Key Words: Redox-initiated polymerization; Cerium(IV); Methyl
methacrylate; L-methionine

INTRODUCTION

[illegible] methacrylate polymers, in recent years, have found wide applications as self-extinguishing materials[1-3]. Understanding of their thermal or thermo-oxidative degradations, which usually occur prior to ignition at the edge of the flame, would be very important from the point of view of fire protection and retardancy of plastics.

Ceric salts form efficient redox systems in the presence of organic reducing agents such as alcohols[4], aldehydes[5], carboxylic acids[6-10], and amino acids[11-14]. The redox system can be used to initiate the polymerization of vinyl monomers. The redox polymerization of methyl methacrylate in acid aqueous medium has been studied for the ceric-thiourea initiator system[15].

Polymers containing polar groups such as -COOH or -NH₂ adsorb well on pigments and provide improvement in their dispersibility[16]. Cross-linked polymers carrying such groups also are used in ion-exchange processes[17].

In this work, the polymerization of methyl methacrylate monomer initiated by the L-methionine-cerium(IV) sulfate system in an acid aqueous medium was investigated. Three different types of mechanisms were found to be possible for ceric ion initiated polymerizations. Ceric ion is reduced Ce³⁺ and [illegible] radicals according to reaction 1[18]:

$$Ce^{4+} + [illegible] \rightarrow Ce^{3+} + H^{+} + [illegible] \qquad (1)$$

Under strongly acidic conditions, transfer of electrons from the monomer to the ceric ion yields active species which would propagate the chain polymerization according to reaction 2:

$$Ce^{4+} + CH_2{=}[illegible] \rightarrow Ce^{3+} + [illegible] \qquad (2)$$

In monomers containing carbon-hydrogen bonds [illegible] functional groups, [illegible] the formation of primary radicals [illegible]

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Oxidative Polymerization of Methyl Methacrylate in Acid-Aqueous Medium

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ABSTRACT

The polymerization of methyl methacrylate monomer initiated by L-methionine-Ce(IV) sulfate redox system in an acid-aqueous medium was investigated. Partially cross-linked methyl methacrylate polymers with limited solubility in known solvents were obtained. The dependence of polymerization yields on the mole ratio of L-methionine to cerium(IV) sulfate and methyl methacrylate monomer to cerium(IV) sulfate ($n_{Ce(IV)} = n_{Meth}$), polymerization time, acid concentration, temperature, and amount of solvent (acetone and methanol) was investigated. The results of infrared, thermal gravimetric analysis, differantial scanning calorimetry measurements to indicate the thermal oxidative properties of obtained polymers also are given. The possible mechanism for the polymerization reaction is discussed.

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Key Words: Suspension redox polymerization; Cerium(IV); Methyl methacrylate; L-methionine.

INTRODUCTION

Methyl methacrylate polymers, in recent years, have found wide application as surface-coating materials.[1–4] This knowledge of their thermal or thermal oxidative degradation, which occurs prior to ignition at the edge of the flame spread, is very important from the point of view of fire protection and temperature usage.

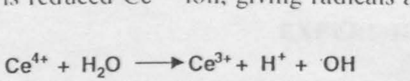
Ceric salts form effective redox systems in the presence of organic reducing agents such as alcohols,[5,6] aldehydes,[7] carboxylic acids,[8–10] and amino acids.[11–14] The redox system can be used to initiate the polymerization of vinyl monomers. The redox polymerization of methyl methacrylate in acid aqueous medium also was studied for the ceric-thiourea initiator system.[15]

Polymers containing polar groups such as –COOH or $-NH_2$ absorb well on pigments and provide stabilization to paint dispersions.[16] Cross-linked polymers carrying such groups also are used as drug-release materials.[17]

In this work, the polymerization of methyl methacrylate monomer initiated by the L-methionine-cerium(IV) sulfate system in an acid-aqueous medium was investigated. Three different types of mechanisms were found to be possible for ceric ion initiated polymerizations. Ceric ion is reduced Ce^{3+} ion, giving radicals according to reaction 1.[15]

