

# Study on Polymerization of Ethylenediaminetetraacetic Acid and Methyl Methacrylate

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**ABSTRACT:** The polymerization of ethylenediaminetetraacetic acid (EDTA) with methyl methacrylate (MMA) was prepared using a cerium(IV) redox initiator system at 60°C under nitrogen. The microstructures of the obtained polymers were characterized by NMR measurement and the DEPT technique, as well as by infrared spectroscopy. The mechanism of the polymerization reaction was determined from the microstructures of the derived polymers. It showed that the reaction leading to the polymerization formation was the carbon site of the ethylene of the EDTA. It was not the same as that suggested in the literature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2311–2317, 1997

**Key words:** ethylenediaminetetraacetic acid; methyl methacrylate; microstructure; mechanism

## INTRODUCTION

Ethylenediaminetetraacetic acid (EDTA), an excellent chelating agent,<sup>1,2</sup> is added to foodstuffs, pharmaceuticals, and high-quality cosmetic products for the control of unwanted trace metal contamination.<sup>1–5</sup> Very good catalysts are made when EDTA forms a complex with cations, but they cannot be isolated from the end products. A polymer-supported metallic catalyst can overcome the separation and purification problem in a homogeneous catalytic reaction. In this study, EDTA-containing copolymers were systematically studied to improve their useful properties. Polymerizations of monomer to chelating agents have been extensively studied<sup>6–10</sup> over many years. Different mechanistic pathways have been suggested by many workers<sup>11–17</sup> to explain the experimental observation concerning redox polymerization. Cerium(IV)–EDTA redox systems have been used as the initiators for aqueous free-radical polymer-

izations.<sup>11–17</sup> Such mechanisms of the polymerization suggest that the reducing agent reacts with the ceric ion to form an intermediate complex and subsequently decomposes to the free radicals which initiate polymer formation. Sarac et al.<sup>11</sup> used the cerium(IV)–EDTA redox initiator system with and without electrolysis to study the polymerization of acrylamide. The polymerization of a monomer to EDTA in water was conducted by Hsu and coworkers<sup>12,13</sup> using cerium(IV) redox as an initiator. They proposed that the initiation polymerization step occurs to release carbon dioxide from EDTA free radicals in the synthesis of polymers. Padhi<sup>14</sup> and Mohanty et al.<sup>15</sup> undertook infrared spectroscopy and found that the polymer contains EDTA as an end group. Tripathy et al. found that the polymer contains EDTA as an end group.<sup>16,17</sup> They also characterized the mechanism of the polymerization of the monomer end group of the polymer by IR spectra. Hence, all the authors<sup>11–17</sup> suggested that the initiation step occurs by the abstraction of hydrogen atoms in the  $\alpha$  position or by the escape of carbon dioxide from the malonic acid.

Over the past decade, <sup>1</sup>H- and <sup>13</sup>C-NMR spec-

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trometry have become important techniques for the investigation of the microstructures of polymers.<sup>18-21</sup> Recently, the distortionless enhancement by the polarization transfer (DEPT) NMR technique<sup>22-24</sup> also has been used to assign peak multiplicities. In this work, the Ce(IV)-EDTA redox system was used to initiate the polymerization of methyl methacrylate (MMA). The microstructures of the PMMA and EDTA polymers were determined using <sup>13</sup>C-NMR along with the DEPT technique, as well as by an IR spectrometer. The mechanisms of the polymerization of EDTA with MMA were proposed.

## EXPERIMENTAL

### Reagents

The disodium salt of ethylenediaminetetraacetic acid (EDTA) was supplied by Sigma. Methyl methacrylate (MMA) was commercially available and purified by double-distillation in a nitrogen atmosphere under reduced pressure. Ceric sulfate (EP grade, E. Merck Co.) was recrystallized in methanol three times. The water was deionized.

### Polymerization

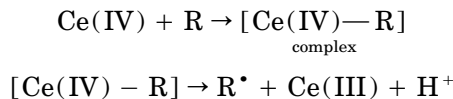
Emulsifier-free polymerization was conducted in a 1-L four-necked borosilicate resin kettle, which was equipped with a stirrer, a condenser, a thermometer, and a nitrogen inlet. The reactor was placed in a well-thermostated water bath controlled at  $60 \pm 0.5^\circ\text{C}$ . The polymerization was carried out under a nitrogen atmosphere for 8 h. The recipe studied was as follows: EDTA = 0.5M, MMA = 0.5M, and cerium sulfate =  $5 \times 10^{-2}$ M. After 8 h reaction time, the resultant polymer was precipitated in cold methanol to stop the polymerization and to separate the unreacted monomer. The polymer was purified by continuous extraction in a Soxhlet thimble with distilled water to remove the residual cerium sulfate and EDTA. The polymer was recovered in a vacuum oven.

