrm{Ce(IV)\text{–}ClCH_2CH_2OH}]} \xrightarrow{\mathrm{k_d}} \underset{(\dot{\mathrm{R}})}{\mathrm{Cl\dot{C}HCH_2OH}} + \mathrm{Ce(III)} + \mathrm{H^+} \tag{119}$$

Initiation

$$\mathrm{M} + \mathrm{R}^{\cdot} \xrightarrow{k_i} \mathrm{M}_1^{\cdot} \tag{120}$$

Propagation

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet} \tag{121}$$

$$M_{n-1}^{\bullet} + M \xrightarrow{k_p} M_n^{\bullet}$$

Termination

$$M_n^{\bullet} + \mathrm{Ce(IV)} \xrightarrow{k_t} M_n + \mathrm{Ce(III)} + H^+ \tag{122}$$

Oxidative termination

$$R^{\bullet} + \mathrm{Ce(IV)} \xrightarrow{k_o} \text{Oxidation product} + \mathrm{Ce(III)} + H^+ \tag{123}$$

It was found that molecular weight of polymer decreases on increasing the concentration of ceric ion (ceric ammonium nitrate, CAN) and increases on increasing the concentrations of acrylamide and 2-chloroethanol.

In the acrylonitrile polymerization by cerium(IV) (CAN)-primary alcohol in nitric acid under nitrogen, by the application of Taft's correlation, it was suggested that the mechanism is free radical mechanism ($\sigma^* \cong 0,\ \rho^* = -0.2$).

$$\mathrm{Ce(IV)} + \mathrm{R{-}CH_2OH} \overset{k_d}{\rightleftharpoons} \mathrm{C} \longrightarrow \dot{\mathrm{R}}\mathrm{CH{-}OH} + \mathrm{Ce(III)} + H^+ \tag{124}$$

Similar to polymerization of acrylamide both increase in cerium(IV) decreases, the molecular weight and increase in alcohol concentration decreases the molecular weight of polymer.

In the polymerization of acrylonitrile by cerium(IV) [cerium(IV) ammonium sulfate (CAS)]–diol (propane 1,2-diol [79] and butane-1,4-diol [80]) systems in aqueous sulfuric acid and under nitrogen, for the primary radical production step, complex formation was not reported between cerium(IV) and diol. This fact probably can be attributed to the small complex formation constant between cerium(IV) and diol by comparison with high complexation of sulfate species with cerium(IV) [93,94] under high sulfuric acid concentrations.

In addition to kinetic results, the infrared spectrum of the isolated both polymers showed the presence of hydroxyl groups along with those of the homopolymer, indicating that the polymer contains the diol as an end-group, which envisages the initiation by primary radicals formed from the reaction of ceric ion with diol and termination by metal ions.

The decrease on R_p with increasing $[H_2SO_4]$ for propane–1,2-diol system, was explained by assuming that the reactive species are covalently bound neutral ceric sulfate species, $[Ce(SO_4)_2]$ and decrease of rate can brought about by increasing acid and HSO_4^- concentration occurs due to depletion of neutral species.

In both cases rate of polymerization was found to be directly proportional to the concentration of diol and inversely proportional to the ceric ion concentration but shows square dependence to the concentration of monomer. The rate of ceric ion disappearance is directly proportional to the initial concentration of ceric ion and diol.

For the polymerization of acrylonitrile with cerium(IV) (CAS)–glycerol in aqueous sulfuric acid the termination step is postulated to be mutual at lower concentrations of Ce(IV) where the rate of monomer disappearance was found to be proportional to $[\text{Monomer}]^{1.5}$ $[\text{Glycerol}]^{0.5}$ and $[\text{Ce(IV)}]^{0.5}$ and the rate of ceric ion disappearance was proportional to [Ce(IV)] and [Glycerol].

The termination step for the same system at high concentrations of Ce(IV) ($[\text{Ce(IV)} > 2.0 \times 10^{-2}$ mol/l) termination step was proposed to be lincar showing that the rate of polymerization is proportional to $[\text{M}]^2[\text{Glycerol}]$. The rate of ceric ion disappearance was found to decrease with increasing sulfuric acid concentration alone and increasing ionic strength by addition of NaHSO_4 to constant sulfuric acid concentration, probably due to formation of neutral disulfato complexes of Ce(IV) $[\text{Ce(SO}_4)_2]$ according to following equilibrium [94].

$$\text{Ce(4)} + \text{HSO}_4^- \leftrightharpoons \text{Ce(SO}_4)^{2+} + \text{H}^+ \tag{125}$$

$$\text{Ce(SO}_4)^{2+} + \text{HSO}_4^- \leftrightharpoons \text{Ce(SO}_4)_2 + \text{H}^+ \tag{126}$$

$$\text{Ce(SO}_4)_2 + \text{HSO}_4^- \leftrightharpoons \text{Ce(SO}_4)_3^{2-} + \text{H}^+ \tag{127}$$

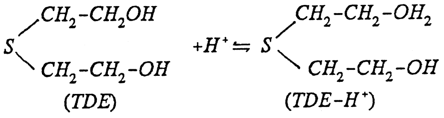
In the polymerization of acrylonitrile, [AN] by Ce(IV)–benzylalcohol [BA] system in nitric acid [217], the first-order dependence of R_p on [AN] observed and the rate of Ce(IV) disappearence was proportional to first powers of [Ce(IV)] and [BA]. The reaction of Ce(IV) benzylalcohol produces the free radical $\text{C}_6\text{H}_5\text{CH}_2\text{O}$ which may partly be oxidized by Ce(IV) to give benzaldehyde. The growing polymer chains get terminated by the mutual annihilation of polymer radicals as evidenced by the dependence of rate of polymerization over square roots of [Ce(IV)] and [BA].

Mutual type of combination of polymer chains was also observed in the case of Ce(IV) (CAS)–malonic acid initiated polymerization of methylmethacrylate and methylacrylate in aqueous sulfuric acid [84] and cerium(IV)–(CAN)–isobutylalcohol initiated polymerization of methylmethacrylate in aqueos nitric acid [78].

In the polymerization of methylmethacrylate by Ce(IV) (CAN)–isopropyl alcohol (IPA) in aqueous nitric acid [95], the polymerization reaction orders were 1/2 and 3/2 with respect to the IPA and monomer concentration, respectively, within the range $(3\text{–}5) \times 10^{-3}$ mol/l), of Ce(IV). But at lower Ce(IV) concentration ($<1 \times 10^{-3}$ mol/l), the order with respect to monomer and Ce(IV) changed to 1 and 1/2, respectively, and the rate of ceric ion disappearance was first order with respect to Ce(IV) concentration and IPA, indicating the possibility of oxidative termination in addition to termination of the polymeric radicals by bimolecular interaction.

Formation of free radicals was occurs after disproportionation of coordination complex of Ce(IV)–alcohol which is evidenced kinetic and spectroscopically.

Involvement of intermediate complex formation between the cerium(IV) and the protonated species of the 2,2′-thiodiethanol (TDE) in aqueous sulfuric acid in the polymerization of acrylonitrile was reported [81].



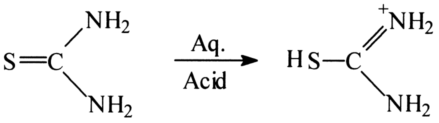
(128)

$$\text{TDE–H}^+ + \text{Ce(IV)} \leftrightharpoons \underset{\text{(C)}}{\text{Complex}} \tag{129}$$

$$C \rightarrow R^{\cdot} + Ce(III) + H^{+} \qquad (130)$$

$$R^{\cdot} + Ce(IV) \rightarrow Products \qquad (131)$$

In the cerium(IV) thiourea initiated aqueous polymerization of methylmethacrylate acidity of the reaction medium played an important role in controlling the polymerization mechanism [96]. Initiating species are reported as [97].



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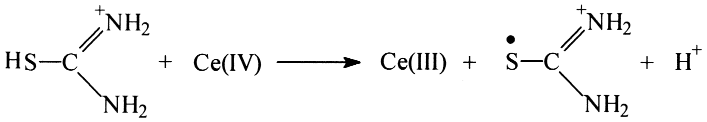


(133)

Increase of sulfate ion concentration caused an increase in R_p, whereas decreasing pH leads to sharp decreases in R_p. These results generally differ from other reducing agents, probably due to formation of protonated thiocarbamido radicals, which is the initiating species for the MMA polymerization.

The efficiency of initiation (f = rate of initiation, rate of Ce(III) formation) was found to be between 62 and 89% depending on the initiator concentrations.

Degradative chain transfer was not observed in this system. According to kinetic results $[R_p = k[Ce(IV)]^{0.41}[TU]^{0.32}[MMA]^{1.18}$ and low $\bar{P}_n[(0.16 - 2.55) \times 10^{-3}]$ of the polymers comparatively with end-group determination studies of similar systems, in addition to bimolecular mode of termination, termination by primary radicals were also suggested related to following reasons:

- *f* is rather low and a sizable percentage of the primary radicals were wasted by reactions other than initiation.
- The primary radical is resonance stabilized and would be comparatively unreactive toward addition to the π bond of MMA, In addition, the low [MMA] (limited by its solubility in water) used in the present system would increase the possibility of primary radical termination.

Cerium(IV) carboxylic acid [86,87] hydroxycarboxylic [86–88], amino acid [88–90] and polyamino carboxylic acid [90–92,98–101] systems have also been studied in detail recently. Generation of free radicals, reaction mechanism and initiation ability of free radicals in these systems were studied before. The following scheme was generally proposed for cerium(IV) organic reducing agent redox system.

$$Ce(IV) + R \rightarrow \underset{\text{complex}}{[Ce(IV)\text{–}R]} \qquad (134)$$

$$[Ce(IV)\text{–}R] \xrightarrow{k_d} \underset{\text{(Primary radical)}}{R^{\cdot}} + Ce(III) \quad \text{(decomposition)} \qquad (135)$$

Initiation

$$R^{\cdot} + M \xrightarrow{k_i} RM^{\cdot} \qquad (136)$$

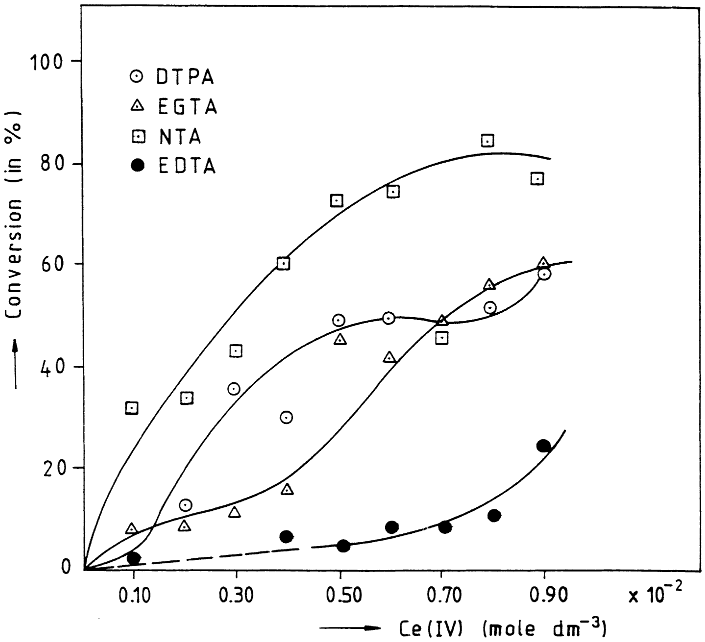


Fig. 1. The effect of Ce(IV) concentration on the conversion. [AM] = 0.60 mol.dm^{-3}; [NTA] = [EDTA] = [DTPA] = [EGTA] = 0.020 mol.dm^{-3}; [H_2SO_4] = 0.050 mol.dm^{-3}; 55°C, $t = 60$ min. From J. Appl. Polym. Sci. 1993;47:1643. ©1993 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. [91].

