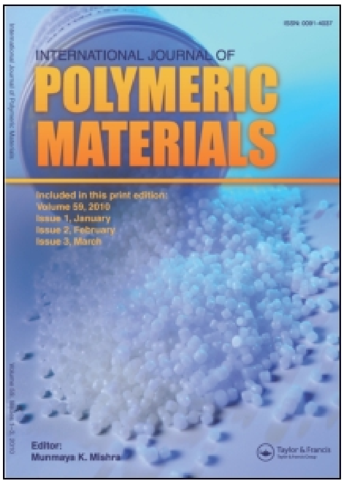

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

ELECTROINDUCED DISPERSIVE POLYMERIZATION OF METHYL METHACRYLATE IN AQUEOUS MEDIA

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To cite this Article Sarac, A. Sezai and Cebeci, Fevzi C.(2004) 'ELECTROINDUCED DISPERSIVE POLYMERIZATION OF METHYL METHACRYLATE IN AQUEOUS MEDIA', International Journal of Polymeric Materials, 53: 9, 763 — 776

To link to this Article: DOI: 10.1080/00914030490498252

URL: http://dx.doi.org/10.1080/00914030490498252

International Journal of Polymeric Materials, 53:763–776, 2004
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490498252

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ELECTROINDUCED DISPERSIVE POLYMERIZATION OF METHYL METHACRYLATE IN AQUEOUS MEDIA

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The electroinduced and chemical dispersion polymerization of methyl methacrylate was performed in aqueous methanol solution (water/methyl alcohol ratio 50/50 by wt%) in the presence of poly(vinyl pyrrolidone) as a stabilizer with ceric sulfate as an initiator. The effects of various polymerization parameters, for example concentrations of recipe ingredients, temperature, potential, and duration, on polymerization yield were examined. In all cases higher yield was obtained with the electrochemical polymerization procedure. Initiation rates of polymerization processes, thermal properties of polymers, interaction of initiator with monomer and stabilizer were investigated in detail. Possible structure of polymer is proposed, and a tentative polymerization mechanism is suggested.

Keywords: electroinduced polymerization, dispersion polymerization, polyvinyl pyrrolidone, methyl methacrylate, ceric sulfate

INTRODUCTION

On account of the high oxidation power of ceric salts and their well-defined stoichiometry, Ce(IV)-reducing agent redox system is widely used in polymerization of vinyl monomers in aqueous media [1–8]. In recent years, electroinduced polymerization of vinyl monomers, such as polymerization of acrylamide [9], acrylonitrile [10], and N-Vinyl carbazole [11] was achieved successfully, with the use of catalytic amount of oxidant in the absence or in the presence of a reducing agent, which indicated some advantages, for example regeneration of cerium (IV) on the electrode surface without allowing nonconductive surface coating of the electrode preventing further electron transfer.

Received 14 February 2002; in final form 28 July 2002.

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Previously, this method was employed for polymerization of acrylonitrile in the presence of polyacrylic acid and catalytic amount of Ce(IV), and stable micron size polyacrylonitrile particles were obtained [12].

In this study, electroinduced dispersion polymerization of methyl methacrylate was carried out, in the presence of poly(vinyl pyrrolidone) as a stabilizer, catalytic amount of Ce(IV) salt, sulfuric acid, and water-methanol mixture, with an aim of preparing monodisperse particles of poly(methyl methacrylate) [PMMA], to facilitate the preferance of electrochemical method by combination with an oxidant catalyst [cerium(IV)].

Dispersion polymerization [13] made great improvements in the last two decades. It has been reviewed by several authors [14–17]. Fundamental research in dispersion polymerization using common monomers was done since 1982 by Almog et al. [18] at Xerox, by ober et al. [19], and Paine [20–23], and at Lehigh University by El-Aasser's group [24–27]. The dispersion polymerization of methyl methacrylate in non-polar organic media has been extensively studied, whereas the same polymerization of methyl methacrylate in polar media was attempted, but these polymerization processes have encountered various difficulties. The current article describes a redox initiator system composed of cerium(IV)-methanol and/or cerium(IV)-poly (vinyl pyrrolidone) couple, which is more proper for polar media.

