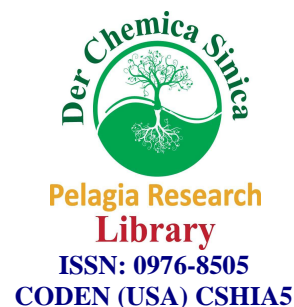




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### Anthracene Iodine Charge transfer complex as degradative chain transfer agent in the polymerization of ethyl acrylate

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#### ABSTRACT

The radical polymerization of ethylacrylate by Anthracene iodine charge transfer complex in DMSO at 60°C for 60 mins under inert atmosphere of nitrogen using dilatometric technique was studied. The initiator and monomer exponent value are 0.5 and unity respectively. The system followed ideal kinetics. The polymerization was inhibited in the presence of hydroquinone. The energy of activation was 42.02 kJ. The structure of polyethylacrylate was confirmed by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectroscopy. The results are explained in terms of a radical mode of polymerization with degradative initiator transfer, the principal mode of termination was bimolecular.

**Keywords:** Anthracene-Iodine charge transfer complex, (A-I.C.T.C.), degradative transfer agent, ethyl acrylate, kinetics and mechanism.

#### INTRODUCTION

Among polyacrylates, polyethyl acrylate is a high temperature resistant elastomer and has a superior resistance to degradation. It has vast applications in loading, textiles, finishing, paper restaurant, oil resistant and leather finishing. Hence it has attracted a number of polymer chemists. Hutton<sup>1</sup> and Nandi<sup>2</sup> polymerized ethyl acrylate and studied the kinetics using AIBN as initiator. Srivastava *et al.*<sup>3</sup> used stibonium ylide as an initiator in studying kinetic and mechanism of polymerization of ethyl acrylate, the system followed ideal kinetics. Ylides containing hetroatom like bismuth, antimony, arsenic, sulphur, phosphorus have been reported as initiator<sup>4,5,6</sup>, retarder<sup>7,8</sup> and degradative transfer agent<sup>8,9</sup> in polymerization of different vinyl monomers. The aim of present work is to study the applications of A-I.C.T.C. in polymerization of ethyl acrylate.

#### MATERIALS AND METHODS

##### Experimental (Merck)

Ethyl acrylate was purified<sup>10</sup> by washing with 4% NaOH and distilled water to neutral reaction and then vacuum distilled. Purified solvent dimethyl sulphoxide and non solvent methonal were used. Anthracene iodine charge transfer complex was prepared as reported in literature<sup>11</sup>.

##### Polymerization procedure:

A solution containing ethyl acrylate (Merck) and the A-I.C.T.C. in DMSO was injected into a dilatometric apparatus and the polymerization reaction was carried out at 60 ± 0.1°C for 60 mins under an inert atmosphere of nitrogen. The progress of reaction, was monitored as meniscus movement per unit volume per unit time, with the help of a cathetometer, was converted into conversion. The polymer was precipitated with methanol was dried to constant weight. The rate of polymerization (R<sub>p</sub>) was calculated from the slope of the linear portion of conversion versus time plots<sup>12</sup>.

The intrinsic viscosity ( $\eta$ ) of the polymers, determined in benzene 30°C using an Ubbelohde viscometer, to calculate the viscosity average molecular weight  $M_v$  with the values of the Mark-Houwink ( $\eta$ ) =  $KM_v^\alpha$  constant<sup>13</sup>

$$K = 27.7 \times 10^{-3} \text{ ml/g}$$

$$\alpha = 0.67$$

## RESULT AND DISCUSSION

Anthracene iodine charge transfer complex failed to initiate the polymerization of EA below 50°C. The polymerization condition and results are summarized in Table 1 to 2 and illustrated in (Fig.1-8). The kinetic studies have been carried out by varying the concentration of A-I.C.T.C., EA and temperature.

The kinetic studies have been carried out by varying the concentration of AIBN, anthracene-iodine charge transfer complex, ethyl acrylate and temperature. The results show that [A-I.C.T.C.] acts as a degradative transfer agent. The results are summarized in Table-I to III and Figs. 1 to 16.