Propagation

$$RM^{\cdot} + nM \xrightarrow{k_p} R(M)_nM^{\cdot} \quad (137)$$

Several termination possibilities reported depending on cerium(IV) concentrations and other factors

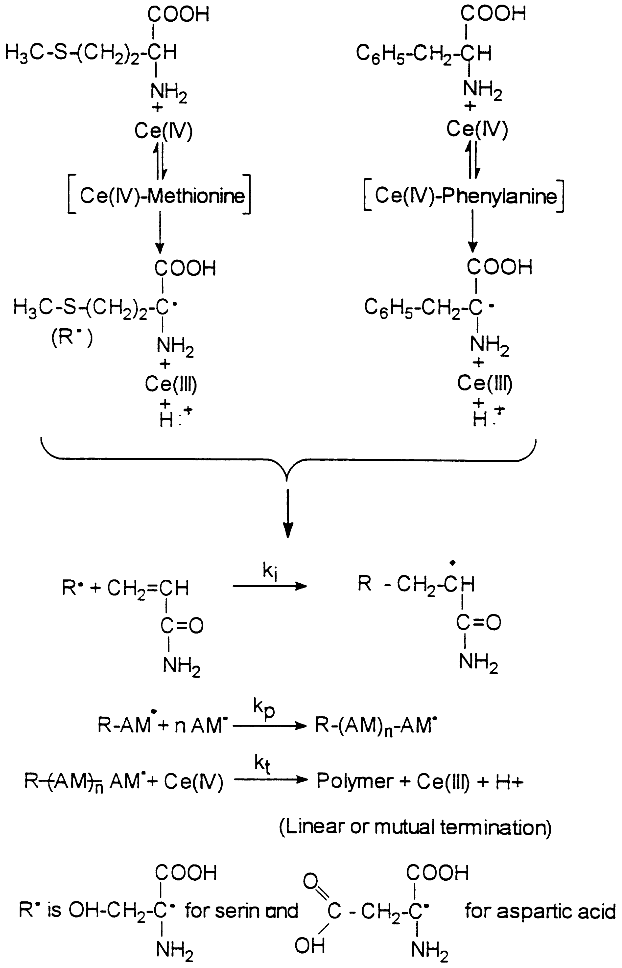
$$R(M)_n\dot{M} + Ce(IV) \xrightarrow{k_t} \text{polymer–Ce(III)} + H^+ \quad (138)$$

(Termination by cerium(IV))

$$R(M)_n\dot{M} + \dot{M}(M)_nR \xrightarrow{k_t} R–M_n–M–M–M_n–R \quad (139)$$

(Mutual termination)

Polymerization of acrylamide initiated with cerium(IV) [cerium(IV) sulfate, CS] in the presence of methionine, phenylalanine, serine and aspartic acid was investigated in sulfuric acid solution. The yield and the molecular weight reach a maximum at about 60–70°C and 0.16 mol/l H_2SO_4 concentration except for the yield with phenylalanine (Fig. 1). Further increase of both temperature and sulfuric acid concentration causes a drop in the yield and molecular weight. This is reflected in the fact that the initiating species is destroyed at higher temperature by side reactions [91–102].



Scheme 3.

The yield increases with the presence of the following substitutions at the amino acid skeleton in the order: –COOH(second carboxyl group of aspartic acid) > OH > Ar > S–CH_3, which can be probably be explained by the electron richness of some of these groups.

Comparison of molecular weight determined by conductometric titration of the carboxy end groups (≈4760) with the viscometric chain length (≈4380) indicated that there were two –COOH groups per chain.

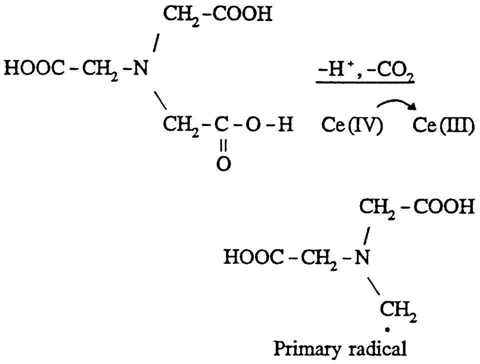
These results at 60 and 70°C and FT-IR spectra of polymers prepared with amino acid support the termination of the mutual type. The following (Scheme 3) was proposed which explains the experimental results.

Cerium (IV) [ceric sulfate]–polyamino carboxylic acid redox system was studied at different hydrogen ion and initiator concentration and reaction time [91]. Highest conversion was found for NTA (nitrilotriacetic acid), following order of conversion for other amino acids are as follows (Fig. 1):

EGTA $\geq$ DTPA $>$ EDTA where, EGTA [(ethylenedioxybis(ethylenenitrilotetraaceticacid)], NTA (nitrilotriacetic acid) and, EDTA (ethylenediamine tetraacetic acid) DTPA (diethylene triamine pentaacetic acid).

The yield is decreased with increasing H_2SO_4, which is due to the coordination of the SO_4^{2-} to form relatively stable ceric sulfate species and the protonation of the amino nitrogens. At high concentrations of H_2SO_4 and low concentrations of Ce(IV), conversions fall probably due to the acidity of the medium acting as an inhibiting agent for the polymer. At lower acid concentration, the cerium ion complex governs the generation of primary radicals and leads to the increase in the conversion. Similarities observed between kinetic studies on Ce(IV)–NTA and Ce(IV)–EDTA systems [100,101] and polymerization of acrylamide in these redox systems, i.e. Inflexion points in the conversion or rate vs. $[H^+]$.

Based on kinetic studies on cerium (IV)–polyamino carboxyclic acid reactions and cerium (IV)–polyamino carboxyclic acid initiated acrylamide polymerization in sulfate medium following step was proposed which an electron transfer from the carboxylic acid to Ce(IV) initiates decarboxylation and leads to the formation of free radicals.



(140)

Cerium(III)–NTA chelated complex was proposed for the production of primary radical by using CAN and the presence of new methylene groups from decarboxylation of one of carboxyl group of NTA was shown by the shifts in ^{13}C and ^{1}H-NMR measurements [100]. The mechanism of the formation of such free radical derived from Ce(IV)–NTA redox pair represented as in Scheme 4.

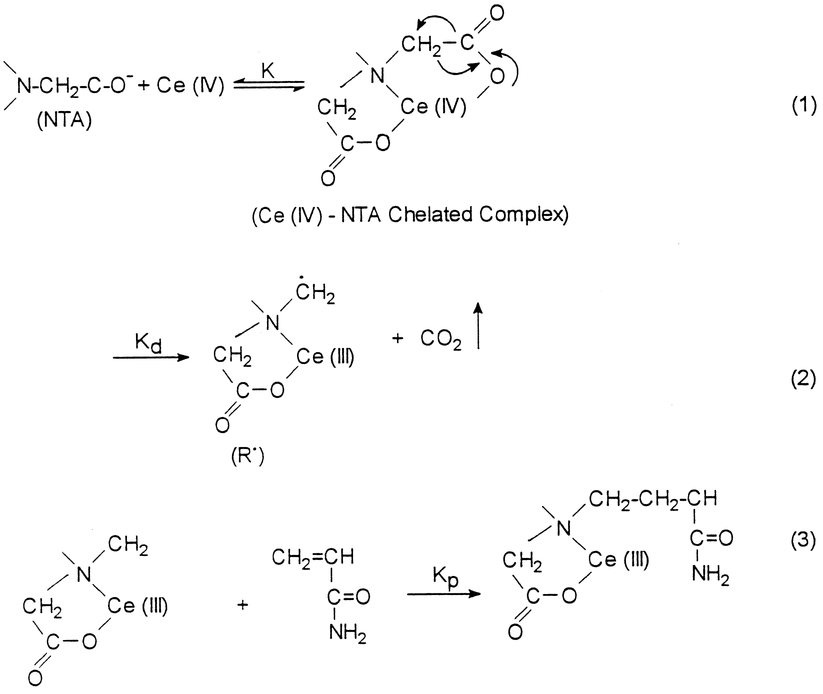
A series of chelating type reductants containing redox pairs, i.e. Ce(IV), or several first-row transition metal coupled with chelating agents of amino acids, dibasic acids or diamine were studied [100], and highest limiting conversion and rates of polymerization were obtained for Ce(IV)–NTA redox pair (Table 1).

Cerium(IV) could initiate significant polymerization in the presence of chelating agent, therefore the chelating agent acts not only reducing agent, but also as a promotor for initiation.

In general, the higher the reductive reactivity of redox pair, the faster the R_{pi} and the higher the X_L.

Among the first-row transition metals such as Co(III), Cr(IV), Cu(II), Fe(III), V(V), Mn(VII)O_4^-, [permanganate, MnO_4^-] and in addition to this cerium, Ce(IV)$(NO_3)_6^{2-}$ which have larger oxidative reactivity with NTA, performs higher limiting conversions.

In general, the performance of Ce(IV) systems are found to be better than that of those of Mn(VII)O_4^- for acrylamide polymerization in the presence of amino acid, dibasic acid and diamine reductants. Cerium (IV)–amino acid type chelating agent redox pairs are not all appropriate initiators for both aqeuous polymerization of acrylic acid (AA) and acrylonitrile (Table 2). End-group determinations of



Scheme 4.

Table 1

Effect of Ce(IV) and various chelating agent redox pairs on acrylamide polymerization at 40°C ([M] = 0.2 M, [Chelating Agent] = 2.5×10^{-3}M, [CAN] = 5×10^{-3}M). (From J. Polym. Sci., Part A Polym. Chem. 1993;31(3):213. ©1993 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. [100])

Chelating agent	$R_{pi} \times 10^5 (\mathrm{M\ s^{-1}})$	Limiting conversion (X_L (%))	$E_{1/2}$
None	0.05	0.29	0.95
NTA (nitrilotriacetic acid)	16.93	80.97	0.88
NPA (nitrilotripropionic acid)	2.55	78.77	0.98
IDA (iminodiacetic acid)	7.07	61.72	1.04
EDTA (ethylenediamine tetraacetic acid)	5.05	43.99	0.75
DTPA (diethylenetriamine pentaacetic acid)	0.25	1.82	0.59
Glycine	1.52	10.43	0.91
Oxalic acid	4.82	67.57	0.89
Malonic acid	1.37	44.44	1.06
Succinic acid	0.25	1.45	1.06
Glutaric acid	0.12	0.54	1.06
Ethylenediamine	0.25	1.40	1.06
Acetic acid	0.27	1.60	1.06
$K_2S_2O_8$[a]	0.55[b]	20.89[b]	1.06

[a] Thermal initiator without Ce(IV).

[b] With inhibition time of 1 h.

Table 2
Aqueous polymerization of vinyl monomers initiated by Ce(IV)–amino acid chelating redox pairs at 40°C [AM] = 0.2 M, [AA] = [AN] = 0.5 M; $[\mathrm{Ce(IV)}] = 5 \times 10^{-3}$ M, [Chelating Agent] $= 2.5 \times 10^{-3}$ M. (From J. Polym. Sci., Part A Polym. Chem. 1993;31(3):213. ©1993 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. [100])

	Chelating agent			
Monomer	EDTA	NTA	NPA	IDA
$R_{pi} \times 10^5 (\mathrm{M\ s^{-1}})$				
Acrylamide (AM)	5.1	16.9	2.6	7.1
Acrylic Acid (AA)	11.8	45.7	3.5	2.8
Acrylonitrile (AN)	4.5	19.7	8.3	30.7
X_L (%)				
Acrylamide (AM)	44.0	81.0	78.8	61.7
Acrylic Acid (AA)	53.8	76.6	7.7	9.5
Acrylonitrile (AN)	14.5	37.4	50.5	72.3

acrylonitrile and acrylamide polymers containing functional end-groups, i.e. citric, tartaric and malonic acids in aqueous and nonaqueous media by conductometric and potentiometric methods, confirmed the proposed mechanism [87,88].

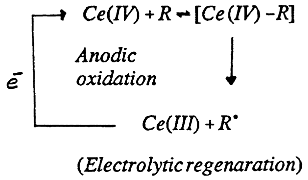
3.2.2. Electrochemically regenerated Ce(IV)

For cerium (IV)–malonic acid redox system [86], primary radical ($R^{\bullet}$) was suggested as $(HOOC)_2\dot{C}H$. Electrochemical regeneration of Ce(IV) during the polymerization with different electrode systems, C, Ag, Cr/Ni, Pb, Pt, stainless steel was carried out with a highest yield (66%) of polymerization for stainless-steel but high molecular weight obtained for Cr/Ni in citric ($M_n = 210\,500$).

A sharp increase in the yield up to about $4\text{–}5 \times 10^{-3}$ mol/l CAN concentration was observed. (Fig. 2)

Further increase in Ce(IV) concentration did not increase the conversion. At lower Ce(IV) concentration, polymerization of acrylamide in the presence of electrolysis showed much higher conversion values; at 6.25×10^{-4} mol/l Ce(IV) concentration, conversion is about 25% and 5% with and without electrolysis, respectively. The effect of Ce(IV) ion concentration, temperature and reaction time clearly indicated that at low Ce(IV) concentration and temperature a significant conversion increase was achieved in about 60 min of polymerization time, if the electrolysis was applied (Fig. 3). Further increase in polymerization time does not affect the conversion considerably, because the Ce(IV) concentration reaches a constant value.

Cerium(IV)–EDTA redox system also indicated that at low concentrations of cerium (IV), the electrolytic method continuosly supplying Ce(IV) from Ce(III) has an advantage over the nonelectrolytic method for which polymerization did not occur under these conditions [92].