### Characterization

Infrared spectra were obtained in the range of 4000-400  $\text{cm}^{-1}$  on a Perkin-Elmer system 2000 FTIR spectrophotometer using KBr pellets. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker WP 100 spectrometer. Deuterated acetone and deuterated dimethyl sulfoxide were used as a solvent for the polymers.

## RESULTS AND DISCUSSION

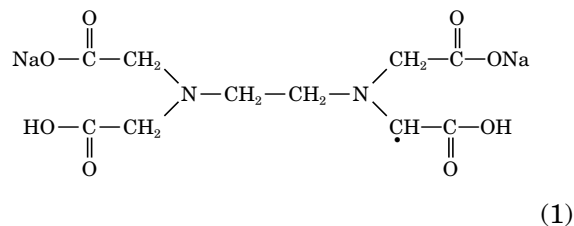
The mechanism of the redox system polymerization may be depicted as follows<sup>6-10</sup>:



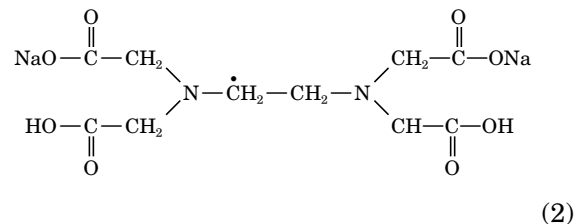
where R and R<sup>•</sup> are the chelating agent and the initiator fragment radical, respectively. Thus, the radicals which are capable of initiating the polymerization of MMA perhaps occur via the reaction of the ceric ion and the chelating agent.

The radical formation may be proposed as follows:

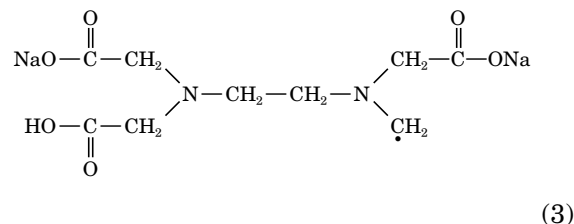
1. Abstraction of hydrogen of the acetate  $-\text{CH}_2-$  of EDTA by the cerium ion:



2. Abstraction of hydrogen from ethylene  $-\text{CH}_2\text{CH}_2-$  of EDTA by the cerium ion:



3. Escape of carbon dioxide of EDTA:



The microstructures of the polymer were thoroughly characterized by IR and <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. Figure 1 shows the IR spectrogram

