Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Saraç, A. Sezai , Özkara, Serife , Ustamehmetoglu, Belkis and Sezer, Esma(2003) 'Controlled Electroinduced Polymerization of Methyl Methacrylate in the Presence of Catalytic Amount of Cerium(IV)', Journal of Macromolecular Science, Part A, 40: 2, 193 — 207

To link to this Article: DOI: 10.1081/MA-120017260

URL: http://dx.doi.org/10.1081/MA-120017260

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. 40, No. 2, pp. 193–207, 2003

Controlled Electroinduced Polymerization of Methyl Methacrylate in the Presence of Catalytic Amount of Cerium(IV)

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ABSTRACT

By using the advantage of the electroinduced system being ecologically preferred system to chemical polymerizations, controlled electroinduced Methyl methacrylate (MMA) polymerization was realized with high yields and in short period of times by the use of catalytic amount of cerium(IV) [Ce(IV)] which is continuously regenerated. Progress of polymerization was followed electrochemically (cyclovoltametry, CV) and spectrophotometrically(Uv–vis spectrophotometry, by the absorbance changes of catalyst).

Electroinduced polymerization of methyl methacrylate (MMA) in the presence of Ce(IV), which allows Ce(III) to be converted to Ce(IV) electrochemically during polymerization due to fast electron transfer rate of Ce(IV)/Ce(III) redox system was performed, comparatively chemical method (oxidative). The effect of Ce(IV), monomer and sulphuric acid concentration, temperature, time, air, light and solvent on the polymerization yield was studied and compared with nonelectrolytic conditions.

Resulting polymers were characterized by FT-IR and UV–Visible spectrophotometry and molecular weight of polymers were determined by GPC and viscometric measurements.

Possible polymerization mechanisms are suggested in the case of electrolytic and nonelectrolytic conditions. Electrolytic process has an advantage over the nonelectrolytic method in which 20% higher yields obtained comparing to nonelectrolytic

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DOI: 10.1081/MA-120017260
1060-1325 (Print); 1520-5738 (Online)

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methods with a very narrow molecular weight distribution compared to chemical method.

Key Words: Polymethylmethacrylate; Electroinduced polymerization; Ceric salt; Electrocatalytic polymerization.

INTRODUCTION

Ceric salt-reducing agent system is a well known and effective initiator for vinyl polymerization.[1–4] Graft and block copolymers are also prepared with this system.[5] A free radical is formed when a reducing agent is used in combination with the ceric salt since an electron transfer reaction takes place.

Considerable work on chemical polymerization of MMA by ceric ion-reducing agent[6–13] and the electrochemical initiation of MMA polymerization have been published.[14,15] Initiation of the polymerization of MMA could be accomplished on the cathode only. Cathodic polymerization of MMA on the different cathode materials was studied,[16] and in this study, the effect of the type of the cathodic material to the rate of polymerization was searched. Few papers have been reported on the anodic polymerization of MMA in methanol–H_2SO_4 solution.[14,17] During electrochemical polymerization of vinyl monomers formation of insoluble coat or adsorbtion on the electrode surface inhibits the the polymerization, but recently it was shown that the presence of a suitable catalyst such as Ce(IV) with a high rate of 1 electron transfer and clean stoichiometry gives polymers in preperative yields, which is comparable with the oxidative chemical method. Our previous studies on the electrochemical polymerization of Acrylamide with Ce(IV) and $KMnO_4$ reducing agent initiating systems indicated that the electrolytic method compared with nonelectrolytic method at a very low concentration of initiator has many advantages. One advantage is of ecological importance[18–20] where at low catalysis, [Ce(IV)] concentration which is regenerated in the electrochemical process and therefore, its concentration remains constant during the reaction time.

EXPERIMENTAL

Reagents

Methyl Methacrylate (MMA) was distillated under vacum before use, Cerium (IV) ammonium nitrate (CAN), Cerium (IV) Sulphate (CS), Acetonitrile (ACN), Sulphuric acid, were all Merck reagents and used without further treatment. Other chemicals used were analytical reagent grade. Distillated and deionizated water was used. Mainly CS was used. Since it is not soluble in ACN in this case, CAN was used.

Equipment

Electrochemical measurements were performed by a Wenking POS 575 model Potentiostat connected with a Kipp and Zonen XY recorder and, interfaced to PC.