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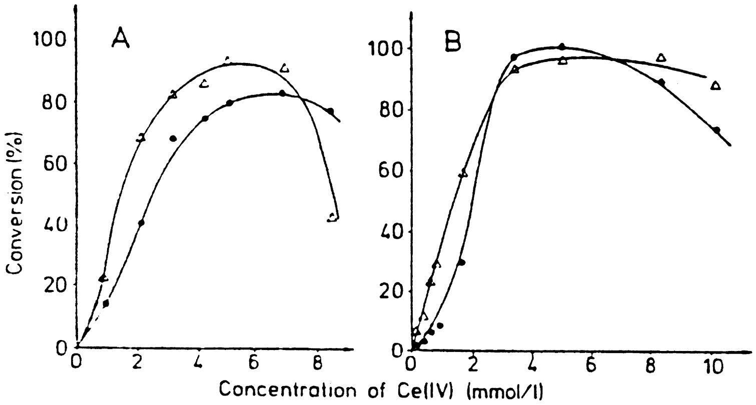


Fig. 2. The effect of Ce(IV) concentration on the polymerization yield: (△) with electrolysis, (●) without electrolysis. A: Reducing agent; [CA] = 16.7 mmol/l. B: Reducing agent: [MA] = 41.7 mmol/l; Graphite electrode, temperature: 50°C, time: 60 min, potential: 3 V [86].

Termination reactions by electrolytic method might be by recombination of polymer radicals or anodic termination.

The most striking feature is found that while there is no polymerization at concentrations below 4 mmol/l ceric sulfate in the absence of electrolysis, at about 0.30 mol AM/l polymer formed from initial concentration of 0.60 mol/l acrylamide monomer concentration. The molecular weights of the polymers in the system with electrolysis also showed a decrease at concentrations below 4×10^{-3} mol/l Ce(IV) (CS) (Fig. 4); these results are presumed to be related to the termination reaction by the recombination of polymer radicals.

The effect of the electrode type on the conversion was studied and showed that the type of electrode on the polymer yield was significant. Although molecular weight of polyacrylamide produced with lead electrode system was significantly higher than the others, graphite was the best electrode among metals tried (Table 3).

An increase in the polymer yield and decrease in the molecular weight by increasing Ce(IV) concentration was also observed in the presence of dicarboxylic and hydroxy carboxylic acids instead of EDTA.

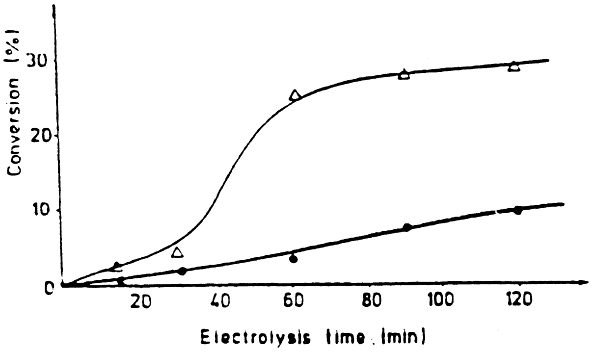


Fig. 3. The effect of time on the polymerization yield; (△) with electrolysis, (●) without electrolysis. [AA] = 417 mmol/l; [CA] = 16.7 mmol/l. [Ce(IV) = 0.625 mmol/l. Graphite electrode, temperature: 30°C, potential: 3 V [86].

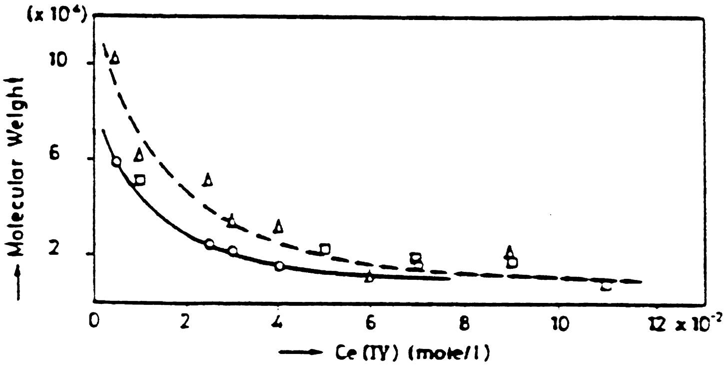
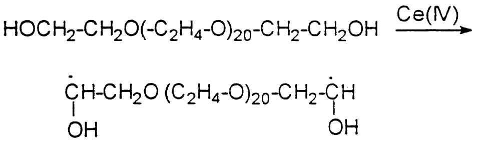


Fig. 4. The effect of Ce(IV) concentration on the molecular weight of polymer formed. (○) with electrolysis [EDTA] = 2.00 × 10^{-2} M; (△) without electrolysis [EDTA] = 2.00 × 10^{-2} M; (□) without electrolysis [EDTA] = 4.00 × 10^{-2} M. From J. Appl. Polym. Sci. 1992;44:877. ©1992 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. [92].

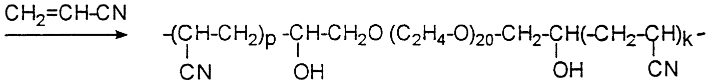
3.2.3. Graft copolymerization by Ce(IV)

Ce(IV) salts are also well known initiators for graft copolymerization of vinyl monomers such as acrylonitrile and acrylamide [102,103]. Starch and cellulose were the most used polymer for grafting. The basic reaction is a redox reaction between Ce(IV) and $-CH_2OH$ groups of celluluse, starch, ketonic resin and free radicals generated initiates the polymerization. This method was also used for the preparation of block copolymer of polyacrylonitrile and polyoxyethylene (PEO) and polyoxypropylene (PPO).

PEO and PPO which contained methylol groups at both chain ends were used as the reducing agent. It was suggested that the polymerization proceed in accordance with the following schemes.



$$HOCH_2\text{-}CH_2O(\text{-}C_2H_4\text{-}O)_{20}\text{-}CH_2\text{-}CH_2OH \xrightarrow{Ce(IV)} \underset{OH}{\dot{C}H}\text{-}CH_2O\,(C_2H_4\text{-}O)_{20}\text{-}CH_2\text{-}\underset{OH}{\dot{C}H} \tag{142}$$

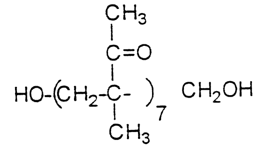


$$\xrightarrow{CH_2=CH\text{-}CN} \text{-}(\underset{CN}{C}H\text{-}CH_2)_p\text{-}\underset{OH}{C}H\text{-}CH_2O\,(C_2H_4\text{-}O)_{20}\text{-}CH_2\text{-}\underset{OH}{C}H(\text{-}CH_2\text{-}\underset{CN}{C}H)_k\text{-} \tag{143}$$

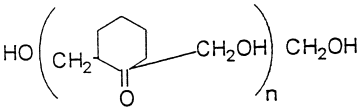
Table 3
Effect of electrode type on yield and molecular weight (Time: 30 min, [Ce(VI)] = 0.010 M[EDTA] = 0.040 M, Voltage = 2.5–3 V, Current: 40 mA and temp = 55°C). (From J. Appl. Polym. Sci. 1992;44:877. ©1992 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. [92])

Electrode type	Yield (mol AM/l)	Mol. weight (10^4)
Graphite	0.661	3.28
Lead	0.599	5.26
Cr/Ni	0.408	2.04

The yield of block copolymer increased with increasing PEO concentration. In this case, copolymerization may proceed mainly from one chain end of PEO and termination by generated free radicals may also be possible. Similarly Ce(IV)– ketonic resin redox system was used to initiate the polymerization of acrylonitrile. Ketonic resins were methyl ethyl ketone/formaldehyde resin and cyclohexanone/formaldehyde resin with the following representative structures. Both ketonic resins contain free $-CH_2OH$ groups



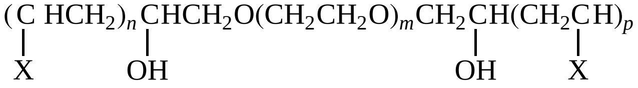
methyl ethyl ketone/formaldehyde resin



cyclohexanone formaldehyde resin

Water-soluble cellulose derivatives such as methyl cellulose (MC) and methyl hydroxy propyl cellulose (MHPC) and polyethylene glycols were also used as reducing agents for block/graft copolymer synthesis of acrylamide and acrylonitrile [103] (Scheme 5).

The copolymers have shown similar solubility properties of polyacrylonitrile (PAN) and polyacrylamide (PAM) homopolymers. It was assumed that homopolymers of acrylamide or acrylonitrile were not produced in this system since no PAM or PAN homopolymers were formed under similar conditions without modified cellulose (blank experiments). The spectrum of copolymer of polyacrylonitrile shows peaks of both modified cellulose and PAN. Peaks due to OH and CN stretchings are observed at 3450 and 2250 cm^{-1}, respectively. (Fig. 5) In the FT-IR spectra of copolymers of modified cellulose–PAM, peaks due to OH, NH and C=O stretching and NH_2 rocking are observed at 3450–3200 and 1670, 1610 cm^{-1}, respectively. (Fig. 5) FT-IR spectrum of, water-soluble copolymer of poly(ethyleneglycol)s–polyacrylamide, shows peaks at 3350–3200, 1670 and 1600 cm^{-1} due to NH, C=O stretching and NH_2 rocking, respectively (Fig. 5, Ref. [103])



$$(\underset{X}{C}HCH_2)_n\underset{OH}{C}HCH_2O(CH_2CH_2O)_mCH_2\underset{OH}{C}H(CH_2\underset{X}{C}H)_p$$

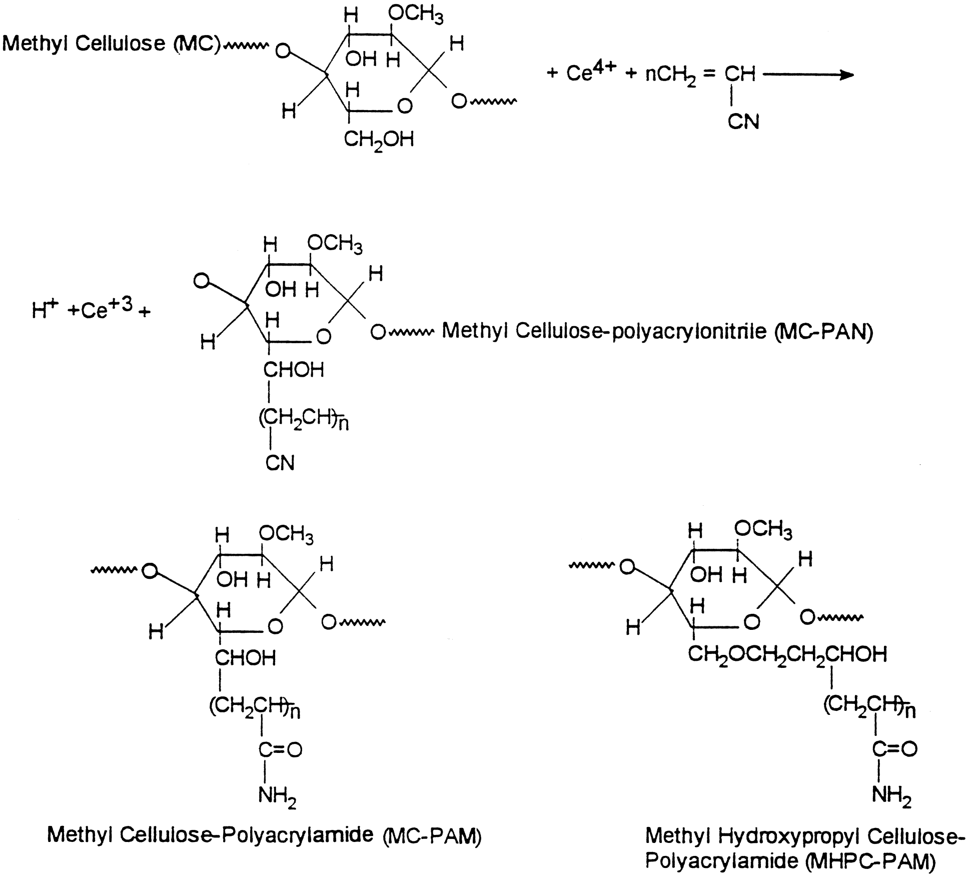
$m = 30$ and 90

$X = -CN, -CONH_2$

Cerium(IV) (CAN) concentration have shown a marked effect on the yield. The yield of acrylonitrile polymerization increased sharply and reached to about 100% at 20 mmol/l Ce(IV) concentration. However, the yield of acrylamide polymerization decreased with increasing Ce(IV) concentration above 5 mmol/l. The molecular weight decreased with increasing HNO_3 concentration, although the yield seems not to change significantly.

3.3. Iron (II and III)

Fenton’s reagent has been extensively used as a redox initiator in graft copolymerization of vinyl monomers onto cellulose, starch, wool, lignosulfonates, viscose and cotton [104–113].



Scheme 5.