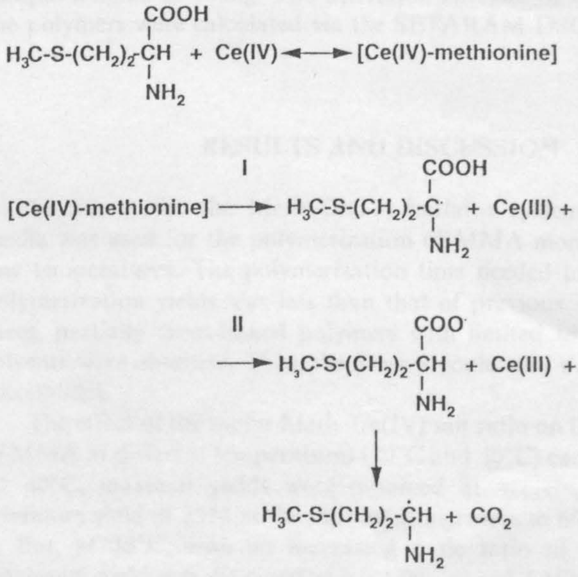
$$Ce^{4+} + H_2O \longrightarrow Ce^{3+} + H^+ + {}^{\cdot}OH \qquad (1)$$

Under strongly acidic conditions, transfer of electron from the monomer to the ceric ion yields active species, which would propagate the chain polymerization, according to reaction 2.



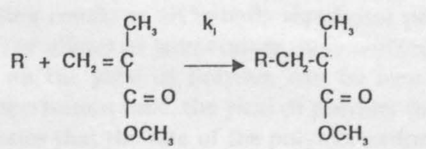
$$Ce^{4+} + CH_2{=}\underset{X}{\underset{|}{C}}H \longrightarrow Ce^{3+} + {}^{+}CH_2\text{-}\underset{X}{\underset{|}{\dot{C}}}H \qquad (2)$$

In this case, the resulting polymer would not carry hydroxyl end groups. But when redox couples, such as ceric-amine or ceric-thiourea, are used, due to an increased production of primary radicals, the induction period is much shorter and the rate of polymerization is considerably faster than with ceric salts alone. In this case, the amount of hydroxyl and amine end groups of the final polymer chains was found to be dependent on the pH of polymerization medium. The ˙OH appear above pH 2, and although they increase up to pH 4.3, the dominance of amino end groups continues, which indicates the redox reaction given for methionine in Eq. (3) is the main mechanism.

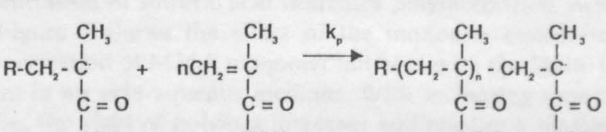


(3)

Initiation:

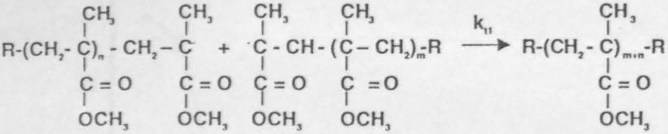


Propagation:

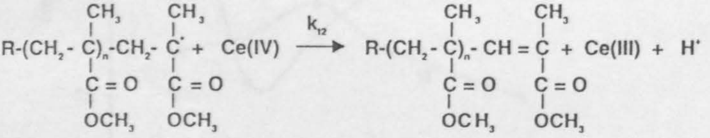


Termination reactions:

a) Combination



b) Mutual termination



If radicals that form in the redox reaction are denoted as $R^{\cdot}$, the polymerization reaction can be shown as given above.

The dependence of polymerization yields on the mole ratio of L-methionine to cerium(IV) sulfate, methyl methacrylate monomer to cerium(IV) sulfate ($n_{Ce(IV)} = n_{Meth}$), polymerization time, temperature, acid concentration, and the amount of solvent (acetone and methanol) was investigated. Infrared (FTIR), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) were used to characterize the polymers.

EXPERIMENTAL

Cerium(IV) sulfate[Ce(IV)], methyl methacrylate (MMA), L-methionine (Meth), methanol, and sulfuric acid of Merck quality and acetone of technical quality were used without further treatment.