EXPERIMENTAL

Chemicals

Methyl methacrylate (MMA) was distilled before using. All other chemicals were used with no further purification; poly(vinyl pyrrolidone) K-30 (PVP) ($M_w = 40000$ g/mol) (Fluka), ceric sulfate (CS) (Fluka), ceric ammonium nitrate (CAN) (Fluka), methyl alcohol (MeOH) (Carlo-Erba), acetonitrile (Carlo-Erba), sodium perchlorate, sulfuric acid (Carlo-Erba), and deionized water.

Instrumentation

FT-IR spectra were obtained by a Mattson 1000 FT-IR spectrophotometer using KBr disks, quantitatively prepared 1/150 (sample/KBr) ratio. A Shimadzu 160A UV-Visible Spectrophotometer was used for absorption measurements. ^{1}H-NMR analyses were recorded on a Bruker 250MHz NMR electro-spin. Samples were dissolved in $CDCl_3$ for measurement. Cyclic Voltammetry measurements were carried out using a Wenking POS model 73 potentiostat connected with a Kipp and Zonen X-Y recorder. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed with Setaram DSC 92-8. TGA curves were obtained on heating the sample at $10\mathrm{K\,min}^{-1}$ from 50°C to 500°C in an inert N_2 atmosphere. Particle size and size distributions were measured using a 256-channel Coulter Multisizer. A computer interfaced to the multisizer was employed to calculate and to plot for size, area, and volume distributions and their parameters. More than 200,000 particles were counted for each size distribution. It is found that particle size distribution of sample 1C3 is narrow, and the mean value of particles is 4 micrometers.

Chemical and Electrochemical Reaction Cell

Similar reaction cells were used for chemical and electroinduced polymerization processes. A glass reaction cell whose anode and cathode compartments were divided by a sintered glass disk of medium porosity was used for divided-cell electroinduced polymerization. The cell was placed in temperature controlled water bath at 50°C.

Preparation of PMMA Dispersions

The dispersion polymerization of MMA was performed in aqueous methanol solution (water/methyl alcohol ratio 50/50 by wt%). All polymerizations were carried out according to a standard recipe. Polymerization conditions are shown in Table 1, and sample codes and reaction conditions of some recipes are given in Table 2. The recipe was changed to yield different concentrations of recipe ingredients but the total amount of recipe was kept at 25 grams. In duration,

TABLE 1 Polymerization Conditions and the Standard Recipe used in Preparing PMMA Dispersions

Variables	Standard recipe	By wt.%
Initiator concentration	Initiator (Ceric Sulfate)	0.1
Sulfuric acid concentration	Sulfuric acid	10
Monomer concentration	Monomer	5
Stabilizer concentration	Stabilizer	2.5
Solvency of the medium	H_2O/MeOH	41.2/41.2
Temperature	Temperature	50°C
Duration	Duration	60 min
Potential	Potential (Volt)	2.4 V
	Stirring speed	100 rpm

TABLE 2 Sample Codes and Reaction Conditions of Some Recipes

Sample code	Initiator wt%	MMA wt%	Potential volt
1C3	0.1	5	—
1E3	0.1	5	2.4
1C5	0.4	5	—
1E5	0.4	5	2.4
4C5	0.1	10	—
4E5	0.1	10	2.4
4E4	0.1	7.5	2.4

H_2SO_4: 10 wt%, PVP K-30: 2.5 wt%, Solvency: H_2O/MeOH: 1/1, Temperature: 50°C, Duration: 60 Min.

potential, and temperature studies a standard recipe was applied as shown in Table 1. The prepared polymers were poured into centrifuge tubes and were centrifuged at 7,200 rpm for 4 h. The liquid phase was separated using a pipette and the separated polymer was washed and dried in a vacuum oven at room temperature for 48 h.

Yields of the polymers were calculated according to the following equation,

$$\text{Yield}\,\% = \frac{\text{Amount of Polymer (g)}}{\text{Amount of Monomer (g)}} \times 100$$

RESULTS AND DISCUSSION

Polymerization Yield

Due to the possibility of initiation with Cerium-PVP and Cerium-MeOH redox couple, and in order to better understand the contribution of PVP and MeOH to the polymerization yield, emulsion polymerization of methyl methacrylate was also carried out. Polymerization of MMA was performed with PVP in the absence of MeOH according to the standard recipe, given in Table 1, modified by using 82.4% by wt. H_2O instead of water-MeoH mixture, and the yield was found to be 60%. Homopolymerization of MMA was carried out with MeOH. In this case PVP was omitted by replacing with equal amount of solution mixture from the standard recipe, and the yield found was 56.7%.