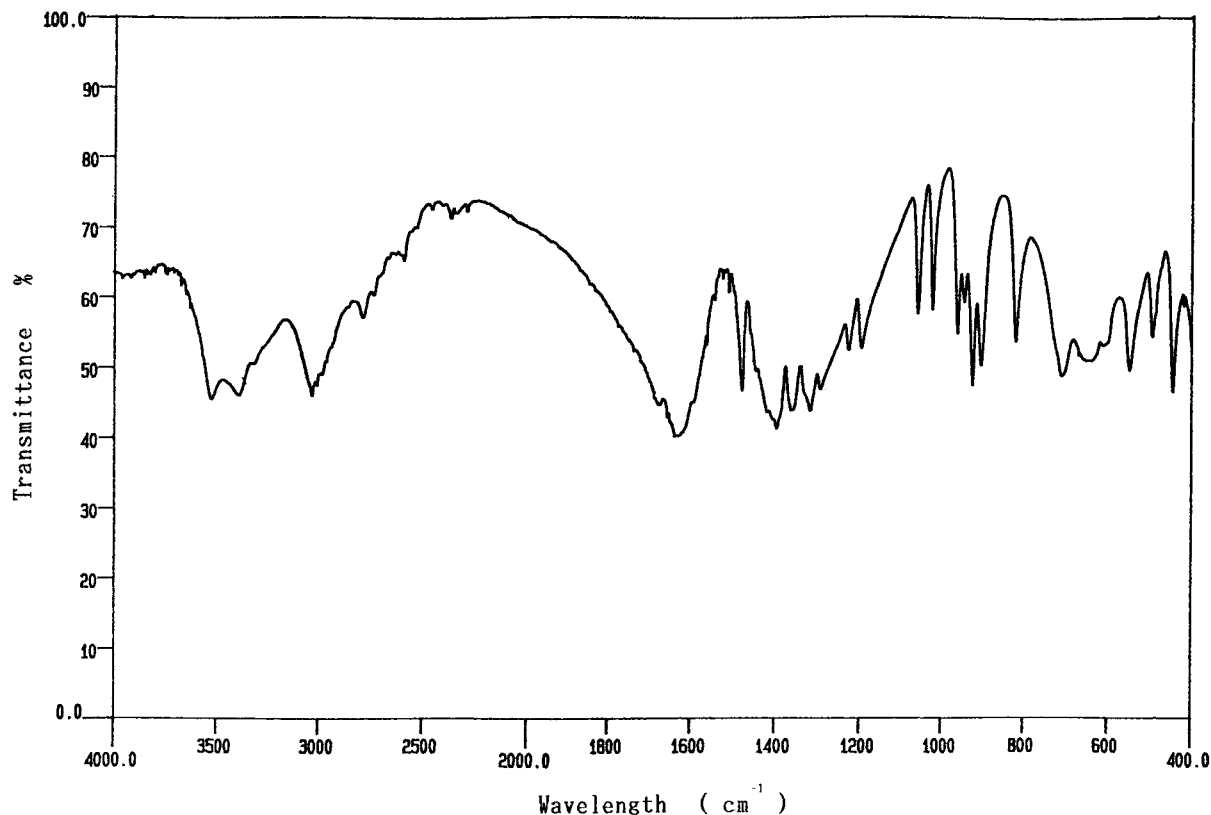


Figure 1 IR spectra of EDTA.

of the EDTA. The peaks at  $3520$  and  $3390\text{ cm}^{-1}$  are due to the stretching vibration of  $-\text{OH}$ ,  $3030$  and  $2780\text{ cm}^{-1}$ ; the stretching vibration of  $\text{CH}_2$ ,  $1640\text{ cm}^{-1}$ ; and the stretching vibration of the  $\text{C}=\text{O}$  group of EDTA. The  $\text{C}-\text{N}$  asymmetric stretching and  $\text{C}-\text{C}$  stretching vibration of acetate groups are assigned at  $1054$  and  $940\text{ cm}^{-1}$ , respectively. Figure 2 shows the IR spectrogram of the isolated polymer to compare it with the absorptions of the IR spectrogram of EDTA. It is found that the appearance of a new absorption peak occurs at  $1725\text{ cm}^{-1}$ . The new peak is assigned to the carbonyl band of PMMA. The peaks at  $1271$ ,  $1240$ ,  $1190$ , and  $1148\text{ cm}^{-1}$  result from the stretching vibrations of the  $\text{C}-\text{O}$  groups. The data indicate that  $-\text{COO}-$  groups of MMA exist on the molecular chains of the polymer. Table I lists the assignments for the absorptions of those IR spectrograms in the figures. Therefore, we suggest that the cerium(IV) reducing agent initiates the polymerization of MMA to EDTA, thus the resulting polymer.

Figure 3 shows the  $^1\text{H-NMR}$  spectrum of the EDTA. Two  $^1\text{H-NMR}$  absorptions are shown in the acetate and ethylenic regions, respectively.

Figure 4 shows the  $^1\text{H-NMR}$  spectrum of the EDTA-PMMA. The chemical shifts in Figure 3 were compared with Figure 4. Figure 4 shows that chemical shifts appear at  $0.8$ ,  $2.1$ , and  $3.6$  ppm. The data indicate that the  $-\text{CH}_2-$ ,  $-\text{CH}_3$ , and  $-\text{OCH}_3$  of MMA exist on the molecular chains of the polymer, which is more evidence of the existence of the polymerization of MMA to EDTA, thus the resulting polymer.