The polymerization reaction was carried out in a round-bottomed flask equipped with a stirrer, which was placed in a constant temperature bath. Ce(IV) in acidic water was added to a suspension of MMA and Meth. The reaction was carried out for a predetermined time up to 1 hr, at 20–60°C. The precipitated polymer was filtered, washed, and dried to a constant weight in a vacuum oven. Effective reaction variables, such as molar Meth/Ce(IV) ratio, MMA/Meth ratio ($n_{Ce(IV)} = n_{Meth}$), polymerization time, temperature, concentration of sulfuric acid, and the amount of acetone or methanol in a suspension medium were investigated.

The FTIR measurement was carried out with ATI Unicam (Mattson 1000) FT-IR spectrometer, and the spectra of polymer was obtained by the KBr disk method.

A Shimadzu TGA-50 was used for the TGA analysis of poly(MMA)s in a nitrogen atmosphere, with a heating rate of 5°C/min and the sample weights of 10 mg.

The DSC analysis of polymers was carried out with the SETARAM DSC 131 in a nitrogen atmosphere with a heating rate of 10°C/min and sample weights of 10 mg. The activation energies of the degradation of the polymers were calculated via the SETARAM DSC 131 software.

RESULTS AND DISCUSSION

In this study, the Meth–Ce(IV) initiator system in acid-aqueous media was used for the polymerization of MMA monomer at high and low temperatures. The polymerization time needed to reach maximum polymerization yields was less than that of previous studies.[9–13] In all cases, partially cross-linked polymers with limited solubility in known solvents were obtained. Thus, the average molecular weight could not be determined.

The effect of the molar Meth–Ce(IV) salt ratio on the polymerization of MMA at different temperatures (30°C and 40°C) can be seen in Fig. 1. At 40°C, maximal yields were obtained at $n_{\mathrm{Meth}}/n_{\mathrm{Ce(IV)}} < 0.5$ and a minimum yield of 25% at the ratio of 1, increases to 60%, at the ratio of 3. But, at 30°C, with an increasing mole ratio of Meth to Ce(IV), maximum yield was obtained at $n_{\mathrm{Meth}}/n_{\mathrm{Ce(IV)}} = 1.5$ (Fig. 1, curve B).

Figure 2 shows the effect of the concentration of Ce(IV) on the polymerization of MMA when the $n_{\mathrm{Ce(IV)}}/n_{\mathrm{Meth}}$ ratio was kept constant at 1. The increase of the Ce(IV) concentration in the polymerization reaction results in an initially significant polymerization yield.

The effects of temperature, polymerization time, and acid concentration on the yield of polymer can be seen in Table 1. With increasing polymerization time, the yield of polymer increases slowly (Table 1). This indicates that the rate of the polymerization reaction is very fast and the reaction is almost complete after a few minutes. Increasing the concentration of sulfuric acid decreases polymerization yield.

Figure 3 shows the effect of the monomer concentration on the polymerization of MMA monomer initiated with the Meth–Ce(IV) redox system in an acid-aqueous medium. With increasing monomer concentration, the yield of polymer increases and reaches a maximum value at

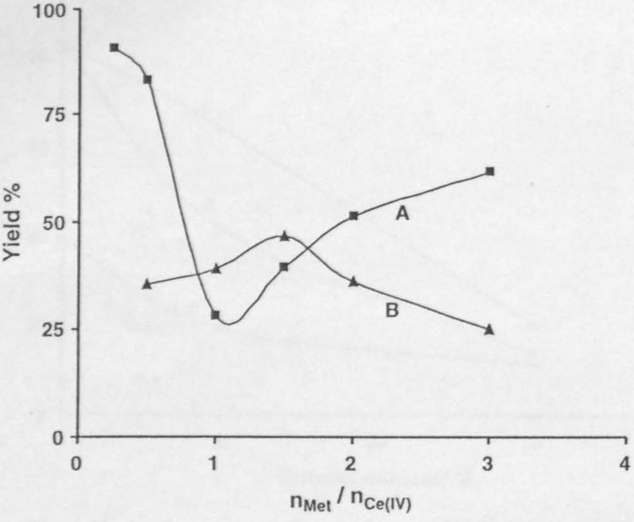


Figure 1. The dependence of mole ratio of L-methionine/Ce(IV) on the yield of polymer at 40°C (A) and at 30°C (B). $C_{MMA} = 0.7$ mol/L, $C_{H_2SO_4} = 0.1$ mol/L, $C_{Ce(IV)} = 0.02$ mol/L, $t = 1$ hr.