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Spectrophotometric measurements were made by the Shimadzu UV-160 A UV–Visible recording Spectrophotometer in a quartz cell. The UV light source used in the polymerization process was provided using a 300 W mercury lamp. FT-IR spectra were obtained by a Mattson 1000 spectrometer, preparing KBr disks. Gel Permeation Chromatography (GPC) and Ubbelohde viscometer were used for determining molecular weight by using the following equation[21]:

$$[\eta] = 55.9 \times 10^{-2} M^{0.5}\ \mathrm{ml\ g^{-1}}$$

(in methanol–toluene mixture 9/5 by volume at 26°C)

Polymerization Procedure

The chemical polymerization was carried out in a three necked flask equipped with a stirrer and a dropping funnel for the addition of a Ce(IV) solution in a water bath connected to a thermostat. MMA was dissolved in 0.3 M H_2SO_4. The initial concentration of MMA was 0.9 M in these studies. The temperature of the reaction media varied from 10°C to 50°C and the concentration of Ce(IV) varied from 1.0×10^{-4} to 1.0×10^{-2}M. The reaction time was chosen as 24 h, since the conversion was low at a shorter reaction duration.

Ce(IV) solution was added using a dropping funnel. Since stirring the reaction during the electrolysis is known to retard the process,[22] the reaction mixture was not stirred in any of the experiments. PMMA dissolved in DMF and reprecipitated several times in water. The conversion of MMA was determined by directly weighing the PMMA dried in vacum. The% conversion was obtained from the ratio between the amount of polymer formed and the initial amount of monomer in the mentioned reaction time.

The Electrochemical polymerization was carried out in a cell divided into two compartments with a sintered disc using two Pt electrodes at 2.5 V (current density = 60 mA/2.6 cm^2). The cathode compartment contained required amounts of monomer and Ce(IV) in the aqueous solution of H_2SO_4, while the anolyte contained only a H_2SO_4 solution, and the yield obtained at the same reaction conditions and reaction time compared with chemical ones.

In order to investigate the effect of the light, the same experiments were carried out under illumination by using a tungsten lamp (20 W) for 2 h.

RESULTS AND DISCUSSION

Effect of Ce(IV) Ion Concentration

The metal ion concentration was varied from 1.0 10^{-4} M to 1.0 10^{-2} M both in the chemical and electrochemical polymerization procedure. The yield increases considerably up to the concentration of 5.10^{-3} M which is used for later experiments and beyond this point the yield decreases. Although the conditions are not the same, similar behaviour was

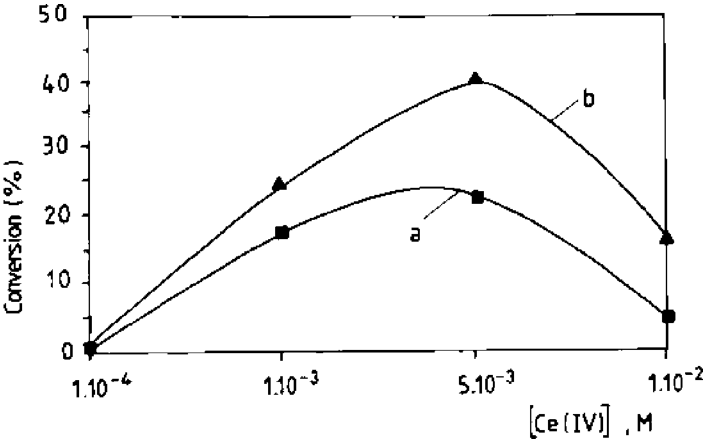


Figure 1. The effect of Ce(IV) (CS)on the conversion of polymerization [MMA] = 0.9M, [H_2SO_4] = 0.3M, t = 25°C, (a) Chemical, (b) Electrochemical polymerization. Electrodes = platinum, voltage = 2.5 V, current = 70 mA, polymerization time = 24 h.

also reported by Fernandez and Guzman et al. in the aqueous polymerization of MMA initiated by the redox couple.[7,8,11–13]

A ~ 20–25% increase in the yield was observed in the case of the electrochemical polymerization method, compared to the chemical method (Fig. 1). This might be due to the effect of both the regeneration of Ce(IV) by electrolytic conditions and the advantage of the electrochemical process alone.

The decoloration of the yellow colour of Ce(IV) solution during the precipitation of polymer in catholyte shows that Ce(IV) reduced to Ce(III), which is colorless:

Ce(IV)(Yellow) + e − → Ce(III) (Colorless)

This reaction can prevent the formation of a polymer film on the cathode surface and results in an increase in conversion. With the same purpose, Albeck *et al.* reported that they changed the polarity every 5 min with the aim of inhibiting the coating of the cathode with a polymer film shortly after the start of the experiment. However, they obtained low conversion (15%), even at high monomer concentration (70% in volume).