In presence of sufficient monomer or other scavenger, OH formed by interaction of hydrogen peroxide and ferrous ion is responsible for initiation of polymerization [114–117]. The nature of the initiating radical may be varied by changing the nature of the medium, i.e. in the presence of methanol the radical may be $HOCH_2^{\cdot}$ [118]:

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + OH^- + \dot{O}H \quad [\text{or } \mathrm{Fe(OH)}^{2+} + {}^{\cdot}OH] \tag{144}$$

$$\mathrm{Fe(II)} + {}^{\cdot}OH \rightarrow \mathrm{Fe(III)} + OH \tag{145}$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{146}$$

$$\mathrm{Fe(II)} + HO_2^{\cdot} \rightarrow \mathrm{Fe(III)} + HO_2^- \tag{147}$$

$$\mathrm{Fe(III)} + HO_2^{\cdot} \rightarrow \mathrm{Fe(II)} + H^+ + O_2 \tag{148}$$

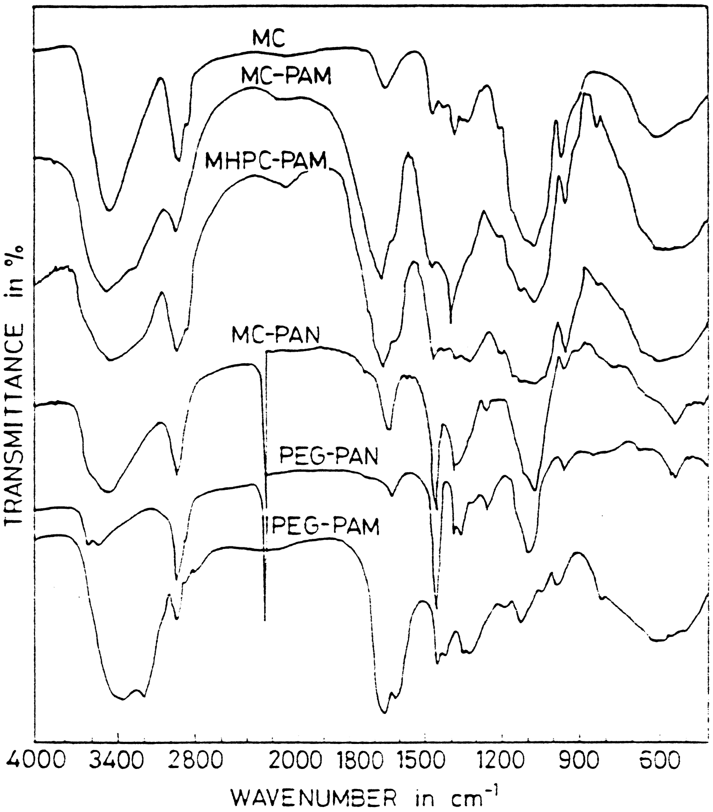


Fig. 5. FT-IR Spectra of Cellulose derivatives and poly(ethylene glycols [103]; methyl cellulose (MC), Methyl-cellulose–polyacrylamide (MC–PAM), methyl-cellulose–poly arcylonitrile (MC–PAN), poly(ethylene glycol), 4000-polyacrylonitrile (PEG–PAN), poly (ethylene glycol) 1500-polyacrylamide (PEG–PAM).

This redox system was also used in the preparation of the methacrylic-acid–styrene block copolymers.

Grafting poly(methylmethacrylate) onto chitosan by using Fenton’s reagent as a redox initiator in an aqueous medium and in the presence of atmospheric oxygen was studied [119]. In this study, it was found that the increase in chitosan increases the percentage of homopolymer up to a certain amount of chitosan according to following reaction:

$$\text{Rchit OH} + \text{M}_n^{\cdot} \rightarrow \text{Rchit O}^{\cdot} + \text{M}_n\text{–H} \qquad (149)$$

An increase in ferrous ammonium sulfate concentration showed a parallel decrease in graft polymer, due to destruction of OH by the reaction

$$\text{OH} + \text{Fe(II)} \rightarrow \text{OH}^- + \text{Fe(III)} \qquad (150)$$

Furthermore, an increase in Fe(II) concentration is accompanied by an increase in Fe(III) concentration by the reaction

$$\text{H}_2\text{O}_2 + \text{Fe(II)} \rightarrow \text{OH}^- + \text{Fe(III)} + {}^{\cdot}\text{OH} \qquad (151)$$

which might participate in the termination process, and the free radicals produced on the backbone might be oxidized to produce the oxidation products. Both effects decrease the percentage of grafting. High concentrations of hydrogen peroxide does not favor grafting due to decrease of OH concentration in the reaction medium:

$$^{\cdot}OH + HO\text{–}OH \rightarrow {}^{\cdot}OOH + H_2O \tag{152}$$

$$^{\cdot}OOH + Fe(III) \rightarrow O_2 + H^+ + Fe(II) \tag{153}$$

Methylmethacrylate onto cellulose using Cu(II) and Fe(III) metal ions along with peracids. Fe(III)–thiourea redox pair has been used for polymerization of methylmethacrylate in *tert*-butyl alcohol, methylmethacrylate in DMSO and in aqueous medium (References in Ref. [1]).

The initiating species is formed by the abstraction of H-atom of the –SH group of the isothiourea form in the presence of ferric ion. In the mechanism of redox polymerization initiated by *N*-haloamines and Fe(II), for the polymerization of methylmethacrylate formation of R_2N radical is reported [120]:

$$R_2NCl + Fe(II) \rightarrow R_2N^{\cdot} + [FeCl]^{2+} \tag{154}$$

In the monovinyl polymerization of ferrous ion coupled with peroxodisulfate ion as an initiator, the generation of sulfate ion radical $SO_4^{\cdot -}$ is important for initiating vinyl polymerization effectively. Normally divinyl monomers yield highly crosslinked and insoluble polymers. But it was found that this type of monomers can occasionally yield soluble, gel free polymers, and a new type of alternating intra- and/or intermolecular propagation was suggested for such cases [121]. Free radical copolymerization was then extended to a variety of symmetrical and unsymmetrical divinyl monomers [122].

A variety of *N*-substituted diacrylamides and dimethacrylamides were copolymerized through free radical initiators [123–127]. In the homocopolymerization of *N*-substituted dimethacrylamide derivatives, cyclization process occurred through repeated intermolecular tail–tail (t–t) propogation with head–head (h–h) cyclization.

Similar to permanganate–oxalic acid [68], thioglycollic acid [69], and ethylene glycol [69] and thiourea [67] initiator systems for the polymerization of *N*,*N′*-MBA, for Fe(II)–peroxidisulfate redox system, a polymerization mechanism involving cyclopolymerization in the propagation step is suggested [128].

The rate of polymerization is found to depend on $[M]^{3/2}$ and $[S_2O_8{}^{2-}]^{1/2}$ and independent of [Fe(II)] over a range and following reaction scheme was suggested for the mechanism.

Initiation

$$Fe(II) + S_2O_8^{2-} \rightarrow Fe(III) + SO_2^{2-} + SO_4^{\cdot -} \tag{155}$$

$$M_1 + SO_4^{\cdot -} \rightarrow M_1^{\cdot} \tag{156}$$

Propagation

$$M_1^{\cdot} \rightarrow M_2^{\cdot} \qquad \text{(intramolecular cyclization)} \tag{157}$$

$$M_1^{\cdot} + M_1 \rightarrow M_1^{\cdot} \qquad \text{(linear propagation)} \tag{158}$$

$$M_2^{\cdot} + M_1 \rightarrow M_1^{\cdot} \qquad \text{(intermolecular propagation)} \tag{159}$$

Termination

$$M_2^{\cdot} + M_2^{\cdot} \rightarrow \text{Polymer} \tag{160}$$

Reaction of primary radicals with Fe(II),

$$SO_4^{\cdot -} + Fe(II) \rightarrow Fe(III) + SO_4^{2-} \tag{161}$$

The head–head (h–h) intramolecular cyclization followed by tail–tail (t–t) intermolecular propagation may give rise to soluble copolymer of *N*,*N*′-MBA with a seven-membered cyclized unit in it.

Comparison of the overall rate of polymerization of *N*,*N*′-MBA with their monovinyl counterparts, acrylamide (AA) and methacrylamide (MAM) shows the order of reactivity as: MBA > AA > MAM, which supports the proposal of cyclopolymerization as the propagation mode for MBA polymerization [69].

Initiation by $SO_4^{\cdot -}$ for the polymerization of acrylonitrile with Fe(II)–peroxidisulfate system was also proposed [129].

3.4. Cobalt(III)

Cobalt(III) is a strong oxidant which oxidizes ^{-}OH to $\dot{O}H$

$$Co(III) + \bar{O}H \rightarrow Co(II) + \dot{O}H \tag{162}$$

as well as other organic substrates [130–132] by participating in single-electron transfer reactions:

$$Co(III) + HCOOH \rightarrow Co(II) + HCO\dot{O} + H^+ \tag{163}$$

$$Co(III) + HCOO^- \rightarrow Co(II) + HCO\dot{O} \tag{164}$$

$$Co(III) + CH_3OH \rightarrow Co(II) + CH_3\dot{O} + H^+ \tag{165}$$

$$Co(III) + CH_3\dot{O} \rightarrow HCHO + H^+ + Co(II) \tag{166}$$

Co(III) was used an initiator for the polymerization of acrylamide, acrylonitrile, methylmethacrylate and methylacrylate [132–134].

The general mechanism is given by following reactions:

$$Co(III) + M \rightarrow Co(II) + R^{\cdot} \tag{167}$$

$$Co(OH)^{2+}M \rightarrow Co(OH)^{+} + R^{\cdot} \tag{168}$$

$$R^{\cdot} + M \rightarrow R{-}M^{\cdot} \tag{169}$$

$$R{-}M^{\cdot} + nM \xrightarrow{k_p} R{-}M_n^{\cdot} \tag{170}$$

$$\text{R–M}_n^{\bullet} + \text{Co(III)} \xrightarrow{k_t} \text{R–M}_n + \text{Co(II)} + \text{H}^+ \tag{171}$$

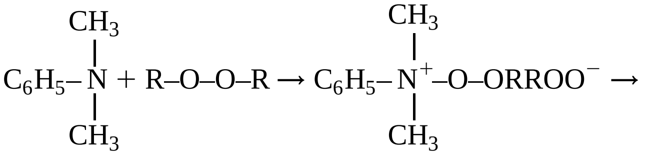
$$\text{R–M}_n^{\bullet} + \text{Co(OH)}^{2+} \rightarrow \text{R–M}_n + \text{Co(OH)}^{+} + \text{H}^+ \tag{172}$$

The polymerization of methylmethacrylate initiated by Co(III)–*tert*-butylalcohol was observed only at high concentration of alcohol as a real redox initiating system.

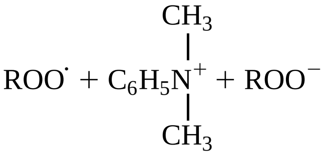
4. Redox initiation in nonaqueous media

4.1. Intermolecular processes

Organic peroxides, i.e. diacyl peroxides and tertiary amines form a complex in nonaqueous solution which cleaves into radicals and radical cations where radical rather than radical cation is the main initiating species [135,136].



$$\text{C}_6\text{H}_5\text{–}\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{N}}} + \text{R–O–O–R} \rightarrow \text{C}_6\text{H}_5\text{–}\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{N}}}{}^{+}\text{–O–ORROO}^{-} \rightarrow \tag{173}$$



$$\text{ROO}^{\bullet} + \text{C}_6\text{H}_5\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{N}}}{}^{+} + \text{ROO}^{-} \tag{174}$$

In the polymerization of styrene chain termination occurs by the normal interaction of propagating radicals, but not with primary radicals or other species [137].

Other reducing agents, i.e. formic acids, sulfonic acids and hydrazines instead of terniary amines have been reported [138–140].

Alkylborons have also been reported which participates in the initiation of redox polymerization in the presence of oxygen by forming a peroxide (R_2BOOR). This trialkyl boron complex interacts with a monomer to form radicals [141,142].

4.2. Transition metal derivative–organic halide initiators

In these systems, radical formation is essentially an electron-transfer process from transition metal to halide by producing a radical fragment from organic halide

$$\text{Me}^{o} + \text{R–Cl} \rightarrow \text{Me}^{+}\text{Cl}^{-} + \text{R}^{\bullet} \tag{175}$$

The redox reaction does not occur directly between halide and metal carbonyl, first conversion of the carbonyl into a more active species by ligand exchange or scission. Electron transfer to R–Cl may occur by two ways and importance of two routes depends on the electron affinity of R [143,144].

$$e^- + \text{R–Cl} \rightarrow \text{Cl}^- + \dot{\text{R}} \qquad (176)$$

$$e^- + \text{R–Cl} \rightarrow \dot{\text{Cl}} + \text{R}^- \qquad (177)$$

Reaction of $Mo(CO)_6$, $Mn_2(CO)_{10}$ (metal carbonyls) and $Pt\{P(C_6H_5)_3\}_4$ with $R = CCl_3$, CBr_3Cl_2CCOOH and $Cl_2CCOOC_2H_5$ mainly proceed by first equation, but with Ni compounds, $Ni(CO)_4$, $Ni(CO)_2$, $\{P(C_6H_5)_3\}_2$, $Ni\{P(OC_6H_5)_3\}_4$ both equations might have comparable importance [145].