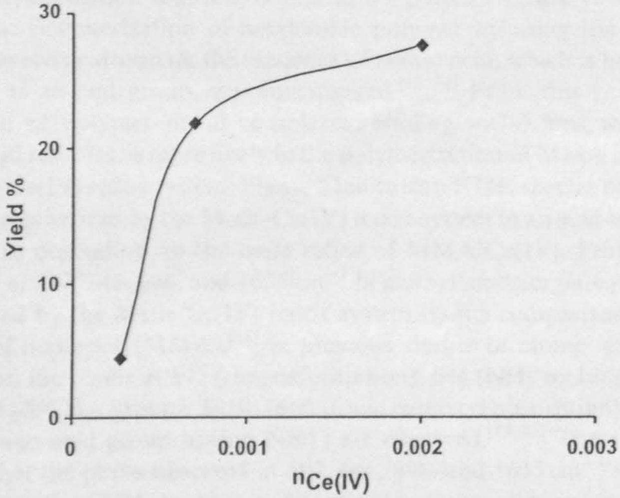


Figure 2. The effect of Ce(IV) concentration on the yield of polymer. $C_{MMA} = 0.7$ mol/L, $C_{H_2SO_4} = 0.1$ mol/L, $t = 1$ hr, $T = 40$°C.

Table 1. The effects of the temperature, the polymerization time, and the acid concentration on the yield of polymer. $C_{MMA} = 0.7$ mol/L, $C_{Ce(IV)} = 0.02$ mol/L.

$n_{Meth}/n_{Ce(IV)}$	Polym time (min)	$C_{H_2SO_4}$ (mol/L)	Temperature (°C)	Yield (%)
1.5	60	0.1	60	29.60
1.5	60	0.1	50	35.50
1.5	60	0.1	40	39.38
1.5	60	0.1	30	46.56
1.5	60	0.1	20	42.46
0.5	10	0.1	40	75.92
0.5	30	0.1	40	76.76
0.5	60	0.1	40	82.52
0.5	60	0.05	40	95.07
0.5	60	0.075	40	89.86
0.5	60	0.2	40	57.76

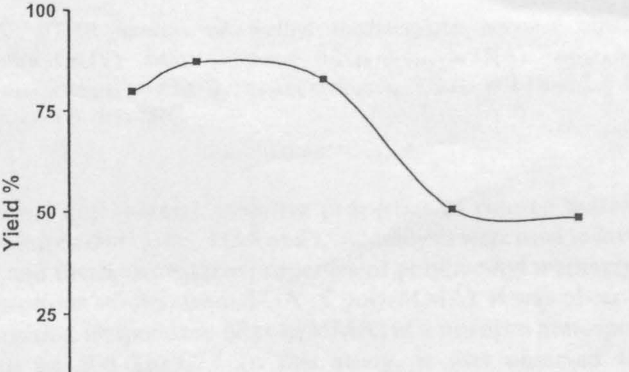


Figure 3. The dependence of monomer concentration on the yield of polymer. $C_{Meth} = 0.01$ mol/L, $C_{H_2SO_4} = 0.1$ mol/L, $C_{Ce(IV)} = 0.02$ mol/L, $t = 1$ hr, $T = 40$°C.

about 0.5 M monomer concentration. A further increase of the monomer concentration decreases the yield of polymerization.

The effect of the amount of solvent in the mixture of solvent–water on the polymerization yield at different temperatures is shown in Fig. 4.