In addition to the advantage of using Ce(IV), since electrochemical oxidation of Ce(IV) takes place simultaneously in the anode compartment, the concentration of Ce(IV) remained almost constant during the polymerization due to fast electron tranfer process, and an additional increase in conversion occurred.

Effect of Monomer Concentration

The effect of controlled feed of monomer on the yield was examined for different concentrations of MMA, keeping the other components constant under the same conditions in chemical and electrochemical process (Fig. 2a and b, respectively). Since the solubility of MMA in water is limited, a homogeneous system can only be obtained at low monomer concentration when an experiment performed beyond 0.15 M the system

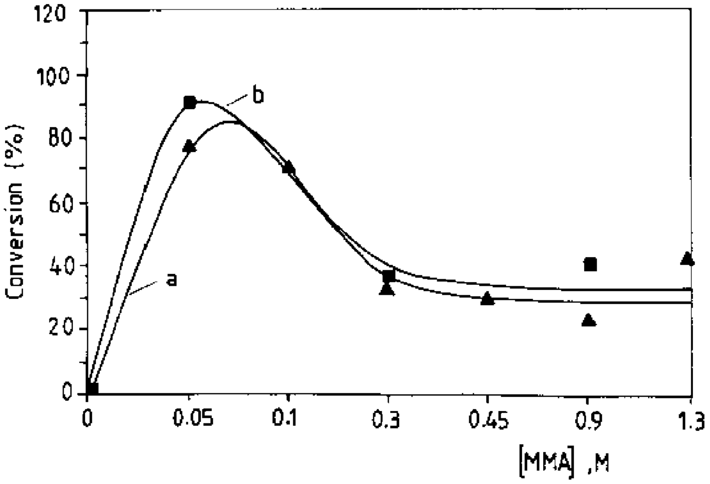


Figure 2. The effect of MMA on the conversion of polymerization. [Ce(IV)](CS) = 5.10^{-3}M, [H_2SO_4] = 0.3t = 25°C (a) Chemical (b) Electrochemical polymerization. Electrodes = platinum, voltage = 2.5 V, current = 70 mA, polymerization time = 24 h.

becomes heterogeneous, decreases in yield at higher monomer concentrations were also observed.

On the other hand, the effect of variation of monomer concentration on the polymer yield has been reported in the literature.[23] It has also been noted that a high number of radicals are adsorbed on the electrode,[24] so that their recombination rate becomes significant, and this may resulting in a decrease in yield at higher monomer concentrations.

Although the electrochemical method shows an increase in the yield about 20% compared to the chemical method up to 0.1 M MMA, beyond this point almost the same yield was observed in both cases.

Effect of Sulfuric Acid

The effect of feed of controlled sulfuric acid on the conversion is shown in Fig. 3. The conversion passes through a maximum by increasing the acid concentration, the same effects have also been reported previously for polymerization with other oxidants.[25]

The maximum conversions obtained for 0.06 M H_2SO_4 in chemical polymerization (Fig. 3a, about 50%) and for 0.3 M H_2SO_4 in electrochemical polymerization (Fig. 3b, about 40%) indicate that in electrolytic conditions conductivity and hydrogen ion concentration increase by increasing sulfuric acid concentration, which results in an increase in the yield in the electrochemical process. The increase in sulfuric acid concentration causes the formation of less reactive complexes of Cerium (IV) namely di and tri sulphate complexes,[26,27] which is responsible for decreasing the yield in both

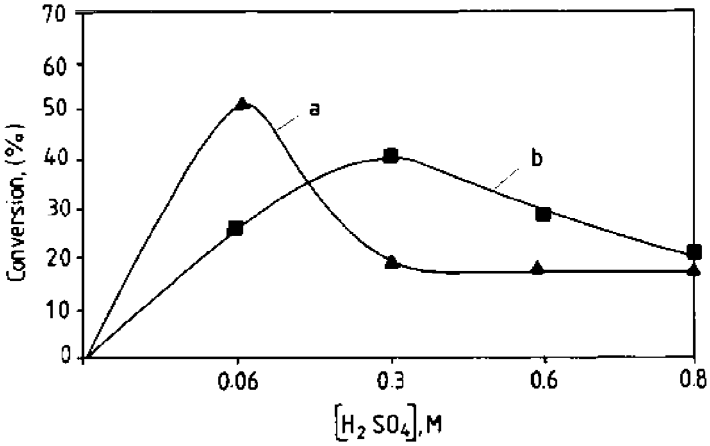


Figure 3. The effect of sulphuric acid on the conversion of polymerization. [MMA] = 0.9M, [Ce(IV)](CS) = 5.10^{-3}M, t = 25°C, (a) Chemical, (b) Electrochemical polymerization. Electrodes = platinum, voltage = 2.5 V, current = 70 mA, polymerization time = 24 h.