4.3. Intramolecular processes

Metal chelates have been used for initiation of different types of polymerizations. Metal acetylacetonates, i.e. $MoO_2(acac)_2$, $Mn(II)(acac)_2$ and $Co(II)(acac)_2$ have been reported as initiator for polymerization of chloral by ionic polymerization mechanism. The following order of rates of polymerization has been given:

$$\text{V(III)} < \text{Cr(III)} \equiv \text{Al(III)} < \text{Fe(III)} < \text{Co(III)} < \text{Ce(IV)} < \text{Mn(III)}$$

Vanadium chelates behave as a retarder, chromium and aluminum chelates are inactive [146–148].

Proportionality between Mn(III) and Co(III) chelates and rate of polymerization has been reported which is consistent with free radical mechanism. Initiating radicals are derived from the ligands, so that the processes can be used for incorporating such groups into terminal positions in polymer chains. In Co(III) ethylacetoacetate and styrene monomer [149], it was found that rate of polymerization proportional to $[\text{Monomer}]^n[\text{Chelate}]^{0.5}$ where n varies from 1.3 to 2.4 depending on the solvent. In initiation step, participation of two monomer molecules has been proposed.

A wide range of organic compounds, increase the rate of initiation by metal chelates [150]. Free radical polymerization of acrylonitrile initiated by $Mn(acac)_3$ (Mn acetylacetonate) occurs readily at 25°C in DMSO solution, although there is little reaction in the bulk monomer. Piperidine, and same pyridine derivatives increase the rates of polymerization of several vinyl monomers initiated by $Mn(acac)_3$ at 70°C. Analogous results also reported for $Mn(acac)_3$ and $Fe(acac)_3$ and some carbonyl compounds and effect of ketones depends on their nucleophilicity [151].

5. Factors effecting redox polymerization

5.1. Effect of surfactants

Increase on the initial rate of polymerization of *N*-VP (*N*-vinyl pyrrolidone) by anionic surfactant (sodium oleate) rather than cationic detergent (i.e. cetyl trimethyl ammonium bromide) was proposed as due to the negative charge on the micelles formed by the anionic detergent. The increasing effect of the detergent on the rate of polymerization can be related to the enhancement of the rate of decomposition of the peroxidiphosphate [152] or peptization action of the detergent. Similar behavior was also observed for polymerization of methyl methacrylate [153] was related to the increase of colloidal stability, which causes the accelaration of rate and higher the molecular weight.

In the polymerization of vinyl acetate and methyl acrylate by the presence of certain soaps using

$K_2S_2O_8$ as initiator [154–156], was found that polymerization took place mainly within the polymer particles which causes the formation of stable suspension. A morphological study on the aqueous polymerization of methyl methacrylate (MMA) [95], showed that in the absence of stabilizers and charged end groups, primary particles are unstable [157] and flocculation as well as coagulation seem to be the main process to determine the particle size distribution instead of nucleation [158], which is the case in the presence of emulsifier. Both processes mentioned above will take place until a critical surface potential ψ_c is developed and further coagulation and flocculation is prevented [159]. The evidence of increase of molecular weight with particle growth and SEM results indicates that polymerization of PMMA proceeds in the particles and that of particles are quite large so that it can be considered that type of the polymerization is a bulk polymerization. As the particle size increases, termination can occur between two growing micro radicals and between a macroradical and a primary radical. Two mechanisms of termination of the growing polymer chains were postulated [160]:

- Colloidal macroradicals coagulate prior to termination.
- Chain radicals grow to macromolecular dimensions and undergo mutual termination while still in free solution.

Particle formation and growth occurs subsequently by phase separation and coagulation of ‘‘dead’’ species. It has been shown that termination can occur in both the aqueous and precipitated phase. After precipitation, termination will take place mainly between macroradicals. In the aqueous phase termination will occur between oligomer radicals, resulting in a lower molecular weight than in the above-mentioned case. The addition of anionic detergent also enhances the rate of polymerization of acrylamide in glyceric acid–permanganete redox system [161] due to negatively charged ionic unicelles that probably exert a repelling force between the growing polymer chains and decreases the possibility of bimolecular termination. But the positively charged micelles favors the orientation of the growing polymer chain for termination; hence the rate of polymerization decreases in the presence of a cationic detergent.

5.2. Effect of solvent and retardants

Increase in induction period and a decrease in the yield was observed [53] by addition of 5% (v/v) aliphatic alcohols and DMF to the mandelic acid–permanganate redox system in the acrylamide polymerization in the order of

$\mathrm{EtOH} > \mathrm{MeOH} > \mathrm{DMF} > \mathrm{Isopropyl\text{-}OH}$

These changes might be related to:

- Addition of water-miscible organic solvents to the reaction medium decreases the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of radical end of the growing chain.
- Due to transfer of macroradical chains to these solvents, a decrease in the rate of propagation and thereby that of polymerization is observed the decreasing effect of addition of alcohols on the rate of polymerization of *N*-vinylpyrrolidone was also observed [162], which is due to the transfer of the growing macroradical chain to the added alcohols through hydrogen abstraction from the alcohols. During chain transfer reaction there is a possibility of generation of a solvent radical which is not capable of initiating the polymerization reaction. The order of the retardation effect (Retardation constant, *I*) of the solvents

is following:

MeOH $>$ EtOH $>$ PrOH $>$ BuOH

Besides these, some amount of catalyst might be consumed in the presence of these solvents which result a fall in overall rate of polymerization and limiting conversion.

Complete inhibition was observed by the addition of retarders/chain transfer agents (methylamine) to above system. Carbon tetrachloride and benzene brought about decrease in percentage polymerization due to increased chain transfer. One ml of benzene addition caused 10 times decrease in molecular weight of the polymer. Similar order of decrease in the conversion was also observed for methylmethacrylate polymerization by Ce(IV)–alcohol system [163] which is

MeOH $>$ EtOH $>$ Acetone $>$ Control

and for polymerization of *N*,*N*′-methylenebisacrylamide by peroxidiphosphate–Ag^+ redox system [164], addition of methanol and ethanol shows a prominent retarding effect. In addition to ethanol and MeOH, acetic acid and formic acid (in the presence of 10%) also depressed the initial rate and max. Conversion of acrylonitrile polymerization by thioacetamide–permanganate initiator system [165]. It was related to (a) solvation of the radical end of the growing chain (cage effect) which hinders the propagation process and (b) increase in the regulated rate of production of primary radicals which render the termination rate relatively fast as compared to the rate of growth of the polymer chain [166,167].

5.3. Retardation effect of alkali metal salts

Addition Na_2SO_4, $ZnSO_4$ and KCl into the acrylonitrile polymerization by thioacetamide–permanganate initiator system [165], caused a decrease in the initial rate and maximum conversion which was assumed to depend on the resultant increase in ionic strength of the medium. But in the case of $CuSO_4$ the retardation of the rate was related to an increase in the rate of linear termination of polymer chains by the Cu(II) ion. Similar conclusions were made before for both AIBN-initiated polymerization of acrylonitrile in the presence of $FeCl_3$ and in the AIBN-initiated polymerization of methylmethacrylate in the presence of $CuCl_2$. (References in Ref. [165])

The addition of Na^+ into acrylonitrile polymerization by thioacetamide–permanganate initiator, caused a decrease in the rate due to formation of complexation with Mn(III) which act as poor source of the primary radicals responsible for the initiation of polymerization.

In glyceric acid–permanganate redox system the rate of polymerization decreases in the presence of alkali metal chloride [54]. The effect of the ionic radii [168] of the alkali metal ion is another possible factor in the reduction of the rate of polymerization; i.e. as the ionic radii increases, the effect of alkali metal chloride increases to supress the rate of polymerization and the maximum conversion. The rate of polymerization and maximum conversion also decrease in the presence of NH_4Cl. The retardation effect of these salts are in the order of

None $>$ LiCl $>$ NaCl $>$ KCl $>$ RbCl $>$ NH_4Cl

The effect of the addition of complex forming metal ions Cu^{2+}, Mn^{2+} and Fe^{2+} on the polymerization of acrylamide by thiomalic acid–persulfate redox system was studied. Because the complex forming metal ions reduce the concentration of thiomalic acid, it was found that rate of polymerization reaction was decreased drastically [169]. But in the presence of light even under weak illumination, Fe^{3+}, Fe^{2+}, Mn^{2+} and Co^{2+} ions at very low concentrations act as powerful photosensitizers for photo-initiation of methylmethacrylate by oxalic acid [153]. Manganese salts are however, exceptions and increase the initial rate of polymerization because Mn^{2+} ions are known to autocatalyze the initiating reaction [170].

Increasing sulfate ion concentration leads progressively to an increase in R_p of ceric sulfate–thiourea initiated polymerization of methyl methacrylate [97], which was related to the formation of reactive ceric sulfate complexes, neutral salts like KBr, KCl and KI found to be noticeably depressing R_p, KI was found to be most depressing the rate of polymerization. Further above concentration of 5×10^{-4} M KI inhibited the polymerization completely.

The salts could be reduced by cerium(IV) to the corresponding halogens. In fact liberation of I_2 was observed in the reaction medium, beside the reduction of primary radical due to decrease of cerium(IV), I_2 and Br_2 are inhibitors of radical polymerization which might be responsible for the remarkable reduction in R_p.

5.4. Effect of pressure on the acrylonitrile polymerization

The initial increase in conversion and rate with pressure was observed in $K_2S_2O_8$–$Na_2S_2O_4$ initiated polymerization of acrylonitrile [171] which was also reported for several cases [172]. This behavior might be explained in terms of an increase in chain propagation rate and/or a decrease in the rate of termination of chain ends and lost of primary radicals by increased collision, as the pressure is raised. Beyond the optimum pressure limit, the conversion as well as rate, fall with pressure. It was suggested that under these conditions diffusion of monomer from the aqueous medium to the growing polymer radical site is being gradually impaired as the system becomes much more dense on exposure to higher pressures.

From pressure–volume relation studies with methacrylic/acrylic esters and acrylonitrile that monomer molecules indeed undergo short-range alignment under pressure even in the liquid state [173,174]. Further, acrylonitrile with a planar $CH_2 = CHR$ and rod-like ($-C\equiv N$) arrangement [175] is favored for such high pressure alignment. Such alignments might create a situation, where diffusion of the monomer molecules, thus aligned to the propagation site will be less than if they are randomly distributed in the solution as in the absence of any pressure, which would imply a fall in conversion or rate.

Similar trend was also observed for the molecular weights of the polymer with increasing pressure namely tend to rise initially and fall thereafter (giving a maximum at about 8×10^6 Pa).

The conversion and molecular weight data in DMF and DMSO was also shown a similar trends to the results obtained for the aqueous system. The overall activation volume, $\Delta V^{\neq}_{pol}$ observed for free radical polymerizations of some vinly monomers are shown in Table 4.

5.5. Effect of oxygen

Oxygen plays several roles in radical polymerization reactions; depending upon the experimental conditions it may act as initiator, inhibitor or retarder, in these reactions [179]. The unique case of high-pressure radical polymerization of ethylene, reflects inhibition an initiation roles [180]. Unlike its role in initiation [181,182] the retarding or inhibitory action of oxygen in such reactions was not understood

Table 4
Comparison of activation volumes ($\Delta V^{\neq}_{pol}$) for free radical polymerization (thermal and redox polymerization) of some vinyl monomers under high pressure (abbreviations: AIBN—2,2′-azobisisobutyronitrile, BPO—benzoyl peroxide, DMF—dimethylformamide, DMSO—dimethylsulfoxide)

Monomer	Maximum pressure (MPa)	Temp (°C)	Solvent	Initiator	$\Delta V^{\neq}_{pol}$ (cm^3/mol)	Ref.
Acrylonitrile	200	50	DMF	AIBN	− 22	[176]
Methyl methacrylate	200	40	–	BPO	− 19	[177]
Styrene	100	50	–	AIBN	− 20.2	[178]
Acrylonitrile	19	40	Dearated H_2O	$K_2S_2O_8$–$Na_2S_2O_4$	− 15.7	[171]
Acrylonitrile	18	40	DMF	$K_2S_2O_8$–$Na_2S_2O_4$	− 14.8	[171]
Acrylonitrile	18	40	DMSO	$K_2S_2O_8$–$Na_2S_2O_4$	− 17.3	[171]

well, not withstanding the well-known peroxide scheme [183]. Furthermore, the peroxide-based inhibitory action of oxygen in radical polymerization is temperature dependent, due to the decomposition of peroxides at high temperatures, generating additional radicals that may initiate polymerization.

