

# 嘉南藥理科技大學專題研究計畫成果報告

## Study on Polymerization of Ethylenediaminetetraacetic Acid and $\alpha$ -Methylstyrene

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計畫主持人：劉孟春

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## 嘉南藥理學院專題研究計畫成果報告

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### ABSTRACT

The polymerization of ethylenediamine-tetraacetic acid (EDTA) with  $\alpha$ -Methylstyrene was prepared by using cerium(IV) redox initiator system at 60 °C under nitrogen. The microstructures of the obtained polymers were characterized by infrared spectroscopy. The mechanism of polymerization reaction was determined from the microstructures of derived polymers.

Keywords: Ethylenediaminetetraacetic Acid,  $\alpha$ -Methylstyrene, Microstructure,

### INTRODUCTION

Ethylenediaminetetraacetic acid (EDTA), an excellent chelating agents<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>. They are very good catalysts, when EDTA form complex with cations. But they can not isolate from end products. Polymer supported metallic catalyst can overcome the separation and purification problem in 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 the aqueous free radical polymerizations<sup>11-17</sup>. In such mechanisms of the polymerization suggest that the reducing agent reacts with ceric ion to form a complex intermediate and subsequently decomposes to the free radicals which initiates polymer formation. Sarac et al<sup>11</sup> used cerium(IV)-EDTA redox initiator system with and without electrolysis to study polymerization of acrylamide.

Polymerization of 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> reported the infrared spectroscopy and found that the polymer contains EDTA as an end-group. Tripathy et al<sup>16-17</sup> indicated the mechanism of polymerization of monomer end-group of the polymer has been characterized by IR spectra. Hence, all the authors<sup>11-17</sup> suggested the initiation step occurs by the abstraction of hydrogen atoms in the position or escaping of carbon dioxide from the malonic acid.

Over the past decade, <sup>1</sup>H and <sup>13</sup>C NMR spectrometry have become important techniques for investigation of the microstructures of polymer<sup>18-21</sup>. Recently the distortionless enhancement by 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  $\alpha$ -Methylstyrene. The micro-structures of the poly( $\alpha$ -Methylstyrene) and EDTA polymers were determined by IR spectrometer. The mechanisms of the polymerization of EDTA with the  $\alpha$ -Methylstyrene were proposed.

## EXPERIMENTAL

### Reagents

Disodium salt of ethylenediamine-tetraacetic acid (EDTA) was supplied by Sigma.  $\alpha$ -Methylstyrene 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 1L four-necked a 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  $60 \pm 0.5$  °C. The polymerization was carried out under nitrogen atmosphere for 8hrs. The recipe studied was as follows: EDTA = 0.5M, MMA = 0.5M, cerium sulfate =  $5 \times 10^{-2}$  M. After 8 hrs reaction time, the resultant polymer was precipitated in cold methanol to stop the polymerization and separate unreacted monomer. The polymer was purified by continuous extraction in a soxhlet thimble with distilled water to remove the residual

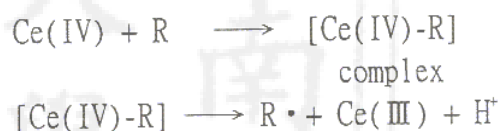
cerium sulfate and EDTA. The polymer was recovered in vacuum oven.

## Characterization

Infrared spectra were obtained in the range of 4000-400  $\text{cm}^{-1}$  on a Perkin-Elmer system 2000 FT-IR spectrophotometer using KBr pellets.

## RESULTS AND DISCUSSION

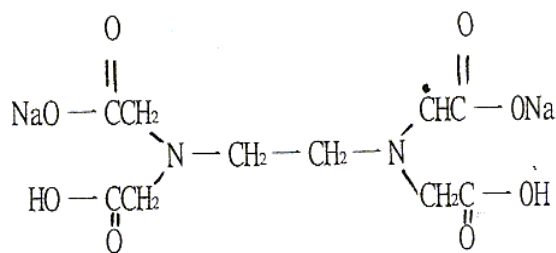
The mechanism of redox system polymerization may be depicted as follows<sup>6-10</sup>:



where R and R $\cdot$  are the chelating agent and the initiator fragment radical, respectively. Thus, the radicals which are capable of initiating the polymerization of  $\alpha$ -Methylstyrene perhaps occur via the reaction of ceric ion and chelating agent.