Effect of Initiator on the Yield

The effect of ceric sulfate (CS) amount on the yield was examined between the range 0.01 and 0.4% by wt. Below this range no yield was

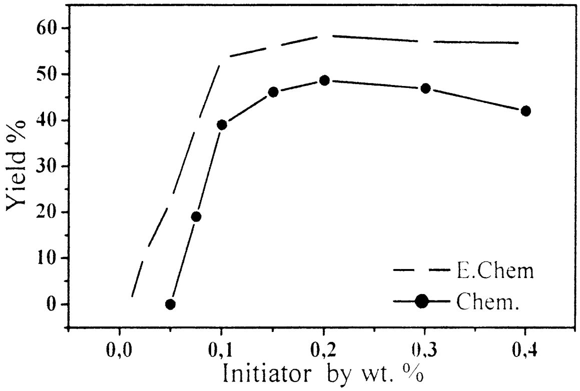


FIGURE 1 Effect of initiator on the yield, curves for both polymerization methods, Chem. Chemical and E. Chem. Electrochemical. $H_2SO_4 = 10.0$ wt.%, PVP k-30 = 2.5 wt.%, MMA = 5.0 wt.%, t = 60 min, T = 50°C, E = 2.4 V.

obtained for both methods. At 0.05% by wt. CS, PMMA was not obtained with chemical method, but with electroinduced method PMMA was obtained at the same experimental conditions, the yield is 24%. Up to 0.2 by wt% Ce(IV) is highly effective on the polymerization yield (Figure 1). At higher concentrations of Ce(IV) the yield started to slightly decrease, which might be due to termination reactions caused by Ce(IV).

Effect of Sulfuric Acid on the Yield

The yield passed through a maximum by increasing the acid percentage. The increase in the yield by increasing the percentage from 5-wt% to 15-wt% might be due to the sulfuric acid behaving as a strong electrolyte and allowing higher currents to pass through the electrolyte. Later decrease in the yield by further increase in the sulfuric acid percentage may be explained by the distribution of species present in solution, which is well established in the previous literature [28–29] (Figure 2).

The amount of the trisulfate complexes is especially increased. It is known as a less reactive species among the other sulfate species due to heavy complexation of Ce(IV) coordination sites, which prevents the electron transfer.

Effect of Monomer on the Yield

The polymerization yield gives a maximum at 10% by wt. Concentration of MMA (Figure 3); similar results were reported for other

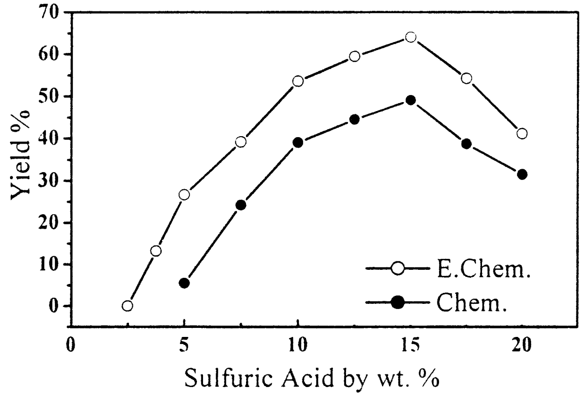


FIGURE 2 Effect of sulfuric acid on the yield, curves for both polymerization methods, Chem. Chemical and E. Chem. Electrochemical. CS = 0.1 wt.%, PVP K-30 = 2.5 wt.%, MMA = 5.0 wt.%, t = 60 min, T = 50°C, E = 2.4 V.

types of polymerizations of MMA. At higher concentration of the MMA a decrease in the yield may be due to mutual termination or heterogeneity of polymerization medium because of solubility problems of the monomer. At higher MMA concentrations, for example, 15% by wt., precipitation was observed for chemical polymerization, whereas at the same conditions for electroinduced polymerization for resulting polymeric product was still dispersed.