The inhibitory role of oxygen during the radical polymerization of styrene initiated by Co^{2+}–BH_4 redox system was explained by the formation of 1-phenyl ethanol [184]. In the absence of an initiator, oxygen might react with a monomer to give a peroxide which may subsequently decompose to give a peroxide radical. Oxygen may also react with a primary radical to give a peroxide radical:

$$R^{\cdot} + O_2 \rightarrow R\text{–}O\text{–}\dot{O} \qquad (178)$$

If these peroxide radicals are not very reactive as compared to their predecessors then oxygen may act as an inhibitor or retarder of polymerization. In the reverse case, oxygen may act an initiator by itself [1]. Catalytic effects of molecular oxygen in vinly polymerization involving hydrazine hydrate [185] and sulfite ion [186] was known. One of the important example of the auto-oxidazible hydroketones or enediols is ascorbic acid. In the presence of oxygen ascorbic acid alone is oxidized to dehydroascorbic, which involves a two-electron transfer. The reaction scheme is as follows [187]:

$$AH_2 \underset{\text{Slow}}{\overset{O_2}{\rightarrow}} \dot{A}H + HO_2^{\cdot} \underset{\text{very fast}}{\overset{O_2}{\rightarrow}} A + H_2O_2 \qquad (179)$$

$$AH_2 + A \underset{\text{very fast}}{\rightarrow} 2\dot{A}H \qquad (180)$$

where AH_2, AH and A represent ascorbic acid, ascorbate radical and dehydroascorbic acid, respectively. The complete absence of polymerization of acrylonitrile with ascorbic acid and oxygen alone shows that the AH radicals and HO_2 radicals are not efficient initiators of polymerization [22]. Reduction in the period of induction time was also observed for peroxydisulfate ascorbic acid initiating redox system for acrylamide polymerization [24].

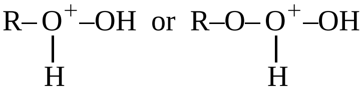
5.6. Influence of accelerators

Since the activation energy for the homolytic decomposition of alkyl hydroperoxide is much lower in the presence of metal salts (40–60 kJ mol^{-1}) than in the case of thermal activation (~170 kJ mol^{-1})

redox systems consisting of a hydroperoxide and a metal salt are able to initiate the radical polymerization of acrylic monomers at room temperature [188]. The high efficiency of these systems in conjuction with the high inhibiting power of oxygen in the radical polymerization of methacrylates [189] made possible the development of anaerobic adhesives and sealants. Industrial applications of single component anaerobic compositions [190] (methacrylates and dimethacrylates) need having a long shelf life (one or more years) and high rates of polymerization (half-life about few minutes). The first requirement is usually achieved by addition of inhibitors, i.e. hydroquinone in the anaerobic composition [188], and on the other hand presence of dialkylarylamine in combination with an organic sulphimide produces a synergistic increase in the polymerization rate [191]. The study on polymerization of methyl methacrylate initiated by cumene hydroperoxide (CHP)/copper saccharinate in the presence of *N*,*N*-dimethyl-*p*-toluidine (DMPT) and *o*-benzoic sulphimide (saccharin, SH) [192] indicated the synergistic effect of DMPT and saccharin which is explained by the fact of formation of primary radicals results almost exclusively from the reaction of Cu^+, $DMPT_2$ with saccharin-activated CHP:

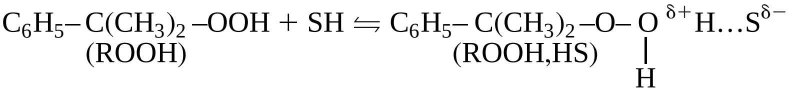
$$Cu^+, DMPT_2 + ROOH, HS \rightarrow Cu^{2+} + RO + H_2O + S^- + 2DMPT \qquad (181)$$

Initiation of MMA with the *tert*-butyl hydroperoxide/H_2SO_4 have explained by assuming that the protonation of hydroperoxide lowers the activation energy for the homolytic scission of the O–O bond [193]. However, hydroperoxide can be protonated in two positions:



$$R{-}\underset{\displaystyle H}{\underset{|}{O^+}}{-}OH \quad \text{or} \quad R{-}O{-}\underset{\displaystyle H}{\underset{|}{O^+}}{-}OH$$

Quantum mechanical calculations [194] have shown that the energy required to induce the cleavage of the O–O bond in methylhydroperoxide is 13 kJ mol^{-1} in the case of $CH_3OOH_2^+$, whereas it would be 74 kJ mol^{-1} in the case of $CH_3O^+(H){-}OH$. Therefore, it is concluded that protonation occurs mainly on the oxygen linked to the hydrogen atom; thus protonation of cumene hydroperoxide represented as [194]:



$$\underset{(ROOH)}{C_6H_5{-}C(CH_3)_2{-}OOH} + SH \leftrightharpoons \underset{(ROOH,HS)}{C_6H_5{-}C(CH_3)_2{-}O{-}}\underset{\displaystyle H}{\underset{|}{O}}{}^{\delta+}H\ldots S^{\delta-} \qquad (182)$$

copper acetate and copper acetylacetonate were also used for the polymerization of MMA, rather than copper(II) saccharinate but this compound was soluble in MMA and it is likely to be formed when an anaerobic sealant containing saccharin is applied on a copper-containing alloy. The rate of polymerization of acrylonitrile in peroxidisulfate–ascorbic acid redox system and in the presence of O_2, showed an increase by addition of Fe(III) ions. This activation effect attributed to the fact that Fe(III) itself may from an efficient redox pair with ascorbic acid, producing an increased quantity of initiating species [22].

5.6.1. Catalyzing effect of silver ions

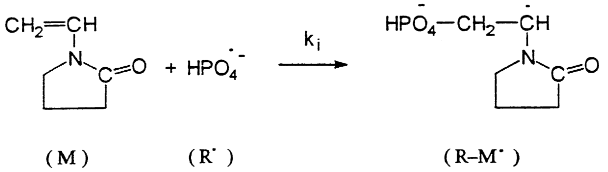
In presence of peroxidiphosphate and Ag^+, kinetics of redox polymerization of *N*-vinylpyrrolidone [195] (*N*-VP) shows that peroxidiphosphate alone does not initiate the polymerization of *N*-VP at the ambient temperature but in the presence of the Ag^+ the reaction occurred at a faster rate even at low temperature. These observations suggested the generation of phosphate ion radicals and a phosphate salt of Ag(II) from unstable complex of the peroxidiphosphate with silver ions, which initiates the polymerization of *N*-VP. It was also presumed that salt of Ag(II) acts as a cocatalyst in activating the reactivity of the monomer through interaction of Ag(II) with the lone pairs of the nitrogen in *N*-VP. This interaction of Ag(II) and the inductive effect of the carbonyl group of the monomer reduces the negative charge of the vinly group, which is generated during the attack of the phosphate ion radical at the monomer molecule the increase of the ionic strength, increased the rate of polymerization, was also supported the idea of metal ion interaction with the monomers. Following mechanisms have been proposed for free radical formation

$$H_2P_2O_8^{2-} + Ag^+ \overset{K}{\leftrightharpoons} AgH_2P_2O_8^- \tag{183}$$

$$AgH_2P_2O_8^- \xrightarrow{k_1} HPO_4^{\cdot-} + AgHPO_4 \tag{184}$$

$$AgHPO_4 + H_2O \xrightarrow{k_2} H_2PO_4{}^- + \dot{O}H + Ag^+ \tag{185}$$

Initiation



(186)

The participation of $\dot{O}H$ radicals in the initiation and termination was excluded on the basis of indication of absence of related functional groups in the polymer by qualitative tests and IR results.

Comparative study of the rate of *N*-VP with *N*,*N*′-methylenebisacrylamide indicated the rate of polymerization of the *N*-VP is low, due to steric hinderances of the pendant group present in the propagating chain.

In the presence Ag^+ in the redox system of peroxidiphosphate for the polymerization of *N*,*N*′-methylenebisacrylamide, rate of polymerization was found to be square root dependent both on the concentration of Ag^+ and peroxidiphosphate which was suggested as a better initiator than peroxidisulfate in vinyl polymerization [164].

Radical formation was suggested by following mechanism, similarly to *N*-vinyl pyrrolidone case.

$$H_2P_2O_8^{2-} + Ag^+ \leftrightharpoons AgH_2P_2O_8^- \tag{187}$$

$$AgH_2P_2O_8^- \rightarrow HPO_4^{\cdot-} + Ag^{2+} + H_2PO_4^{2-} + OH^{\cdot} \tag{188}$$

$$HPO_4^{\cdot-} + M_1 \xrightarrow{k_i} M_1^{\cdot} \tag{189}$$

Peroxydisulfate alone can also initiate the polymerization but when silver ion is coupled with peroxydisulfate behaves as a powerful initiator and such catalytic effect has been investigated for several monomers [195,196]. The kinetics of Ag(I)-catalyzed oxidation of isoamyl alcohol [197], polymerization of acrylonitrile initiated by peroxydisulfate–isoamyl alcohol catalyzed by silver ion was also shown an order of 0.5 with respect to silver ion, due to low activation energies it is considered that the homolytic fission of peroxydisulfate to yield two sulfate radicals were not suggested. In the

Table 5
Effect of ionic strength (μ) on R_p ([N-VP] = 5.0×10^{-2} mol dm^{-3}, [$H_2P_2O_8{}^{2-}$] = 8.0×10^{-3} mol dm^{-3}, [$AgClO_4$] = 5.0×10^{-4} mol dm^{-3}, Temp = 298 K). (Reprinted by courtesy of Marcel Dekker, Inc. from J. Macromol. Sci., Pure Appl. Chem. A 1994;31(7):805. ©1994 Marcel Dekker, Inc. [164])

μ (mol dm^{-3})	$R_p \times 10^6$ (mol dm^{-3} s^{-1})
0.20	6.15
0.35	8.22
0.50	10.00

peroxydisulfate–malonic acid (PS–MA)-initiated polymerization of MMA in the presence of Ag^+ [198] gave a dependence on R_p as $[Ag^+]^{0.5}$, following mechanism was proposed for initiation

$$2Ag^+ + MA \leftrightharpoons (Ag_2MA) \tag{190}$$

$$S_2O_8^- + Ag_2MA \xrightarrow[H_2O]{} MA^{\cdot} + 2HSO_4^- + \dot{O}H + 2Ag^+ \tag{191}$$

$$\dot{O}H + MA \rightarrow M\dot{A} + H_2O \tag{192}$$

$$M\dot{A} + M_1 \rightarrow M_1^{\cdot} \tag{193}$$

lower order of (0.25) on [MA] and [PS] suggested as the possibility of bimolecular decay of primary radicals, which controls the concentration of initiating primary radicals. Polymerization of some monomers by persulfate–Ag(I), i.e. acrolein [199], acrylonitrile [200] and acrylamide [201] (in the presence of lactic acid) were also studied and reaction of persulfate with Ag^+, produces highly reactive Ag^+ which react in the presence of lactic acid producing initiating free radicals.

5.7. Effect of complexing agent acid and ionic strength

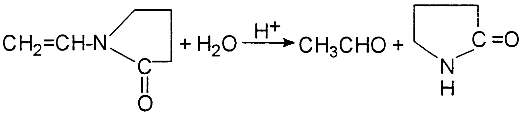
In the peroxidiphosphate–Ag^+ redox polymerization of *N*-VP [164], the presence of sodium flouride decreased both initial rate and maximum yield substantially.

This decreasing effect of sodium fluoride was considered to be, due to the complexation of the fluoride ions with the silver ion, thus slowing down the decomposition of the peroxidiphosphate, which ultimately resulted in a decrease of rate of polymerization and maximum yield.

On the other hand, addition of neutral salt, and increase on the ionic strength in the same system resulted an increase on the rate of polymerization (Table 5).

The anionic surfactant (sodium oleate) was found to be more efficient in increasing the initial rate of polymerization than the cationic detergent (cetyltrimethyl ammonium bromide, CTAB).

In the same system, the rate of polymerization and maximum percent yield decreased to a greater extent by the addition of acid. It was assumed that the presence of acid decomposes the *N*-VP into acetaldehyde and pyrrolidone as given below:



(194)

Similarly the interaction of the acid anions with the peroxidiphosphate ion might decrease the oxidizing power of the peroxidiphosphate which results in a decrease in the rate of polymerization.