### Effect of AIBN:

The effect of AIBN on rate of polymerization ( $R_p$ ) is studied by varying its concentration from  $1.21 \times 10^{-2}$  to  $3.65 \times 10^{-2}$  mol l<sup>-1</sup> keeping A-I.C.T.C, EA and temperature constant at  $43.85 \times 10^{-6}$  mol l<sup>-1</sup>, 2.45 moles and 65°C respectively shown in Table-I and Fig.1. It is found that the rate of polymerization increases with increase in initiator concentration as expected for free radical polymerization. The order of reaction with respect to initiator calculated from the slope of the plot  $R_p$  vs. log AIBN is 0.5 (Fig.2). The induction period is 2 to 8 minutes. The average molecular weight increases with increase in concentration.

### Effect of [A-I.C.T.C]:

The effect of [A-I.C.T.C.] on the rate of polymerization was studied by varying its concentration from  $21.92 \times 10^{-6}$  to  $65.78 \times 10^{-6}$  mol l<sup>-1</sup> while keeping the [EA] constant at  $1.84$  mol l<sup>-1</sup> (Fig.3 and Table-II). The polymerization was associated with an induction period of 2 to 7 minutes. The percentage conversion and rate of polymerization decreased with increasing [A-I.C.T.C.]. A plot of log  $1/R_p$  versus log [A-I.C.T.C.] Fig.4 is linear, the slope of which gives the initiator exponent 0.6. The value is little more than 0.5, as expected for ideal radical kinetics. The plot of  $1/M_v$  vs  $\sqrt{A-I.C.T.C.}$  passes through origin Fig.5 which shows radical polymerization with bimolecular termination<sup>14</sup>. The values of  $k_p^2/k_t$  as determined from the plot of  $1/M_v$  versus  $R_p/(M)^2$  (Fig.6) is  $0.40 \times 10^{-2}$ .

### Effect of [EA]:

Table-IV.6.2 illustrates the influence of the monomer on the rate of polymerization upon varying monomer concentration from  $1.22$  mol l<sup>-1</sup> to  $3.68$  mol l<sup>-1</sup> with [A-I.C.T.C.] constant at  $43.85 \times 10^{-6}$  mol l<sup>-1</sup> (Fig.7). It is note worthy that rate of polymerization is a direct function of ethyl acrylate. A plot of log  $R_p$  versus log [EA] is linear with monomer exponent as 1.20 (Fig.8). The polymerization run are associated with an induction period of 2 to 6 mins. This confirm the system follows non-ideal kinetics.

### Causes of non-ideality:

The value of initiator and monomer exponent suggests that the system follows non-ideal kinetics. The kinetic non ideality can be explained by analyzing the role of A-I.C.T.C. as primary radical termination and degradative chain transfer agent. Various explanation<sup>15-18</sup> for non-ideality in vinyl polymerization have been proposed but with limited success. It is now accepted that primary radical termination and degradative chain transfer are the most important causes of non-ideality.

To analyze the effect of primary radical termination a suitable modified expression given by Deb and Meyerhoff<sup>19</sup> in following form is used.

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_i} - 0.8684 \frac{k_{prt}}{k_g \times k_p} \times \frac{R_p}{[M]^2}$$

where I and M represent initiator and monomer concentration. A plot of above versus  $\frac{R_p}{[M]^2}$  gave a negative slope (Fig.9) indicating primary radical termination due to the initiator for the present system.

The following equation derived by Deb<sup>20</sup> and later simplified by Ghosh and Mitra<sup>21</sup> was used to examine the role of A-I.C.T.C. as degradative chain transfer agent.

$$\log \frac{R_p^2}{(I)(M)^2} = \log \frac{2f_k k_a k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \times \frac{k_{rt} I}{k_i / k_p} \times C_1 \frac{I}{M}$$

where  $C_1$  is initiator transfer constant, the plot of above equation versus  $I/M$  also gave a negative slope Fig.10 suggesting chain transfer reaction due to [A-I.C.T.C.].

The polymerization of few vinyl monomers initiated by nitrogen and phosphorus ylide also follows non-ideal kinetics due to primary radical termination and degradative chain transfer.

### Effect of Temperature

The polymerization runs also carried out at 50°C, 55°C, 60°C, 65°C and 70°C in order to evaluate energy of activation (Fig.11). The value calculated from the plot of  $\log R_p$  versus polymerization temperature is 42 kJ mol<sup>-1</sup> (Fig.12).