Figure 5 shows the regular  $^{13}\text{C-NMR}$  spectrum and the  $\text{CH}_n$  ( $n = 1, 2, 3$ ) subspectra obtained with DEPT  $\theta = \pi/2$  and  $3/4\pi$  for the EDTA-PMMA. It shows chemical shifts at  $178.1$ ,  $177.8$ , and  $177.0$  ppm which belong to the carbon of carbonyl group of PMMA, and the shifts at  $45.1$ ,  $44.9$ , and  $44.6$  ppm belong to the quaternary alkyl carbon of PMMA. The peaks at  $54.3$ ,  $52.0$ ,  $18.6$ , and  $16.5$  ppm are assigned to the carbons of methylene, the methyl of the ester, and the  $\alpha$ -methyl of PMMA, respectively. It indicates that polymerization of MMA onto EDTA has occurred. In addition to the characteristic  $^{13}\text{C}$  chemical shifts of the EDTA and PMMA, it was found that there is one new peak that occurs at  $52.0$  ppm. Again, it was found that this peak does not only belong to methyl carbons

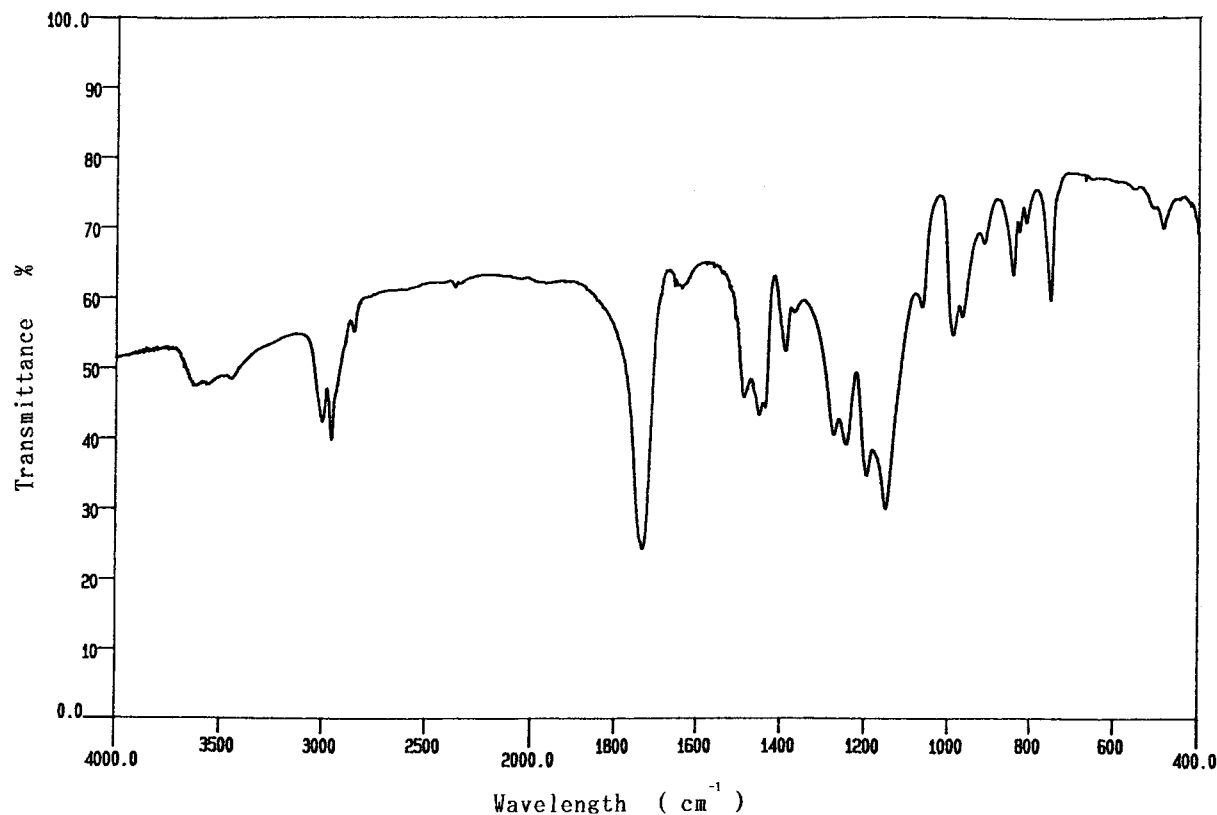


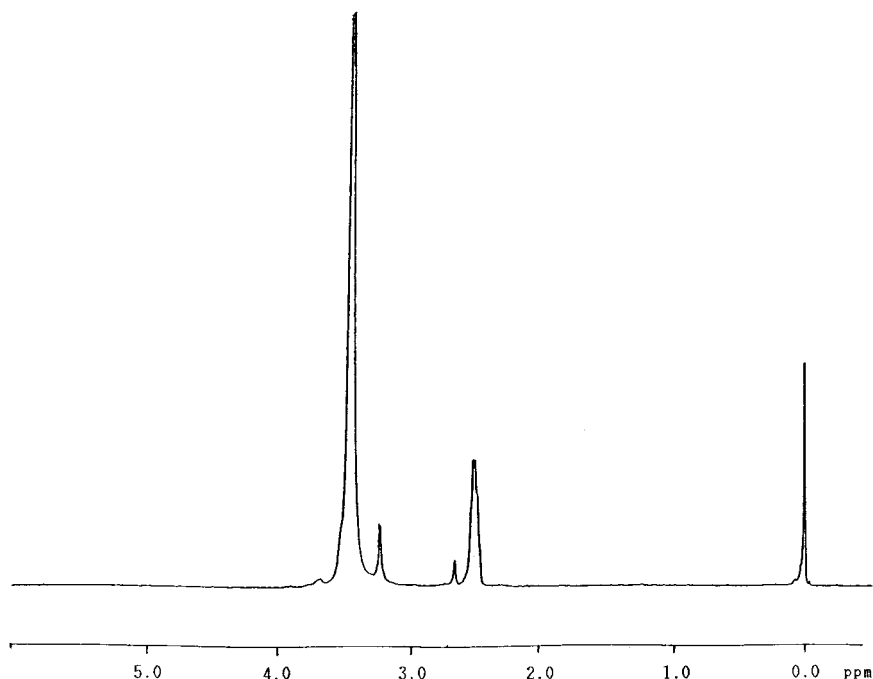
Figure 2 IR spectra of EDTA-PMMA.

but also belongs to methine carbons. This further supports the evidence for the polymerization reaction suggested above. The carbon of the acetate of the EDTA gives chemical shifts at 57.0 ppm,<sup>25</sup>