6. Determination of functionalities

The end group analysis both for addition polymers having functional end groups prepared by redox systems is carried out by using suitable techniques. For linear polymers, determination of end groups gives the number average molecular weight:

$$\bar{M}_n = n \times 10^6/\mathrm{m}$$

where n is the number of groups which can be determined per macromolecule and m is the end-group concentration (in microequivalents per gram). Moreover, study of the polymer chain end provides very useful information for understanding the initiation and termination mechanisms in radical polymerizations. However, the number and kind of end groups present cannot always be predicted with accuracy because of the very low concentration of them.

Redox systems have prime advantage of operating at reasonable rates at very moderate temperatures. Furthermore, they offer an efficient way to attach a functional group at the end (s) of the polymer chains formed.

The purpose of Palit and Konar was to study the general features of permanganate–oxalic acid initiator system in aqueous polymerization, and, in particular, to throw light on the nature of the initiating free radical by detecting the end-groups of the resulting polymer. Carboxyl and strong acid end-groups were detected by both the dye partition and the dye interaction technique [153]. These tests are also suitable for detecting hydroxyl, amino, ammonium and halogen groups. Most of the potentiometric titration techniques permit acid groups of different strengths to be distinguished. As many as three or four inflections detected in this manner. The quantitative determination of the acid group content of acrylics is particularly useful in predicting the basic dye acceptance. The primary purpose of Kirby and Baldwin was to permit differentiation of acid groups of different strengths in the polymers which is initiated with the persulfate–bisulfite redox system [202]. In their work, strong acid groups refer to polymer end groups of the mineral acid type such as sulfonate or sulfate, whereas weak acid groups refer to those groups similar in strength to carboxylic acids. Polyacrylonitrile prepared with azobisisobutyronitrile or hydrogen peroxide catalysts exhibits only weak acid break, which is due to a sulfur free acid. These second breaks are attributed to the hydrolysis of nitrile groups to give weak carboxylic acid groups. Several authors have reported successful measurements by infrared absorption techniques, for example infrared spectra of acrylonitrile polymers prepared with different initiators using the potassium bromide disc technique [203]. The results showed that poly(acrylonitrile) prepared with a redox initiator containing a bisulfite reducing agent exhibited a shoulder at 1043 cm^{-1}. Polymer prepared with azobisisobutyronitrile or benzoyl peroxide showed no similar absorption. In addition, the intensity of the 1043 cm^{-1} absorption band was found to decrease proportionately as the degree of polymerization

Table 6
Aqueous polymerization of acrylamide and acrylonitrile with various concentrations of Ce(IV), H_2SO_4, monomer and carboxylic acid. (Reprinted from Eur. Polym. J. 1994;30:149, ©1994, with permission from Elsevier Science [87])

Polymer	Carboxylic acid (mol/l) $\times 10^2$	Ce (IV) (mol/l) $\times 10^2$	H_2SO_4 (mol/l) $\times 10^2$	Monomer (mol/l)
MA–AAm	2.22	2.20	22.50	0.60
TA–AAm	22.20	22.20	45.00	0.60
CA–AAm	22.20	22.20	45.00	0.60
MA–AN	2.22	0.89	2.60	0.60
TA–AN	22.20	9.44	27.50	1.75
CA–AN	22.20	22.20	22.10	2.00

increased. Further evidence confirming the linear relationship between the 1043 cm^{-1} band and the $-SO_3H$ end groups was obtained by radiochemical tagging experiments. Dyeability of the polymer with basic dyes also correlated with the 1043 cm^{-1} absorption.

Infrared absorption technique is suitable for quantitative estimations of end groups after being calibrated with polymers of known and group content. Chemical determination according to titration methods would serve as a basis for calibration.

Ceric salts such as the nitrate, perchlorate and sulfate in aqueous acidic solution are used as initiators in vinyl polymerization [71,204,205] which are effective redox systems in the presence of organic reducing agents such as alcohols, aldehydes, carboxylic acids, amino acids, hydroxycarboxylic acids and polyaminocarboxylic acids [72,84,86,92,206]. In these systems, Ce(IV) ions are formed a complex with organic reducing agent and this complex acts as source of free radicals which initiates polymer formation.

The resulting polymer was suggested to have corresponding chain end. The 3-chloro-1-propanol and 1,3-bis(dimethylamino)-2-propanol were chosen as reducing agents by Mino etal. and Renders et al., respectively. These substrates added together with Ce(IV) salt in the presence of acrylamide and acrylonitrile to obtain chains containing chlorine and hydroxyl end groups, respectively. $\bar{M}_n$ values of the polymers were determined by titrimetric methods [72,73]. In another work the presence of carboxyl group at the end of poly(methyl methacrylate) chains which is initiated by Ce(IV)–malonic acid redox system were also expected [84]. The comparison of the molecular weights obtained by titration of the carboxyl end groups with the viscometric chain length indicated that there was a mutual type termination.

It is known that when a carboxylic acid reducing agent is used the same functional group may be present as an end group at the end of the polymer chain. If the molecular weights of these samples are high, the accurate determinations of the functional end-groups are difficult because of the very low concentration of them. Therefore polymers which have short chain lengths were synthesized. In addition, to obtain vinyl polymers which have different numbers of carboxyl groups at the end of the chains, Ce(IV)–malonic acid (MA), tartaric acid (TA) and citric acid (CA) redox initiated systems were used [87,88]. Polymerizations were carried out in a round-bottomed flask with a calculated amount of Ce(IV) salt dissolved in inorganic acid, added to the monomer and organic reducing agent, all operations being conducted in water under air at 25 ∓ 0.1°C (Table 6). The purified polymers were determined viscometrically by using an Ostwald viscosimeter, conductometrically using a WTW-LF 95 model conductometer and potentiometrically with a Metrohm E-576 potentiograph (Figs. 6 and 7). All

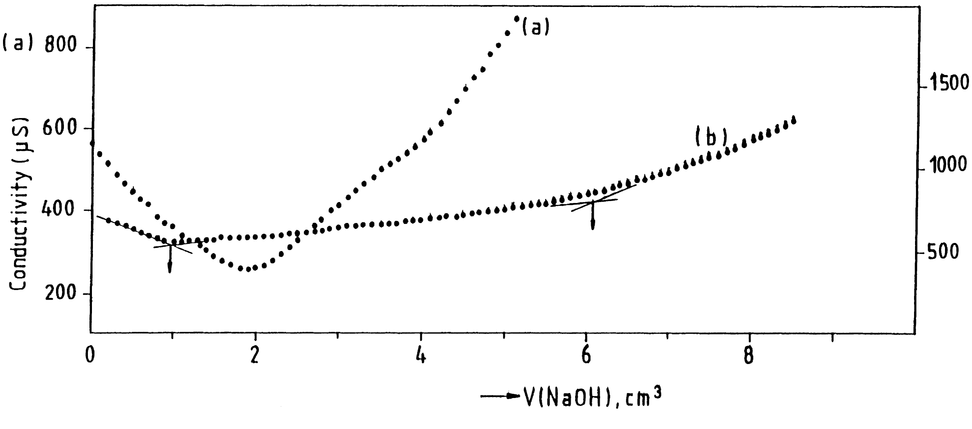


Fig. 6. Titration of carboxyl end groups of polyacrylamide initiated by MA–Ce(IV) redox system in water. Reprinted from Eur. Polym. J. 1994;30:149, ©1994, with permission from Elsevier Science [87].

titrations were carried out in a glass cell kept at constant temperature of 25°C. *N*,*N*-dimethylformamide (DMF) and ethylene–propylene carbonate (80:20 by weight) (EC–PC) and, water and ethylene glycol–water mixture (EG–H_2O) were used as solvent with alcoholic NaOH, tetrabutylammonium hydroxide (TBAOH) in toluol/isopropyl alcohol (9:1) and aqueous NaOH as titrant for polyacrylonitrile (PAN) and polyacrylamide (PAM), respectively.

Although the potentiometric determination method in nonaqueous media by glass–calomel electrode

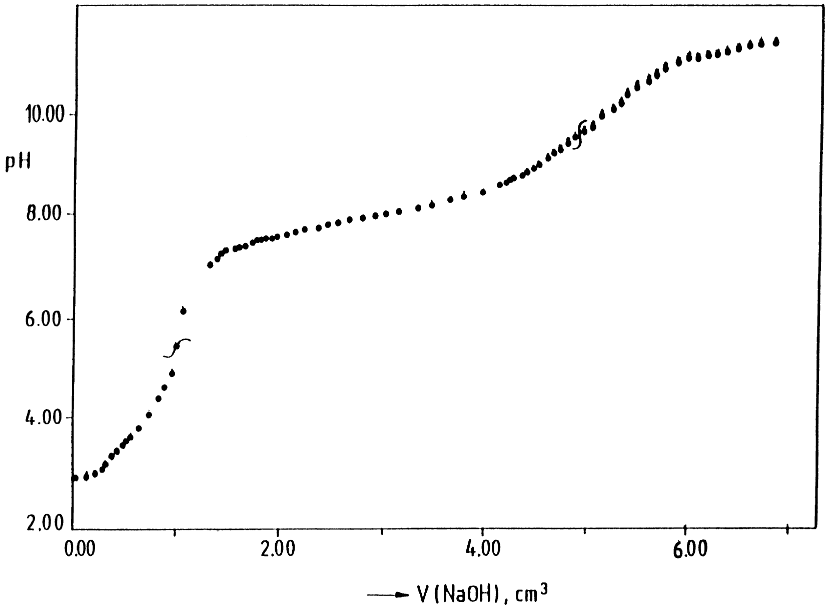


Fig. 7. Titration of carboxyl end groups of polyacrylamide initiated with Ce(IV)– MA redox systems in H_2O. Reprinted from Eur. Polym. J. 1994;30:149, ©1994, with permission from Elsevier Science [87].

Table 7
Number-average molecular weight estimated by end-group determination (Reprinted from Eur. Polym. J. 1994;30:149, ©1994, with permission from Elsevier Science [87])

Polymer	Solvent	Titrant	End group number	$\overline{M}_n$ [a]	$\overline{M}_v$ [b]
MA–AAm	H_2O	NaOH	4	2400	2700
TA–AAm	H_2O	NaOH	4	1600	1250
CA–AAm	H_2O	NaOH	6	3900	7900
	EC–PC	C_2H_5OH–NaOH		16700	17400
MA–AN			2		
		TBAOH		16700	
TA–AN	DMF	C_2H_5OH–NaOH	2	11800	11000
	EC–PC			11400	

[a] Number average molecular weight obtained by conductometric determination of the polymers.

[b] Molecular weight calculated from the intrinsic viscosity for polyacrylonitrile $[\eta] = 3.92 \times 10^{-4}\overline{M}_n^{0.75}$, for polyacrylamide $[\eta] = 6.80 \times 10^{-4}\overline{M}_n^{0.66}$

system is suitable for acids and bases [207,208], Pt–glass and glass–calomel electrode systems give similar results in respect to $\bar{M}_n$ values of low molecular weight polymers [88]. No comparable results were observed with the viscosity-average molecular weights at high molecular weight products. Furthermore, good correlation was obtained with $\bar{M}_n$ and $\bar{M}_v$ for high molecular weight of PAN polymers by the conductometric method [87] rather than potentiometric results (Table 7). A comparison of these systems shows that the use of an appropriate electrode permits titration of acid end-groups in polymers and avoids the problem of alkali metal poisoning encountered with glass–calomel electrode. In spite of only inflection is obtained from PAN polymers initiated by TA–Ce(IV) and MA–Ce(IV) redox systems, an interesting feature of conductometric titration curves of PAM samples which are initiated by carboxylic acid–Ce(IV) and aminoacid–Ce(IV) redox systems are the appearance of two inflections on the curves [87–90].

The neighboring amine groups on the repeating units of the acrylamide may react with each other to form a salt. According to this hypothesis, that salt formation was responsible for the first break, further addition of base suppresses ionization of the $-NH_3$ ion and the reaction is complete at pH $\simeq 11$ and stochiometrically measured carboxyl groups in the polymer. The $\bar{M}_n$ was calculated by assuming that polyacrylonitriles initiated with MA–Ce(IV) and TA–Ce(IV) contain two carboxyl end groups (linear termination), and polyacrylamides initiated by MA–Ce(IV), TA–Ce(IV) and citric acid–Ce(IV) contain four, four and six carboxyl end groups (mutual termination), respectively (Table 6). On the other hand, dissociation constant of the carboxyl group in the methionine molecule in aqueous solution is much higher than that of NH_2. Therefore, after ionization of the –COOH groups is complete (first break), further addition of sodium hydroxide solution of known normality determined the number of amino groups. If this is true the distance between two breaks on the curves should be a fair measure of the total number of amino groups coming from amino acids and acrylamide. Comparison of molecular weight determined by conductometric titration of carboxyl end groups ($\sim$4760) with the viscometric chain length ($\sim$4380) indicated that there were two –COOH groups per chain for polyacrylamide initiated by Ce(IV)–methionine redox system (mutual termination) [90].