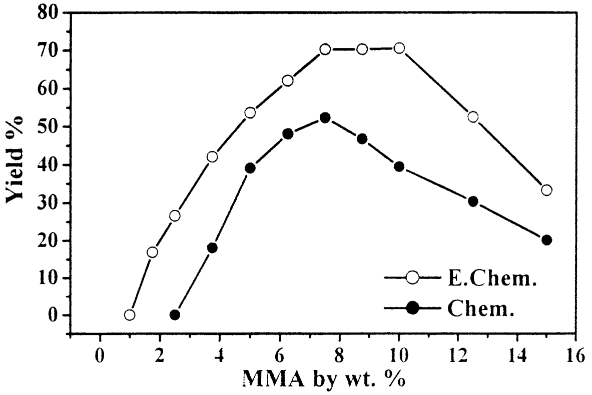


FIGURE 3 Effect of MMA on the yield, curves for both polymerization methods, Chem. Chemical and E. Chem. Electrochemical. CS = 0.1 wt.%, H_2SO_4 = 10.0 wt.%, PVP K-30 = 2.5 wt.%, t = 60 min, T = 50°C, E = 2.4 V.

Effect of Duration on the Yield

Yield of all polymerization processes increase within 20 min and then the time slightly affected the yield for both chemical and electro-induced polymerization conditions. In the former 68% of the yield and in the latter 74% of the yield were obtained in the first 20 min. After 60 min the conversion became constant. It should be noted that the polymerization rate in aqueous methanol solutions was much faster than in pure methanol. At higher content of water in the solution mixture, faster conversion rates were seen. These results are explained as follows. In highly hydrophilic solvent, the hydrophobic monomer MMA is easily absorbed in the particle cores, and thus, the polymerization proceeds mainly inside the particles. Therefore, the polymerization proceeds fast in such solvent [30].

Effect of Solution Composition, Potential, and Temperature on the Yield

Up to H_2O/MeOH: 30/70 solvent ratio no polymerization occurred in chemical polymerization, but at the same solvent composition polymer was obtained electrochemically (Figure 4). The yield was raised by increasing water content of the polymerization medium for both polymerization methods. Possibility of graft copolymerization of PMMA with PVP would increase, with increasing water content, resulting in higher polymerization yield.

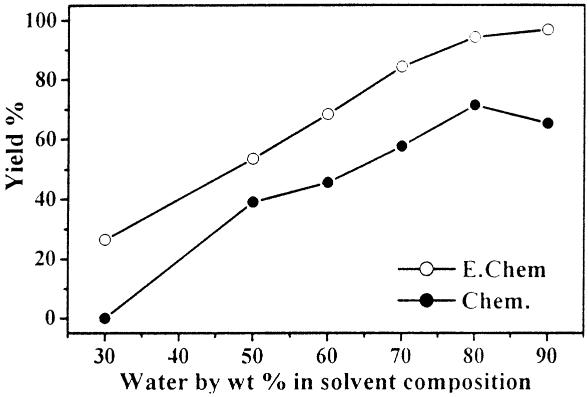


FIGURE 4 Effect of solvent composition on the yield, curves for both polymerization methods, Chem. Chemical and E. Chem. Electrochemical. CS = 0.1 wt.%, H_2SO_4 = 10.0 wt.%, MMA = 5.0 wt.%, PVP K-30 = 2.5 wt.%, t = 60 minutes, T = 50°C, E = 2.4 V.

Effect of potential in the range of 1.8 V and 3.0 V was investigated; the maximum yield was obtained at 2.4 V, and this potential value was applied for other reactions. The cell conditions do not allow enough current to pass through the electrolyte up to 1.8 V, and a further decrease in the yield above 2.7 V could be due to some side reactions.

Temperature is effective until about 55°C and then loses its effect up to 65° C. This result is expected for conventional free radical polymerizations.

Spectral Analysis

Investigation of Ce(IV)-methyl alcohol and Ce(IV)-PVP interaction with UV-Vis Spectroscopy were carried out based on decreasing absorbance of Ce(IV). Reaction rate (k) can be calculated from the slope of the graph log $(A_t - A_\infty)$ vs. t. where; A_l, is absorption of Ce(IV) at any time of reaction, A_0 absorption of Ce(IV) at the beginning of the reaction and A_∞ is absorption of Ce(IV) at the end of the reaction. A graph relating the absorbance values of Ce(IV) and time was plotted. log $(A_t - A_\infty)$ values were calculated and graph of log $(A_t - A_\infty)$ vs. t was re-plotted. From the slope of each graph reaction rate and correlation coefficient (r) were calculated. Results are given in Table 3. It can be concluded from these data that the reaction between Ce(IV)-methyl alcohol and Ce(IV)-PVP is pseudo-first order.