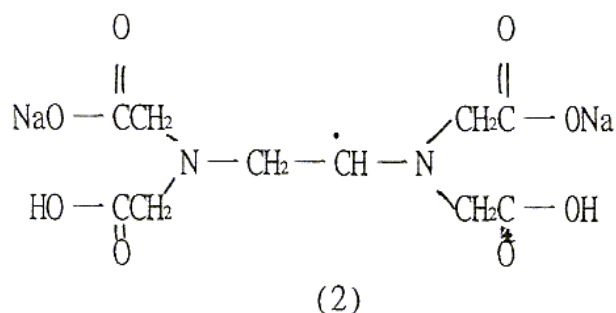
Radical formation may be proposed as follows:

1. Abstraction of hydrogen of the acetate -CH<sub>2</sub>- of EDTA by the cerium ion.

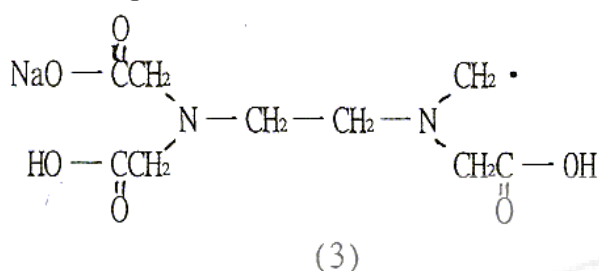


(1)

2. Abstraction of hydrogen from thylene -CH<sub>2</sub>CH<sub>2</sub>- of EDTA by the cerium ion.



### 3. Escape of carbon dioxide of EDTA



The microstructures of polymer were thoroughly characterized by IR spectroscopy. Figure 1 shows the IR spectrogram of the EDTA. The peak at 3520 and 3390  $\text{cm}^{-1}$  are due to the stretching vibration of -OH, 3030 and 2780  $\text{cm}^{-1}$  the stretching vibration of  $\text{CH}_2$ , 1640  $\text{cm}^{-1}$  the stretching vibration of the C=O group of EDTA. The C-N asymmetric stretching and C-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 with the absorptions of IR spectrogram of EDTA. It is found that the appearance of new absorptions peak occurs at 1668 and 1595  $\text{cm}^{-1}$ . The new peak is assigned to C=C stretch band of aromatic compound. The C=C bending of aromatic group are assigned at 1000-650  $\text{cm}^{-1}$ . The peaks at 748 and 698  $\text{cm}^{-1}$  result from the monosubstituted aromatic groups. The data indicates that aromatic groups of  $\alpha$ -Methylstyrene exist on the molecular chains of the polymer. Table I lists the assignments for the absorptions of those IR spectrogram in the figures. Therefore,

we suggest that cerium(IV) reducing agent initiates olymerization of  $\alpha$ -Methylstyrene to EDTA, resulting polymer. It is evidence of the existence of polymerization of  $\alpha$ -Methylstyrene to EDTA, thus resulting polymer.

### CONCLUSION

In this study, the  $\text{Ce}^{+4}$ -EDTA redox system was used to initiate the polymerization of  $\alpha$ -Methylstyrene. It was observed that the polymerization reaction proceeds.

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Fig.1 IR spectra of EDTA

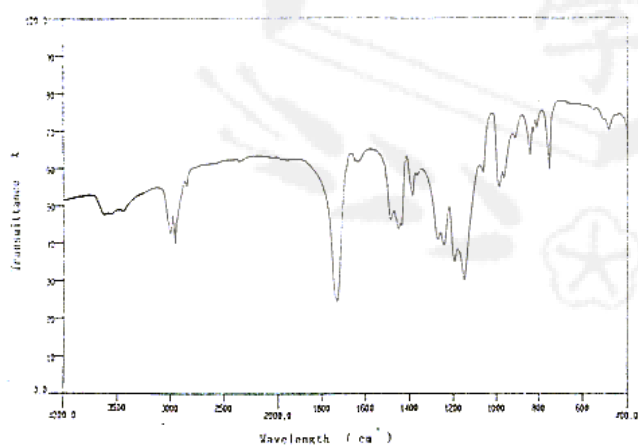


Fig.2 IR spectra of EDTA-Poly( $\alpha$ -Methylstyrene)