The termination mechanism as well as the polymerization rate and the radical production depend

Table 8
K and K′ values of acid and corresponding polymers (Reprinted from Eur. Polym. J. 1994;30:149, ©1994, with permission from Elsevier Science [87])

Acid	Literature values [38]	K concentrated medium	Concentration range $C \times 10^2$ (mol/l)	K diluted medium	Concentration range $C \times 10^2$ (mol/l)	Polymer	K′	Concentration range $C \times 10^2$ (mol/l)
MA	1.6×10^{-3}		6–0.1			MA–AM	0.94×10^{-3}	0.22–0.03
		1.95×10^{-3}	4–0.1	1.32×10^{-3}	0.29–0.029	MA–AN	0.6×10^{-3}	0.07–0.01
TA	9.6×10^{-4}		6–04			TA–AM	7.1×10^{-4}	0.27–0.023
		8.9×10^{-4}	6–0.01	5.6×10^{-4}	0.21–0.02	TA–AN	8×10^{-4}	0.1–0.03
CA	8×10^{-4}		6–0.1			CA–AM	6.15×10^{-4}	0.11–0.03
				4.42×10^{-4}	0.11–0.006			
	8.32×10^{-4}	5.50–0.08						

accordingly on the choice of the experimental parameters. Furthermore, the monomer can be completely soluble (i.e. acrylamide) or not (i.e. acrylonitrile) in the reaction medium [73,209]. Termination mechanisms are also related to the complexity of redox processes involving both an organic substrate and an inorganic salt [86–92]. Complexes are formed but their nature and relative concentrations are affected by any change in the experimental conditions. For all of these reasons experimental results are usually only valid for the particular conditions defined in that work.

Ionization of weak acids and polymers which are initiated by these acids can be shown as follows:

$$\mathrm{HA} \overset{\mathrm{K}}{\rightleftharpoons} \mathrm{H}^{+} + \mathrm{A}^{-} \tag{195}$$

$$\mathrm{AH} \overset{\mathrm{K}'}{\rightleftharpoons} \mathrm{A}^{-} + \mathrm{H}^{+} \tag{196}$$

where K and K′ are ionization constants of acids and polymers, respectively. In order to calculate these constants the conductivity values of polymers and acids which correspond to the end groups were measured at different concentrations. $1/\Lambda$ values were plotted vs Λc by using the Ostwald dilution law, and calculated from the equation K = –(OY)(OX) (Table 8).

The end groups of polymers were studied in a medium which is diluted depending on its molecular weight. Because of the inconsistencies of K′ and K values in concentrated solutions, the acid solutions at the same concentration with the polymer ones are also studied. It can be seen from Table 6 that K values of acids depend on concentration. The difference of K′ values of polymers and the K constants of acids at the same concentration show that the ionization mechanism is influenced by the chain length, solvent medium and the monomer character.

7. Physical and functional properties of redox-initiated polymers

Due to different redox systems conditions and additional agents, i.e. metal ion–persulfate, peroxide, peroxomonosulfate, peroxidiphosphate or metal ion–organic reducing agent, resultant polymers might show different properties especially for low molecular weight polymers. There is not much studies concerned with this aspect mainly related to the amount of end groups are in very low percentage in

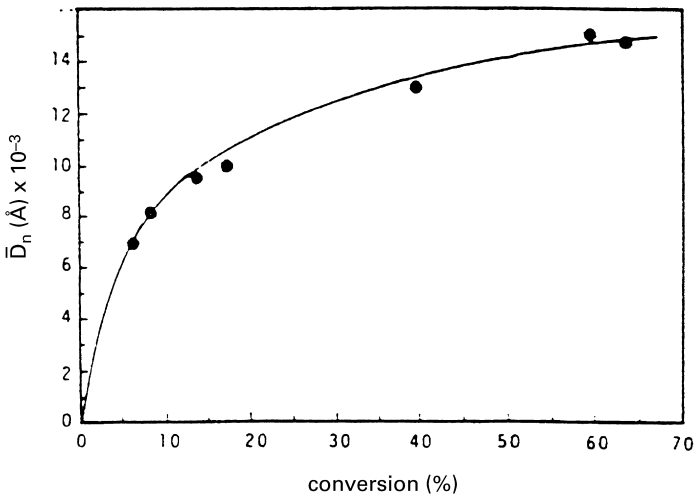


Fig. 8. Average diameter of particles of PMMA as a function of conversion. From J. Polym. Sci., Part A Polym. Chem. 1989;27:3439. ©1989 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. [95].

whole polymer, but the possibility of having different mode of termination steps, in redox polymerization, results some different physical properties in the synthesized polymers.

The structure of the monomer and the solubility of the monomer in its insoluble polymer and in water are some of the factors determining the nature of the polymerization apart from the redox pair, ionic strength and temperature conditions. The separating phase after initiation has been found to play also an important role in heterogeneous polymerization [211]. Detergents increase the solubility of the monomer by emulsifying it as well as protecting thee polymer particles from coalescence by acting as peptisers [212].

The addition of surfactants decreased the rate of polymerization of methylmethacrylate [212,213] with Fenton's reagent ($FeSO_4$ and H_2O_2), which is attributed to the greater stability of the colloid formed.

The polymerization of vinylacetate and methylacrylate has been studied in the absence and presence of certain soaps using $K_2S_2O_8$ as initiator [154–156] showed a stable suspension due to formation of polymerization in the polymer particles. In the study of morphology of PMMA with cerium(IV) isopropylalcohol [95], it was found that the particle size increases as conversion increases, and molecular weight distributions displaces to higher molecular weight as conversion increases (Fig. 8). Most of the particles were found to be spherical, only at the lowest conversion some oval particles are observed. The increase of molecular weight with particle growth was an indication of that the polymerization proceeds in the particles.

The thermal stability of poly(MMA) as polymerized in aqueous nitric acid solution using Ce(IV) alone and in combination with isobuthylalcohol (IBA), isopropyl alcohol (IPA), glucose, maltose and cellobiose as initiator systems has been investigated using differential thermal analysis (DTA) and thermogravimetry (TGA) in dynamic nitrogen [214]. The most stable polymer was found to be the PMMA obtained with Ce(IV), and the Ce(IV)–IBA, Ce(IV)–maltose polymerized samples were the least stable, by indicating that the initiator used in the polymerization of PMMA has an effect on the course of thermal degradation of the polymer.

Three reactions were identified in the thermal degradation of the PMMA obtained with Ce(IV),

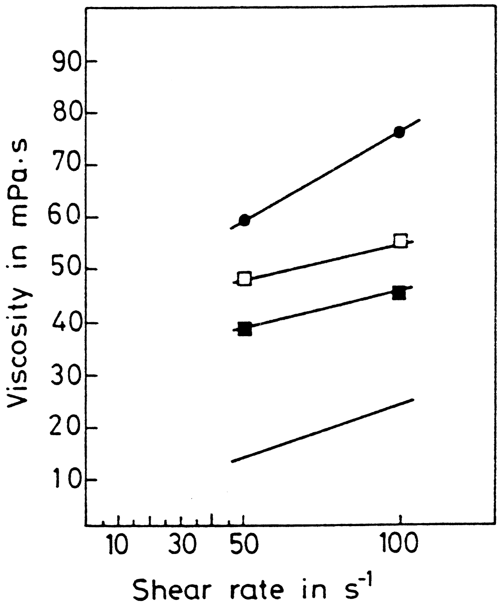


Fig. 9. Effect of shear rate on apparent viscosity of 2% cellulose–polyacrylonitrile and poly(ethylene glycol)– polyacrylonitrile solutions in DMF: (●) methyl cellulose–polyacrylonitrile, (□) poly(ethylene glycol) 1500-polyacrylonitrile, (■) poly(ethylene glycol) 4000-polyacrylonitrile, (—) poly(acrylonitrile-*co*-vinyl acetate) [103].

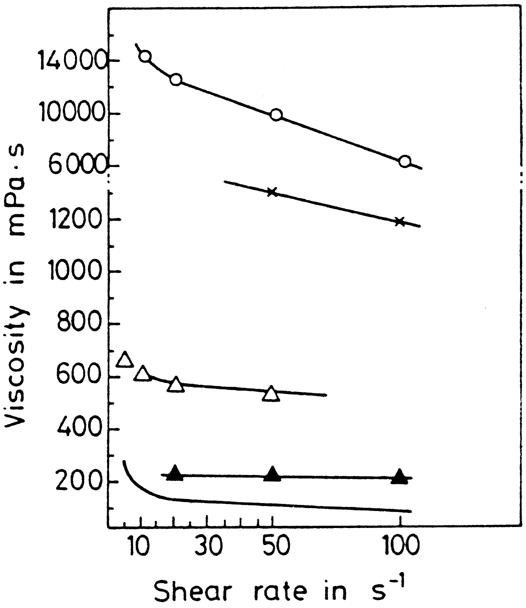


Fig. 10. Effect of shear rate on apparent viscosity of 2% cellulose–polyacrylamide solutions in water: (○) methyl hydroxypropyl cellulose–polyacrylamide; (×) methyl hydroxypropyl cellulose, (△) methyl cellulose–polyacrylamide, (▲) methyl cellulose, (—) polyacrylamide [103].

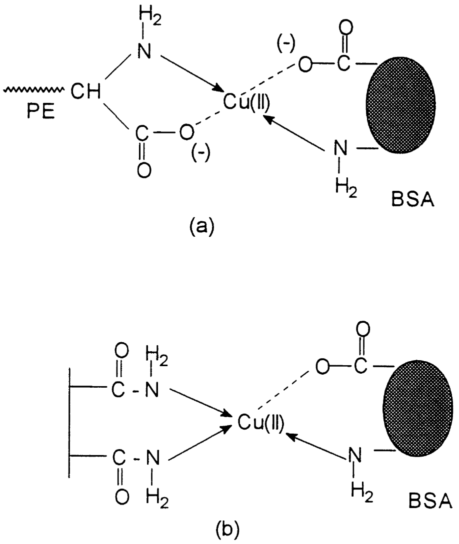


Fig. 11. Schematic illustration of the formation of chelate units between the functional groups of the PE (PAM with glycine end-group) and the protein antigen with participation of copper ions: (a) participated end groups; (b) participated side groups [216].

Ce(IV)–IPA, Ce(IV)–glucose and Ce(IV)–cellobiose, while only two reactions take place in the pyrolysis of Ce(IV)–IBA and Ce(IV)–maltose polymerized samples.

Methyl cellulose–polyacrylonitrile copolymers synthesized with cerium(IV) [103], showed much higher water absorption than commercial poly(acrylonitrile-*co*-vinylacetate), water absorption is 3.2 and 0.9 mg/cm^2, respectively. Accelerated weather test results showed that both copolymers were not effected after 150 h test time, by indicating that used redox system gives a copolymer of methyl cellulose–polyacrylonitrile with higher water absorption and similar weatherability properties to commercial polyacrylonitrile copolymer. Copolymers of this study showed similar rheological properties with corresponding homopolymers of vinyl monomer (Figs. 9 and 10).

In the radical graft polymerization from ultrafine silica surface, a redox system consisting of ceric ion and the silica particles carrying reducing groups, i.e. alcoholic hydroxyl, amino and mercapto groups used which is capable of initiating the polymerization of acrylamide [215].

Amino or mercapto groups were introduced onto the silica by reactions of surface silanol groups with 3-aminopropyltriethoxylsilane or 3-mercaptopropyltrimethoxysilane, respectively. Alcoholic hydroxyl groups were introduced onto the surface by the treatment of the silica with 3-glycidoxypropyltrimethoxysilane.

The percentage of grafting onto the silica reached about 25%, and the silica obtained by this redox graft polymerization gave a stable colloidal dispersions in water. Glycine end-group containing polyacrylamide prepared by Ce(IV)–glycine [216,217] or MnO_4^-–glycine redox systems [217] were used for the construction of immunologically active high molecular structures containing weakly bound sructures destroyed at physiological conditions.

Water soluble or insoluble complexes are formed when divalent copper ions were added to these solutions. Contracts between protein and polyelectrolyte were achieved via chelate formation in which the copper ion is attached at the center. The solubility of the polycomplexes depends on the protein/polymer ratio.

FT-IR and atomic absorption spectrometric measurements indicated that the reduced form of metal ion bound to polymer as a complex, changes with initial concentration of metal ion.

Mainly two peaks were observed in the size exclusion chromatography (SEC) of polymers. Such bimodal character of the molecular weight distribution was explained by the fact that the polymeric product consists of two fractions; free polymer unbounded to metal ions and polymer metal complexes [217].

Structure of ternary complex of polyelectrolyte–copper and bovine serum albumin (BSA) was illustrated in Fig. 11.

The immunological effects of a polyelectrolyte in the ternary complex depends on the structure, chemical transition and conformation of the macromolecules [217]. 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.

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