FT-IR spectra of chemically and electrochemically obtained polymers of the standard recipes (1C3 and 1E3) were taken and the results are given in Figures 5a and 5b, respectively.

All of the spectra of the polymers, which were obtained chemically and electrochemically with different MMA/PVP ratios, resemble the characteristic pattern of PMMA. They have strong bands at 1753 cm $^{-1}$, which corresponds to $-C{=}O$, (carbonyl of ester group), and 1100 cm $^{-1}$, which corresponds to $-C-O$, (ether) and 2950 cm $^{-1}$,

TABLE 3 The Reaction Rate Constant ($k = min^{-1}$) and the Correlation Coefficient (r) were Calculated from UV-Vis Spectra

	Interaction of Ce(IV) with			
	Methyl Alcohol		PVP	
	258 nm	305 nm	257 nm	305 nm
k	0.095	0.087	0.171	0.127
r	−0.998	−0.999	−0.968	−0.998

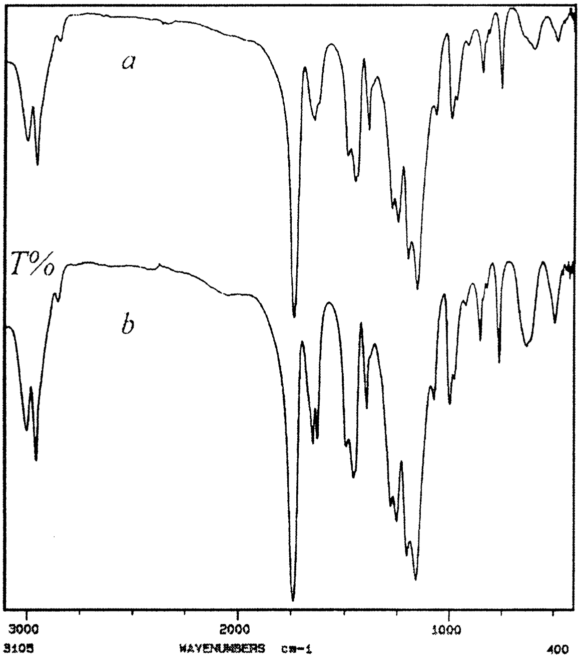


FIGURE 5 FT-IR spectra of chemically and electrochemically obtained polymers of standard recipe (a) 1C3 and (b) 1E3.

which corresponds to aliphatic –C–H. In addition to characteristic bands of PMMA, presence of a band at 1651 cm^{-1}, which corresponds to carbonyl group of PVP, gives evidence for the inclusion of PVP in the structure. When the MMA/PVP ratio increase, the intensity of the characteristic bands for the PMMA increase as expected. It is obvious that there is no significant difference between the PMMA, which was obtained in aqueous solution [31] with Ce(IV).

Effects of the PVP and methyl alcohol on the polymerization mechanism were also followed by FT-IR spectra. In the absence of methyl alcohol, polymerizations of MMA with PVP, and in the absence of PVP, the polymerization of MMA with methyl alcohol were carried out. In the former case, the ratio of the band intensities, which are attributed to carbonyl group of PMMA and PVP at 1753 cm^{-1} and 1651 cm^{-1}, respectively, is lower than in the methanol case. These results indicate that initiation through stabilizer is also possible. However, FT-IR spectra of other polymers obtained in the latter case, this ratio is almost the same for each of the polymers and it is close to the methanol case.

In accordance with the results obtained from FT-IR spectra, the possibility of incorporation of PVP into PMMA structure seems low.

The H-NMR Spectra of the chemically obtained sample 4C5, and the electrochemically obtained sample 4E5, Figures 6a and 6b, are identical. And there are no peaks belonging to PVP in either. The NMR spectra of polymers obtained in high MMA/PVP ratio have characteristic peaks of the PMMA at 0.84 and 1.02 ppm, peak of methylene groups at 1.82, and 1.89 ppm and the methyl ester proton at the 3.60 ppm indicate that the structure of the polymer chain is predominantly syndiotactic.