### Characterization of polymers

#### (i) Fourier Transfer Infrared Spectroscopy (FTIR):

The Fourier transfer infra red spectroscopy Fig.13 of poly ethyl acrylate show<sup>22</sup> a band of carbonyl stretching vibration of the ester group at 1725 cm<sup>-1</sup>. The band at 1025 cm<sup>-1</sup> 3000 cm<sup>-1</sup> appears due to C-O-C stretching of ester and aromatic phenyl respectively.

**<sup>1</sup>H-NMR:** The <sup>1</sup>H-NMR spectrum<sup>23</sup> shows (Fig.14) the ester methyl protons at 3.9 δ ppm. The peak of methine protons are observed at 2.7 δ ppm. Signals at 7.3-7.6 δ ppm corresponds to phenyl protons.

**<sup>13</sup>C-NMR:** The <sup>13</sup>C-NMR spectrum shows<sup>24</sup> (Fig.15) the carbon signals of -CH<sub>3</sub>-CH<sub>2</sub> at 12.2 δ ppm and 35 δ ppm respectively. The backbone methine carbon signals appear at 42.0 δ ppm. The resonance signals around 54.1 δ ppm and 172 δ ppm can be assigned to -OCH<sub>3</sub> and >C=O carbon in poly ethyl acrylate respectively.

**TGA:** TGA curve (Fig.16) exhibits weight loss with temperature<sup>25,26</sup>. There are three distinct steps of weight loss. 20<sup>0</sup> - 270<sup>0</sup>C = 6.07%, 271<sup>0</sup> - 350<sup>0</sup>C = 19.8%, 351<sup>0</sup> - 450<sup>0</sup>C = 80%

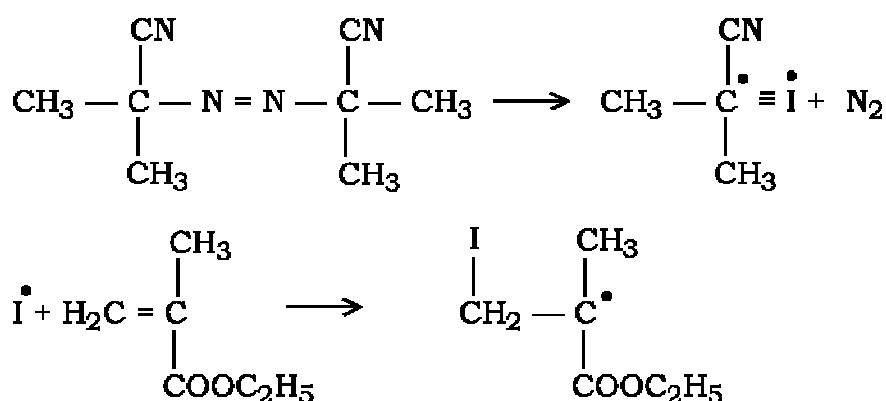
**Scanning Electron Microscopy:** SEM report Fig.17 shows the absence of iodine in the polymer mechanism.