cases, distributions of such species governed by following equilibra:

$$Ce(4) + HSO_4^- \rightleftarrows Ce(SO_4)^{2+} + H^+ \quad K_1 = 2300*$$

$$Ce(SO_4)^{2+} + HSO_4^- \rightleftarrows Ce(SO_4)_2 + H^+ \quad K_2 = 120*$$

$$Ce(SO_4) + HSO_4^- \rightleftarrows Ce(SO_4)_3{}^{2-} + H^+ \quad K_3 = 5*$$

Where Ce(4) total of Ce^{4+}, $Ce(OH)^{3+}$, $Ce(OH)_2{}^{2+}$(at ionic strength of *I = 1)

Effect of Temperature

Polymerization was carried out with Ce(IV) (Ceric sulfate, CS) salt in a H_2SO_4 solution at different temperatures. The results of electrochemical polymerization are shown in Fig. 4. A maximum conversion was obtained at 25°C and this temperature was chosen for other experiments. This conversion is higher than that of the non-electrochemical polymerization.

Ce(IV) is regenerated in the electrochemical process, and therefore its concentration remains constant during the reaction time, but in the chemical one this is not the case as Ce(IV) consumption progresses with the extent of the reaction. The maximum conversion decreases with an increase of temperature from 25°C to 50°C. (Fig. 4. The values are in good agreement with those reported in the literature.[9] The decrease in the maximum conversion as the temperature increases may be due to the side reaction as suggested in the literature.[19]

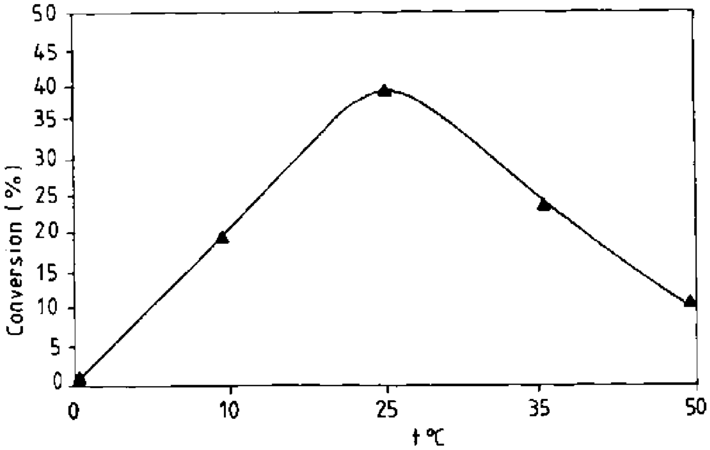


Figure 4. The effect of temperature on the conversion by the electrochemical polymerization. [MMA] = 0.9M, [Ce(IV)](CS) = 5.10^{-3}M, [H_2SO_4] = 0.3 M. Electrodes = platinum, voltage = 2.5 V, current = 70 mA, and polymerization time = 24 h.

Effect of Additives

Hydroquinone Effect

It was suggested that when the polymerization was carried out with the post-electrolysis technique, the conversion was near to 100%.[14] According to previous findings,[28] this would result in the formation of stabilized long-lived radicals capable of continuous growth. The inhibiting effect on the polymer formation of hydroquinone on the polymerization of methyl methacrylate in a two-phase system has also been reported.[15]

Although in the first two hours, a remarkable yield was not observed in the polymerization system, the inhibition test of hydroquinone on the polymerization can be followed by UV–Visible spectrophotometric measurements. It is shown in Fig. 5 that the extinction coefficient of the polymer is smaller than the monomer and the high absorbance value of polymerization medium at the end of the reaction in the absence of hydroquinone supports the conclusion that the polymerization of MMA is a radical polymerization and that hydroquinone has an inhibiting effect on the polymerization.

Effect of Air and Light

All reactions were performed in the presence of air in all experiments. In order to understand the effect of air and light in our experimental conditions, the next experiment was carried out in N_2 atmosphere in the dark. The results are collected in Table 1.