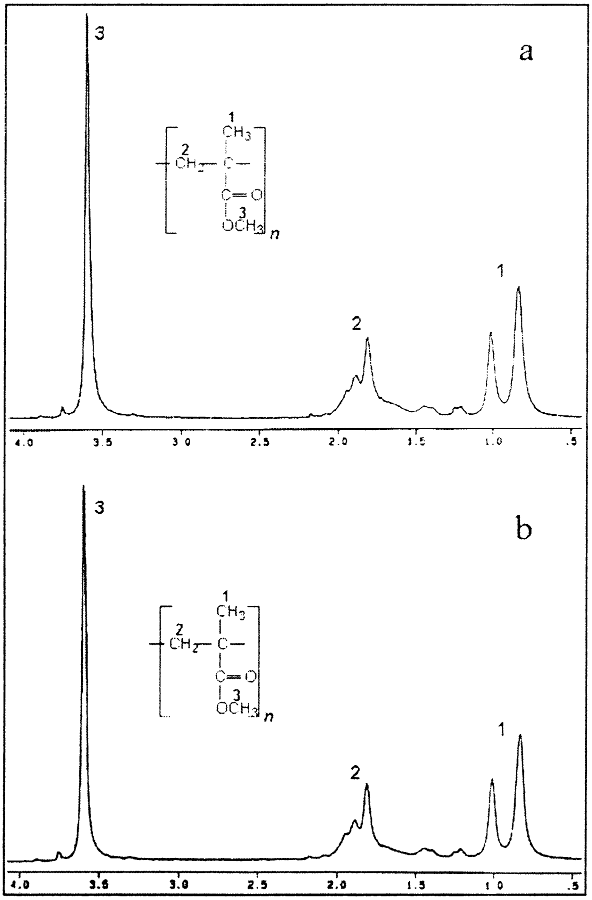


FIGURE 6 (a) NMR spectra of chemically obtained sample, 4C5; (b) NMR spectra of electrochemically obtained sample, 4E5.

Thermal Analysis

TGA and DSC were performed in order to establish the thermal properties as well as to understand the effect of the Ce(IV) incorporated within the polymer matrix, and the effect of the PVP on the resulting polymer. Depending on the conditions of polymerizations of PMMA two degradation reactions occur. These have different energies of activation and these energies depend on chain length, the mechanism of the degradation process, range of conversion, and the percentage of double-bonded chain ends in the system [32].

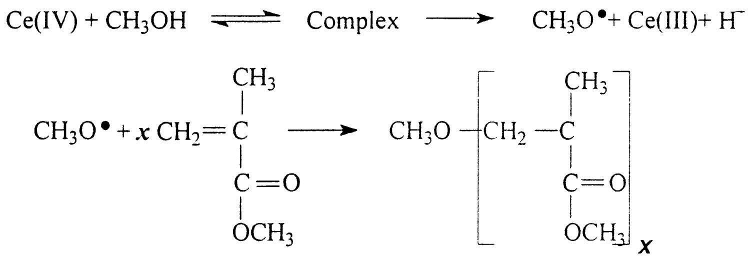
Evaluation of TGA analyses indicated that the temperature region up to 500°C is divided into two events, one between ~125–225°C and another above it. In the first thermal region (125–225°C) there is no significant difference in the weight loss. This would therefore imply that any weight loss must be linked to the monomer or short chain length polymers. In the next thermal region ~225–4250°C), the weight loss was attributed to loss of material possibly from the breakdown of the polymer that would be strongly endothermic. Electrochemically obtained samples, 1E3 and 1E5, have lower decomposition temperature compared to chemically obtained samples, 1C3 and 1C5. This result indicates that electrochemical termination will be favored rather than termination with Ce(IV) in electroinduced system. These results demonstrate that more stable PMMA was obtained with the highest Ce(IV) content and the least stable material includes the least amount of Ce(IV) and MMA. The broad endotherms for the sample 1C5 and 1E5, which contain higher Ce(IV) concentration, reveal the possibility of unreacted cerium within the polymer matrix causing polymer degradation. In the case of high MMA/PVP ratio high endotherm was seen. The results would lead to the conclusion that the percentage of MMA, PVP, and Ce(IV), and the way of polymerization affect the polymer stability.