and the ethylene  $-\text{CH}_2\text{CH}_2-$  of the EDTA gives a chemical shift at 50.0 ppm. The EDTA reacts with MMA, thus resulting in the chemical shift downfield and producing a peak at 52.0 ppm.

Table I IR Bands of EDTA and EDTA-PMMA ( $\text{cm}^{-1}$ )

EDTA		EDTA-PMMA	
IR	Assignment	IR	Assignment
3518	$\text{H}_2\text{O}$	3500	$\text{COO}-\text{H}(\text{st})$
3376	$\text{H}_2\text{O}$	2996	$\nu\text{CH}_2$
3030	$\nu\text{CH}_2$	2954	$\nu\text{CH}_2$
2780	$\nu\text{CH}_2$	1727	$\text{C}=\text{O}(\text{st})$ (PMMA)
1644	$\nu_a\text{COO}^-$	1646	$\nu_a\text{COO}^-$
1475	$\delta(\text{C}-\text{H})\text{CH}_2$	1485	$\delta(\text{C}-\text{H})\text{CH}_2$
1384	$\nu_s\text{COO}^-$	1387	$\nu_s\text{COO}^-$
1351	$\delta\text{NH}^+$	1271	$\text{C}-\text{O}-\text{C}$ (PMMA)
1225	$\text{C}-\text{O}(\text{st})$	1240	$\text{C}-\text{O}-\text{C}$ (PMMA)
1054	$\nu\text{C}-\text{N}$	1190	$\text{C}-\text{O}-\text{C}$ (PMMA)
940	$\text{C}-\text{C}(\text{CH}_2-\text{COO}^-)$	1148	$\text{C}-\text{O}-\text{C}$ (PMMA)
920	$\delta\text{COO}^-(\text{st}, \text{sy})$	1062	$\nu\text{C}-\text{N}$
703	$\text{rCH}_2$	965	$\text{C}-\text{C}(\text{CH}_2-\text{COO}^-)$
		911	$\delta\text{COO}^-(\text{st}, \text{sy})$