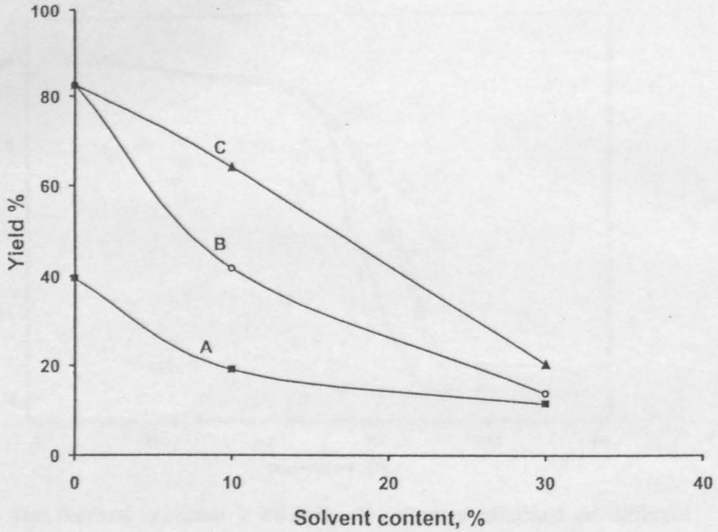


Figure 4. The effect of amount of acetone at 30°C (A) and 40°C (B) and methanol at 40°C (C). $C_{MMA} = 0.7$ mol/L, $C_{Meth} = 0.01$ mol/L, $C_{H_2SO_4} = 0.1$ mol/L, $C_{Ce(IV)} = 0.02$ mol/L, $t = 1$ hr.

As seen from the figure, increasing the amount of acetone and methanol in the polymerization solution, decreases the polymerization yield.

In the polymerization of acrylamide polymer by using the Ce(IV) sulfate–amino acid system, the existence of amino acid, which is bound to polymer as an end group, was investigated.[12–14] From this point, the formation of polymer–metal complexes, binding metal ions with two amino acid residues, is more likely in the polymerization of MMA initiated by Meth–Ce(IV) redox system. Figure 5 indicates a FTIR spectra of MMA polymer synthesized by the Meth–Ce(IV) redox system in an acid-aqueous medium as depending on the mole ratios of MMA/Ce(IV). Peaks were observed at 597, 646, 696, and 1635 cm^{-1} in methyl methacrylate polymer synthesized by the Meth–Ce(IV) redox system by the comparison of the spectra of homopoly(MMA).[17] In previous studies of amino acid with metal ions, the bands at 592 (ring deformation), 644 (NH_2 roching), 650–750 (-CH_2-S-CH_2- group), 1610–1660 (ionic carboxyl absorption), 1600–1640 (amino acid group having NH_3^+) are observed.[19–22] These results suggest that the peaks observed at 597, 646, 696, and 1635 cm^{-1} indicate ring deformation, NH_2 roching, a -CH_2-S-CH_3 group, and ionic carboxyl absorption or amino group having NH_3^+, respectively.

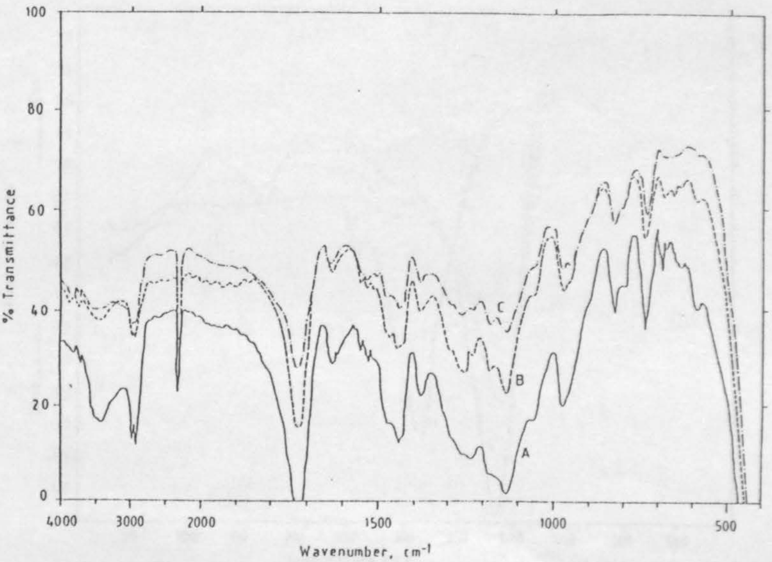


Figure 5. FT-IR spectra of methyl methacrylate polymer obtained by L-methionine–Ce(IV) redox system. $n_{MMA}/n_{Ce(IV)} = 35$(A), $n_{MMA}/n_{Ce(IV)} = 100$(B), $n_{MMA}/n_{Ce(IV)} = 250$(C), $n_{MMA} = n_{Ce(IV)}$, $C_{MMA} = 0.7$ mol/L, $C_{H_2SO_4} = 0.1$ mol/L, $t = 1$ h, $T = 40$°C.