In the case of N_2 atmosphere, a 5–6% increase in yields was obtained showing the inhibiting effect of air (Table 1). Since the aim of this study was to investigate

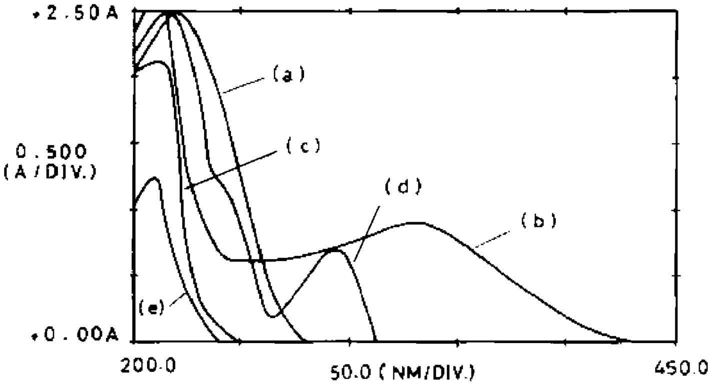


Figure 5. The spectrums of monomer, (a) monomer + Ce(IV) (CAN), (b) polymerization medium at the end of the reaction (t = 24 h) in the absence of hydroquinone, (c) polymerization medium in the presence of hydroquinone, (d) and polymer solution, (e) in ACN.

the differences between chemical and electrochemical process, although light and N_2 were affected our experiments, all polymerization were carried out in air without any illumination.

The Molecular Weight of Polymers

The molecular weights of the products were obtained both with a viscometric method and with GPC measurements. The results are collected in Table 2.

Studies in heterogeneous medium reported low yield of polymer and low molecular weight due to the deposition of the polymer produced on the electrodes.[29]

In our system, a molecular weight of 370,000 by 49% yield and 280,000 by 22% yield was obtained by using CAN and CS, respectively in the chemical polymerization of MMA while 54,000 molecular weighted polymer was obtained (yield = 40%) in the electrochemical method with CS, probably due to termination by Ce(IV) regenerated during the polymerization. In addition to this, since the concentration of Ce(IV) remained constant during the electropolymerization, Ce(IV) initiates smaller polymer chains than

Table 1. The effect of air and light on the conversion of MMA polymerization.$[H_2SO_4] = 0.3\,M$, $[MMA] = 0.9\,M$, $[CS] = 5.10^{-3}\,M$, t = 25°C, polym. time = 24 h, chemical polym.

Conditions	Conversion (%)
Light	20
Light + N_2	25
Dark	10
Dark + N_2	16

Table 2. Molecular weight of PMMA obtained by GPC and viscometric methods. [PDI ~ 1.2] $[\mathrm{Ce(IV)}] = 5.10^{-3}$ M(CS, CAN), [MMA] = 0.9 M.

		Molecular weight	
Polymerization	Method	GPC	Viscometric
Chemical	(CAN)	204,000	370,000
Chemical	(CS)	177,000	280,000
Electrochemical	(CS)	57,000	54,000

the chemical process, resulting in low molecular weight. Since a type of anion (NO_3^- or $SO_4{}^{2-}$) affects the rate of Ce(IV) oxidation, different molecular weight distribution was obtain for chemical polymerization.

FTIR Spectra

The FTIR spectra of polymers obtained by chemical and electrochemical polymerization methods are shown in Fig. 6a and b, respectively. Characteristic peaks observed at 1750, 1000–1300, 2800–3000 cm^{-1}corresponding to —C = O (Carbonyl), C—O (etheric) and —CH_3 (sp^3 CH stretch), respectively. The peak at 1100 cm^{-1} due to $SO_4{}^{2-}$ indicates the cooperation of Cerium (III) sulphate into the polymer as suggested before.[4,18]

The Effect of Solvent

Cyclic Voltammograms

The addition of water-miscible organic solvents to the reaction mixture causes the rate of polymerization to increase.[11] However, the maximum conversion and molecular weight decrease in their presence, which is deduced in the literature[30] that the ceric ion reacts with the solvent, which causes the polymerization rate to increase and the molecular weight to decrease.

In order to see the effect of organic solvent on the polymerization reaction of MMA the next experiment was performed by cyclic voltammetry(CV) measurements in ACN. Fig 7a shows the typical CV curve for Ce(IV) in ACN containing 0.1 M $NaClO_4$. There is no difference in CV shortly after the addition of monomer into this solution. The general features of this curve are marked by an anodic peak at Epa = 1.15 V and a complementary cathodic peak at Epc = 0.95 V. Fig. 7b–d shows the C.V of the same solution in the presence of MMA in 50 min, 90 min, and 120 min reaction periods, respectively.