**Figure 3**  $^1\text{H}$ -NMR spectra of EDTA.

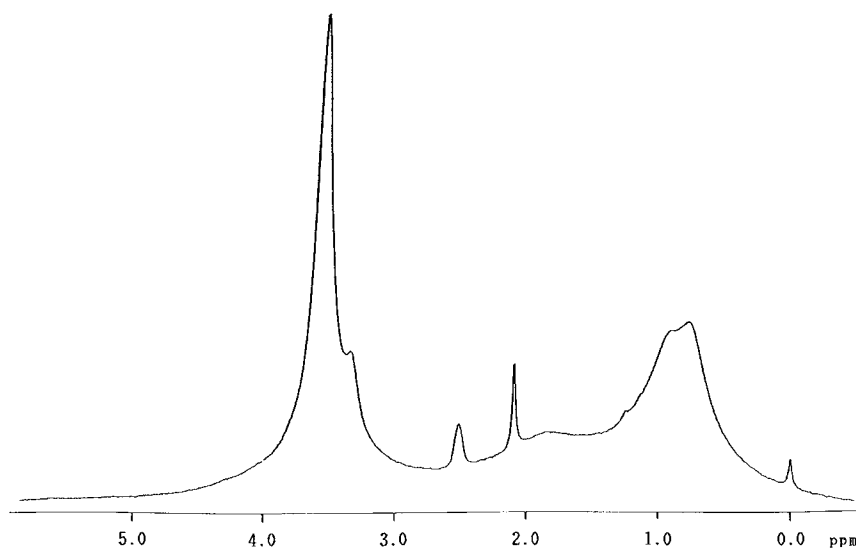
Thereby, it appears that the methine units in the molecular chain of the resulting EDTA-PMMA can be ascribed to the consequences. These results suggest that the polymerization reaction takes place on the abstraction of hydrogen of the ethylene of the EDTA by the cerium ion.

From the IR and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, it is impossible to obtain information about mecha-

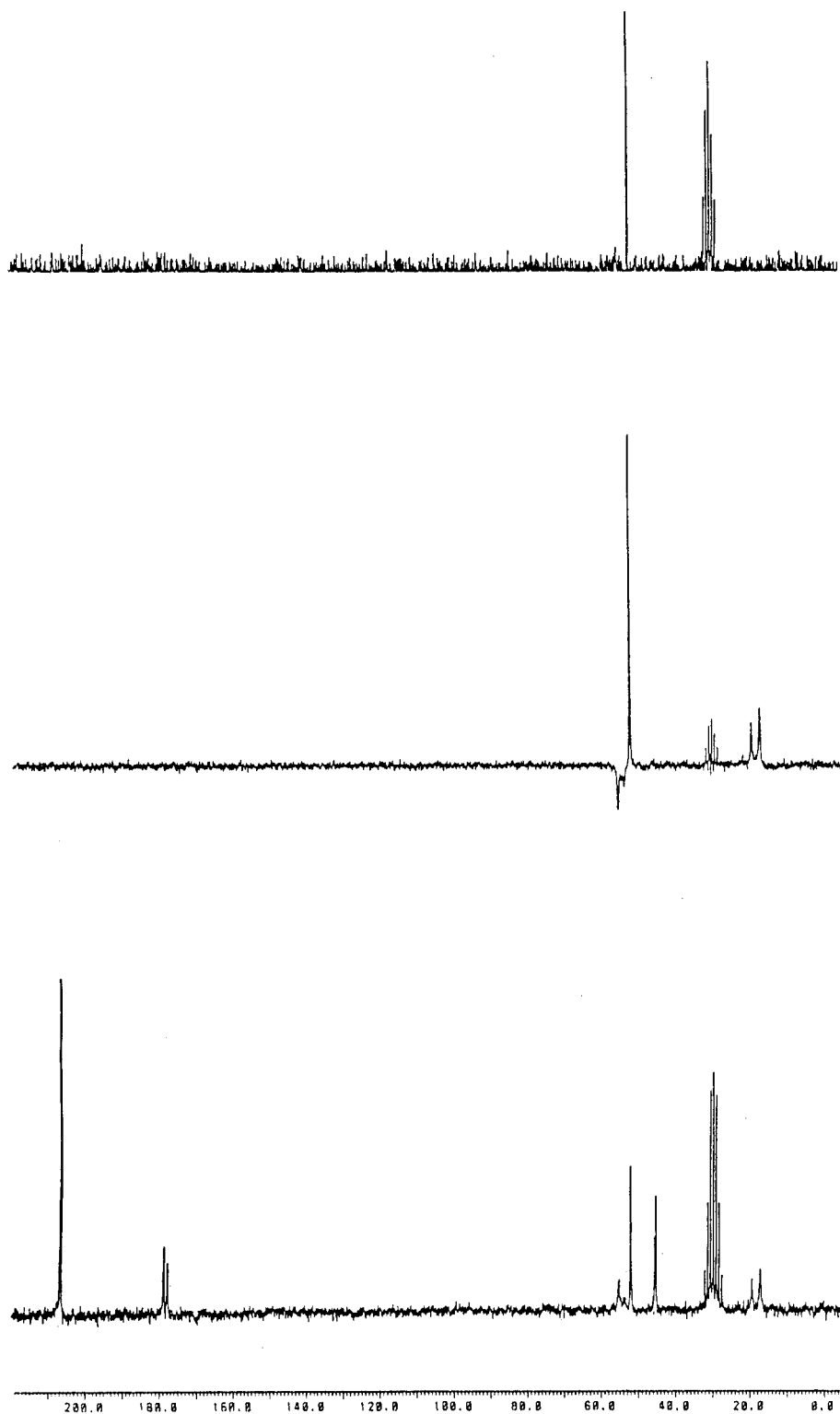
nisms (1) and (3). We suggested that the polymerization initiation step occurs to abstract the hydrogen of the ethylene of the EDTA.