Thermal and thermal oxidative properties of coating materials are naturally important. Thus, TGA and DSC analysis were used to investigate thermal and thermo-oxidative properties of poly(methyl methacrylate)s.

In previous studies, from TGA of poly(MMA), it was observed that decomposition temperature of poly(MMA) in a nitrogen atmosphere was found to be 300–320°C.[4] In this study, it was observed that the decomposition of MMA in nitrogen atmosphere depends on the mole ratio of monomer to Ce(IV) in the polymerization reaction. When the mole ratio of monomer to Ce(IV) equals 35, a maximum weight loss occurred at 400°C and weight loss reached 93.90% at 596°C (Fig. 6, curve A). When $n_{MMA}/n_{Ce(IV)} = 100$, the polymer degraded in two stages. In the first stage, a maximum weight loss of 2.26% formed at 295°C. In the second stage, the rate of weight loss reached to a maximum value at 394°C, and the weight loss was observed to be 95.88% at 432°C (Fig. 6, curve B). At $n_{MMA}/n_{Ce(IV)} = 250$, the polymer degraded also in two stages. In the first stage, a maximum weight loss of 30.5% formed at 321°C. In the second stage, the rate of weight loss reached a maximum

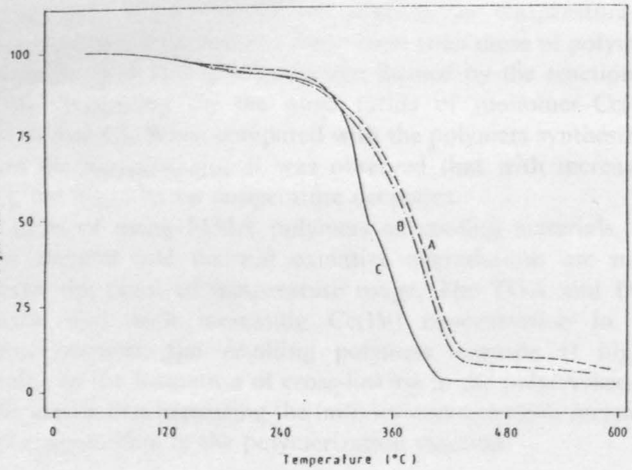


Figure 6. The thermal gravimetric analysis of polymers obtained on different mole ratios of monomer/initiator. $n_{MMA}/n_{Ce(IV)} = 35$ (A), $n_{MMA}/n_{Ce(IV)} = 100$ (B), $n_{MMA}/n_{Ce(IV)} = 250$ (C). $n_{MMA} = n_{Ce(IV)}$, $C_{H_2SO_4} = 0.1$ mol/L, $t = 1$ hr, $T = 40°C$.

value at 356°C with 63.06% and at 422°C, the weight loss of 96.47% occurred (Fig. 6, curve C).

As can be seen from the results, bimodal polymerization reaction takes place, as depending on the mole ratio of MMA monomer–Ce(IV). At the mole ratio of MMA–Ce(IV) = 35, the polymer degrades at higher temperature. With increasing of the mole ratio of MMA–Ce(IV), bimodal decomposition occurs. This indicates that with decreasing of Ce(IV) content in the polymerization reaction, the obtained polymers show two degradation fractions: cross-linked polymer degrading at a high temperature and linear polymer degrading at a low temperature.

The DSC analysis of MMA polymers obtained by using different mole ratios of monomer–Ce(IV) salt ($n_{MMA}/n_{Ce(IV)}$) in polymerization reactions were examined (Fig. 7, curves A and C). The DSC analysis of the homopolymer of MMA prepared by bulk polymerization at 65°C, with azoisobutyronitrile as an initiator is shown in Fig. 7 as curve H. The activation energies of the polymers were calculated via the SETARAM DSC 131 software, and results are given in Table 2.