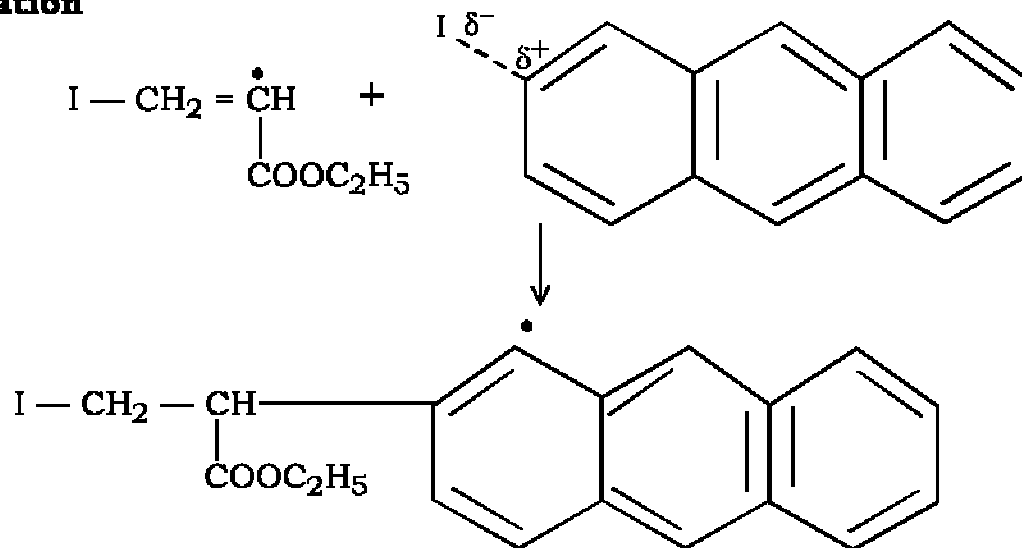
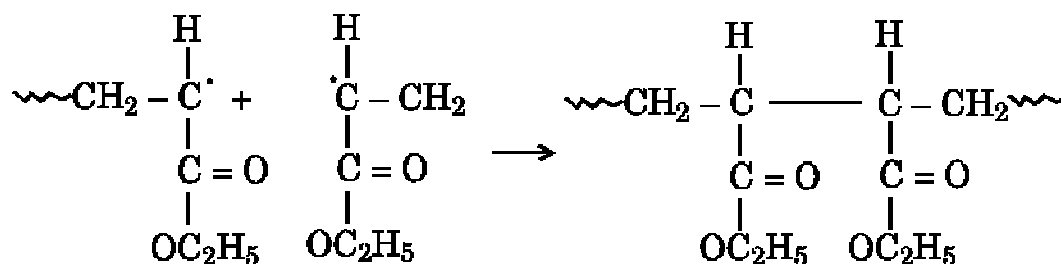
### MECHANISM

The quantitative test of iodine in the polymer showed its absence. The FTIR spectrum also did not show bands in the region, due to iodine at about 500 cm<sup>-1</sup>.

A comparison of the FTIR of the polymer with that prepared in the absence of charge transfer complexes shows that the bands in the regions of 3000 cm<sup>-1</sup> due to phenyl group is absent, which with the polymer prepared in the presence of charge transfer complexes shows the bands in the region of 3000 cm<sup>-1</sup>. Further, the peak area due to phenyl protons in <sup>1</sup>H NMR spectrum is also observed when prepared in the presence of charge transfer complexes. From these observation we can conclude that anthracene has been incorporated in the polymer therefore the following mechanism has been proposed.

#### Initiation



**Propagation****Termination**TABLE-I: Effect of concentration AIBN on the rate of polymerization ( $R_p$ ) of EA

Run No.	AIBN $\times 10^{-2}$ (mol $l^{-1}$ )	Conversion %	$R_p \times 10^6$ mol $l^{-1} s^{-1}$
1	1.21	6.7	1.96
2	1.82	7.5	2.12
3	2.43	8.6	2.49
4	3.04	10.5	3.10
5	3.65	11.4	3.60

$$[A-I.C.T.C.] \times 10^{-6} = 43.85 \text{ mol } l^{-1}$$

$$[EA] = 2.45 \text{ mol } l^{-1},$$

$$\text{Temperature} = 60^\circ C \pm 1^\circ C$$

$$\text{Time} = 60 \text{ mins.}$$

TABLE-II: Effect of A-I C.T.C. concentration on the rate of polymerization ( $R_p$ ) of ethyl acrylate

Run No.	A-I.C.T.C. $\times 10^{-6}$ mol $l^{-1}$	Conversion %	$R_p \times 10^6$ mol $l^{-1} s^{-1}$	$M_v$ —
1.	21.92	10.2	8.16	60432
2.	32.89	9.4	6.12	48556
3.	43.85	8.6	4.90	44791
4.	54.82	7.3	4.08	34120
5.	65.78	6.1	3.47	20036

$$[AIBN] = 2.43 \times 10^{-2} \text{ mol } l^{-1}$$

$$[EA] = 2.45 \text{ mol } l^{-1}$$

$$\text{Temperature} = 60 \pm 0.1^\circ C$$

$$\text{Time} = 60 \text{ mins.}$$

TABLE-III: Effect of ethyl acrylate concentration on the rate of polymerization ( $R_p$ )