CONCLUSIONS

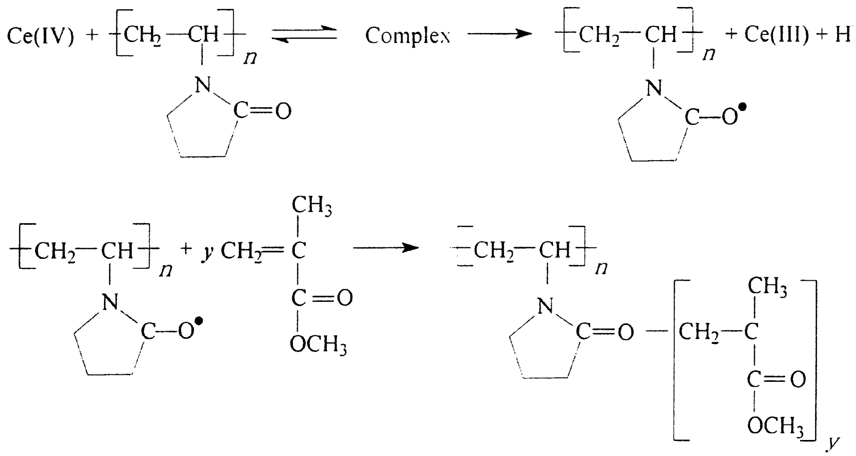
Higher yields were obtained compared to chemical dispersive polymerization of MMA, by electroinduced dispersive polymerization method. In chemical initiation of MMA polymerization by Ce(IV) (Scheme 1) is dominant.

Although neither NMR results nor FT-IR results give strong evidences of inclusion of PVP in the polymer structure, it seems that an initiation with PVP oxidation by Ce(IV) (Scheme 2) is possible as supported by UV-vis and FT-IR results.

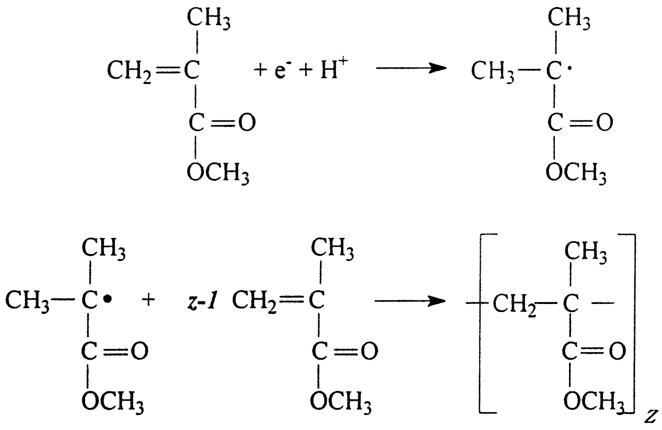
Higher yields obtained in the electroinduced method can be attributed to the electrochemical regeneration of Ce(IV) to Ce(III) and



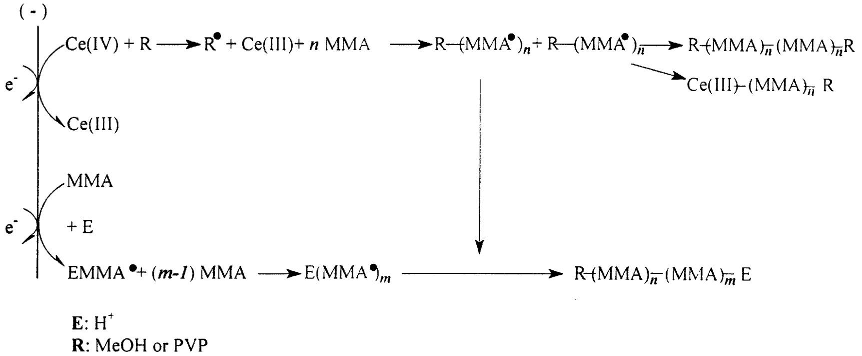
SCHEME 1 Initiation with Ce (IV) + Methyl alcohol.



SCHEME 2 Initiation with Ce (IV) + PVP.



SCHEME 3 Electrochemical initiation of the monomer.



SCHEME 4 Schematic representation of the electrochemical polymerization mechanism.

electrochemical reduction of MMA by generating redicals, in addition to chemical oxidation initiation (Schemes 3 and 4).

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