Since all voltammograms were identical for Ce(IV) alone, after the fourth cyclic scan (in 120 min), shifts in the peak potentials towards to a positive value and

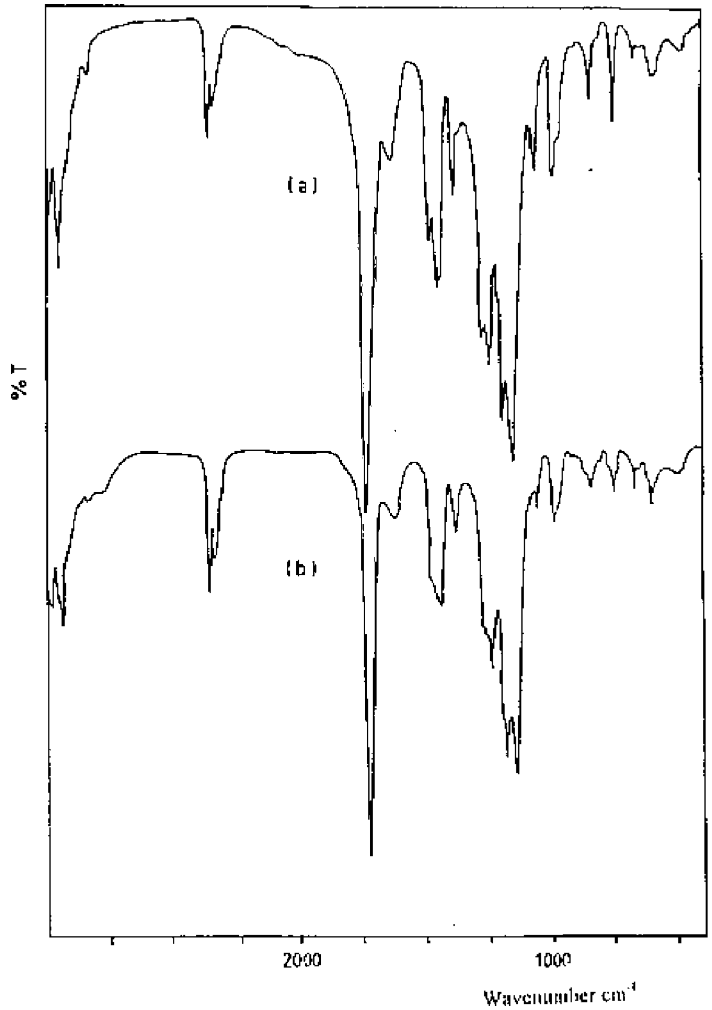


Figure 6. FTIR spectrum of (a) chemical (b) electrochemical polymerization products.

decrease in the peak current provide evidence of the polymerization of MMA with Ce(IV).

Soluble oligomers in CH_3OH in this polymerization were reported.[9] Although C.V. measurements show the reaction with Ce(IV) and MMA, a lack of polymer precipitate due to the solubility of PMMA in ACN and small differences in the viscosity (from $\eta_{sp1} = 0.0207$ to $\eta_{sp2} = 0.0345$) of the resulting solution with ACN might be related to the oligomer formation in the reaction medium (Fig. 5). The shorter disappearing time of Ce(IV) ion during reaction in ACN than in the aqueous medium (4 h and 24 h, respectively) shows the increase in the polymerization rate, resulting in oligomer formation.