#### Mechanism of Polymerization Reaction

Following the microstructure of the polymer obtained above, we proposed the mechanism of the



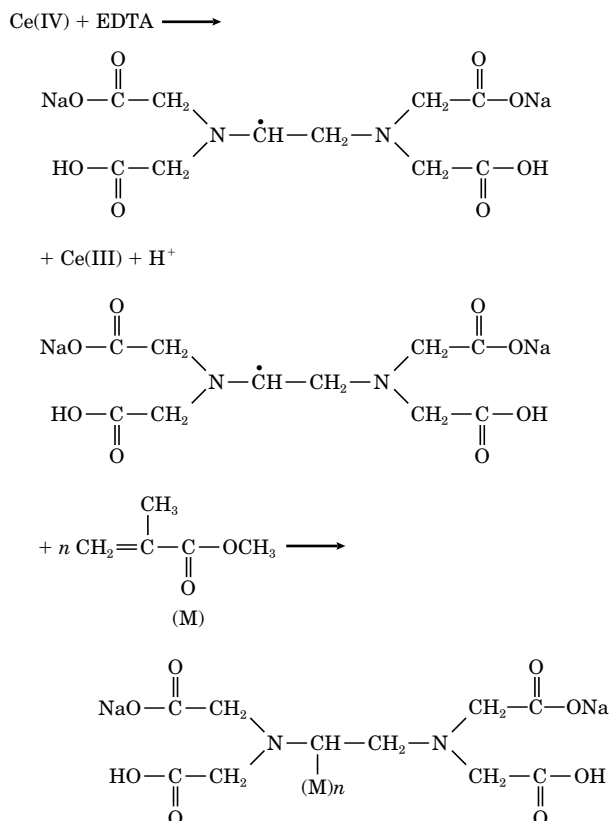
**Figure 4**  $^1\text{H}$ -NMR spectra of EDTA-PMMA.



**Figure 5**  $^{13}\text{C}$ -NMR regular and DEPT spectrum of EDTA-PMMA.

polymerization of MMA to EDTA as follows: EDTA with the ceric ion forms a complex intermediate and subsequently decomposes to the free radicals which initiate polymer formation. The

free radicals produced by the cerium ion abstract the hydrogen of the ethylene of the EDTA. According to the results mentioned above, the mechanism may be schemed as follows:



## CONCLUSION

In this study, the  $\text{Ce}^{+4}$ -EDTA redox system was used to initiate the polymerization of MMA. It was observed that the polymerization reaction proceeds without evolution of carbon dioxide from the EDTA catalyzed by the cerium ion in the  $\text{Ce}^{+4}$ -EDTA redox initiator system. The free radical appears to be produced by abstraction of the hydrogen of the ethylene of the EDTA by the cerium ion, contrary to the mechanisms suggested in the literature.

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