It was observed from the DSC curves, with increasing Ce(IV) content in the polymerization reaction, *Tg*, temperature of polymer increases

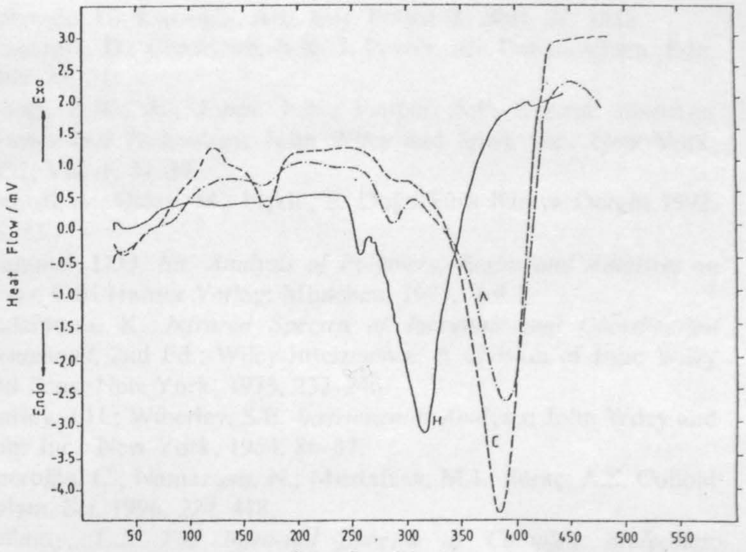


Figure 7. The differantial scanning calorimetric analysis of homopoly(methyl methacrylate) (H) and polymers of the $n_{MMA}/n_{Ce(IV)} = 35$ (A) and $n_{MMA}/n_{Ce(IV)} = 250$ (C). $C_{MMA} = 0.7$ mol/L, $C_{H_2SO_4} = 0.1$ mol/L, $t = 1$ hr, $T = 40°C$.

Table 2. The activation energies and the degradation temperatures of homopolymer and polymers obtained for $n_{MMA}/n_{Ce(IV)} = 35$ and $n_{MMA}/n_{Ce(IV)} = 250$.

	$n_{MMA}/n_{Ce(IV)} = 35$		$n_{MMA}/n_{Ce(IV)} = 250$		Homopolymer of methyl methacrylate	
Peak no.	T(°C)	H(J/g)	T(°C)	H(J/g)	T(°C)	H(J/g)
I	166.5	6.10	169.7	33.69	—	—
II	286.3	15.12	290.1	3.45	253.9	11.63
III	388.4	282.21	383.4	420.23	313.2	411.24

($Tg = 65.55°C$ for $n_{MMA}/n_{Ce(IV)} = 250$ and $Tg = 68.72°C$ for $n_{MMA}/n_{Ce(IV)} = 35$). The peaks attributed to the melting point were observed at 166.5°C and 169.5°C for the polymers, depending on the mole ratios of $n_{MMA}/n_{Ce(IV)} = 35$ and 250, respectively.

As can be seen from Fig. 7, the degradation temperature of homopolymer of MMA (Fig. 7, curve H) is lower than those of polymers of MMA-initiated Meth radicals, which are formed by the reaction of Ce(IV)-Ce(III), depending on the mole ratios of monomer–Ce(IV) (Fig. 7, curve A and C). When compared with the polymers synthesized, depending on the $n_{MMA}/n_{Ce(IV)}$, it was observed that with increasing $n_{MMA}/n_{Ce(IV)}$, the degradation temperature decreases.

On the basis of using MMA polymers as coating materials, the properties of thermal and thermal oxidative degradations are more important from the point of temperature usage. The TGA and DSC results indicate that with increasing Ce(IV) concentration in the polymerization reaction, the resulting polymers degrade at higher temperature due to the formation of cross-linking in the polymerization reaction. This means that increasing the initiator concentration increases the degree of cross-linking in the polymerization reaction.

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