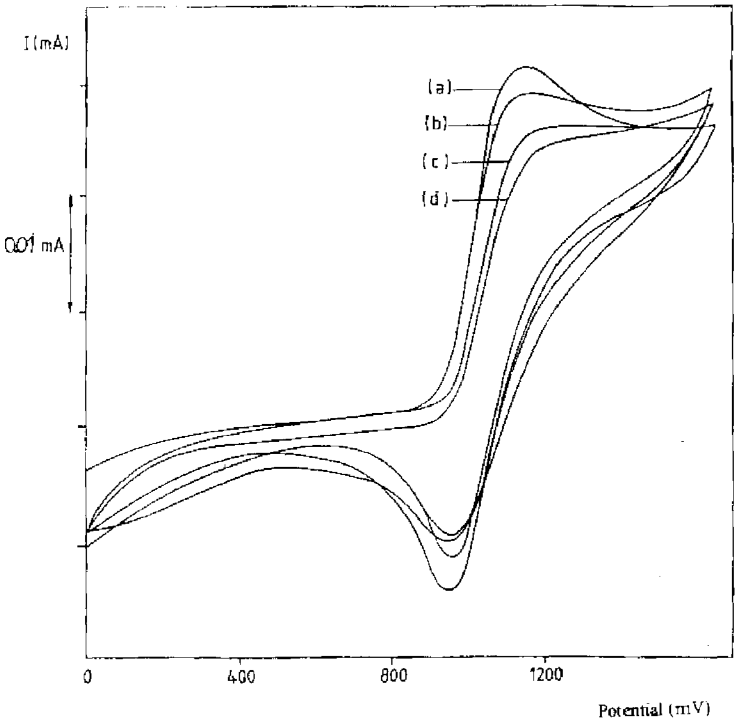


Figure 7. Cyclic Voltammograms of, (a) Ce(IV) (CAN) and mixture of Ce(IV) and MMA at the beginning of the polymerization of MMA, (b) after 50 min, (c) after 90 min, (d) after 120 min in ACN. [MMA] = 0.1M, [Ce(IV)] = 5×10^{-3}M, [$NaClO_4$] = 0.1 M (electrolyte).

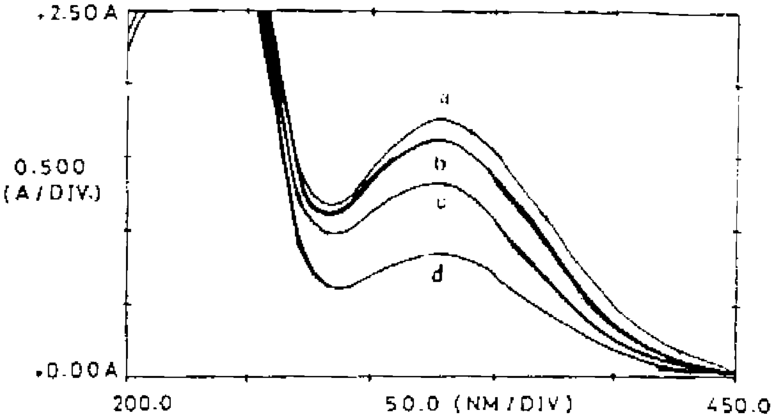


Figure 8. UV–Visible Spectrums of, (a) Ce(IV) (CAN) alone and mixture of Ce(IV) and MMA at the beginning of the reaction, (b) after 20 min, (c) after 40 min, (d) after 80 min.in ACN. [MMA] = 0.1 M, [Ce(IV)] = 5×10^{-3} M (CAN) diluted 1:26 ratio.

UV–Visible Spectra

Since the solubility of monomer is low in water, in order to investigate the reaction between MMA and Ce (IV), acetonitrile was selected and the reaction was followed by UV–Visible measurement in this medium. The absorption spectrum of Ce (IV) alone is given in Fig. 8. It has a maximum absorbance at 327 nm, which gave similar spectrum shortly after the addition of monomer into this solution as observed for C V measurements. Although in the absence of monomer the absorption values do not change, remarkable decrease of absorbance in the presence of monomer was observed in 120 min reaction time (Fig. 8a–d, respectively), showing the reaction between Ce(IV) and MMA.

CONCLUSION

Initiation of polymerization of MMA with Ce(IV) was a predominant case (oxidative chemical polymerization), in addition to radicalic species (to a certain extent) formed from the solvent during oxidative process depending on experimental conditions. Blank experiments from which either Ce(IV) or MMA were excluded gave no detectable polymerization during this period. This indicates that Ce(IV) itself or its catalyzing effect is capable of initiating MMA polymerization. Under the experimental conditions, oxidative radical formation by Ce(IV) by the chemical polymerization is possible.

In order to understand the possibility of anodic polymerization of MMA in H_2SO_4 solution, the anodic compartment was filled with a known amount of ceric sulphate, MMA and H_2SO_4 solutions. The lack of polymer in the anodic compartment shows that the initiation of MMA, which was reported by A. Aurizi et al.[17] in a $CH_3OH–H_2SO_4$ solution, does not occur at the anode through the oxidation of H_2SO_4 to radicals at least for a detectable yield.

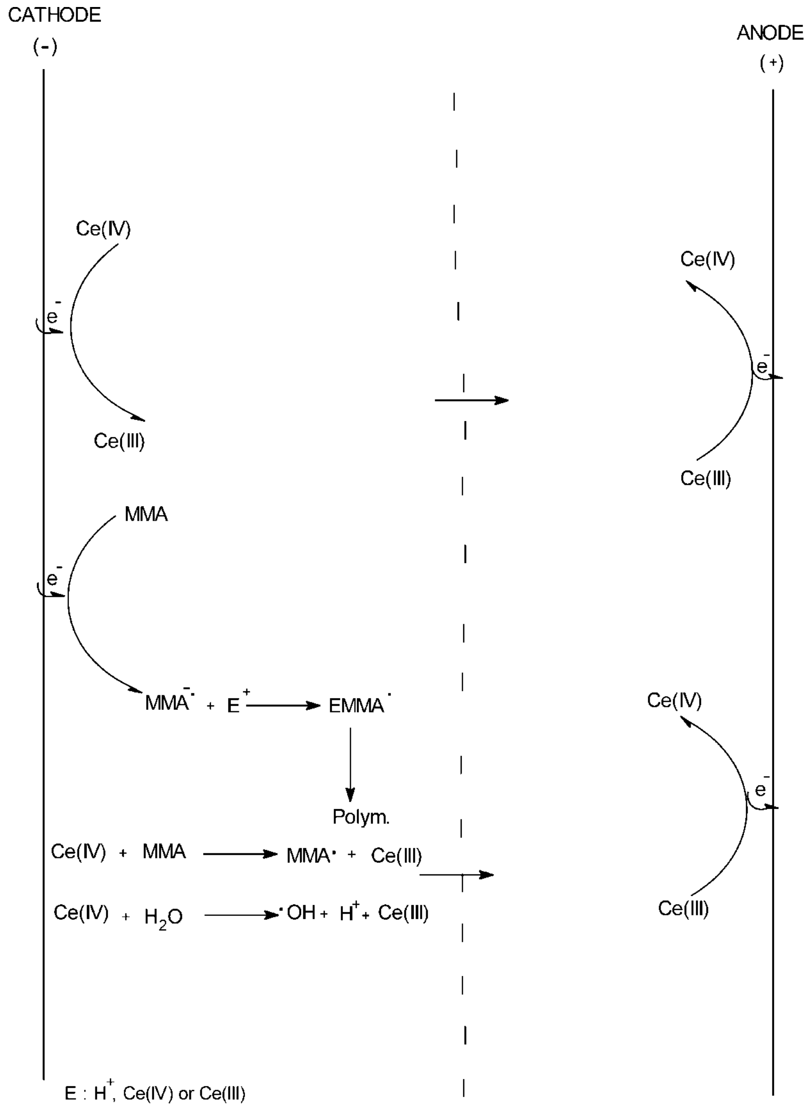
Parravano et al.[16] reported the spontaneous polymerization of MMA in water by free hydrogen radicals. The blank experiment shows that a H_2SO_4 solution alone was not capable of initiating MMA in our experimental conditions for preparative purposes. The studies of the capacitance of the electric double layer on a dropping mercury cathode in the presence of MMA suggested[31] the radicals formed as a result of the reversible electrochemical process initiate that polymerization:

$$\text{Pt–H} + \text{MMA} \rightarrow \text{H–MMA}$$

It is known that in the presence of light, Ce(IV) can produce hydroxyl radicals (•OH) which may initiate the polymerization of MMA.[32,33]

$$\text{Ce(IV)} + H_2O \xrightarrow{h\nu} \bullet OH + H^+ + \text{Ce(III)}$$

In the absence of Ce(IV) no polymerization was observed under illumination, showing that initiation directly from water and MMA alone or together is not possible. In addition to this, polymerization occurred under dark conditions only in the presence of Ce(IV) with a 10% yield (Table 1).According to these results, •OH resulting from reaction under the presence of day light conditions with Ce(IV) also contributes to polymerization of MMA (about 10%).In the presence of Ce(III), polymerization does not occur, which



Scheme 1.

eliminates the possibility of initiation polymerization by Ce(III) at cathode department. The results of these studies indicates that the presence of cerium(IV) can induce the electrochemical polymerization of MMA. Possible reaction mechanisms occurring at anode and cathode compartment can be summarized in Sch. 1. Mainly disproportional termination may occur for MMA as suggested in the literature.[34] By the regeneration of Ce(IV) electrochemically, as well as hindering the formation of polymeric film on the electrode surface, keeping in mind that the electroinduced system has ecological advantages over chemical method. In addition, it is possible to obtain PMMA in a higher yield with a very narrow molecular weight distribution in comparison to oxidative chemical polymerization, by a satisfactory control of feed ratios and other experimental parameters.

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Received April 19, 2002
Revised September 16, 2002