Run No.	EA mol <sup>-1</sup>	% Conversion	$R_p \times 10^6$ mol l <sup>-1</sup> s <sup>-1</sup>	$M_v$
1.	1.22	5.3	1.44	25991
2.	1.84	7.1	1.68	35832
3.	2.45	8.6	4.90	44791
4.	3.06	9.8	6.37	68813
5.	3.68	11.4	9.81	98407

$$[A-I.C.T.C.] \times 10^{-6} = 43.85 \text{ mol l}^{-1}$$

$$[AIBN] = 2.43 \times 10^{-2} \text{ mol l}^{-1}$$

$$\text{Temperature} = 60^\circ\text{C} \pm 1^\circ\text{C}$$

$$\text{Time} = 60 \text{ mins.}$$

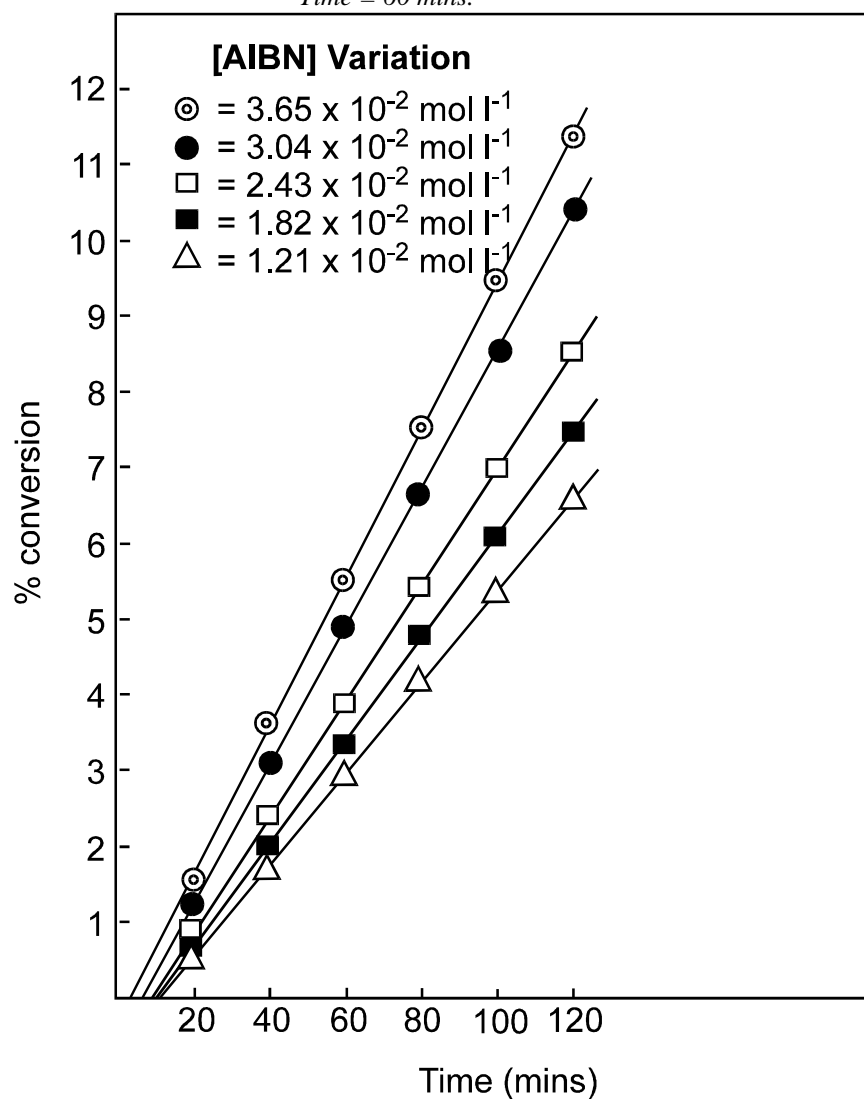


Fig.1 : Percentage conversion versus time plot for polymerization of ethyl acrylate.

$$[A-I.C.T.C.] = 43.85 \times 10^{-6} \text{ mol l}^{-1}$$

$$[EA] = 2.45 \text{ mol l}^{-1}$$

$$\text{Polymerization time} = 60 \text{ mins.}$$

$$\text{Polymerization temp.} = 60 \pm 0.1^\circ\text{C.}$$

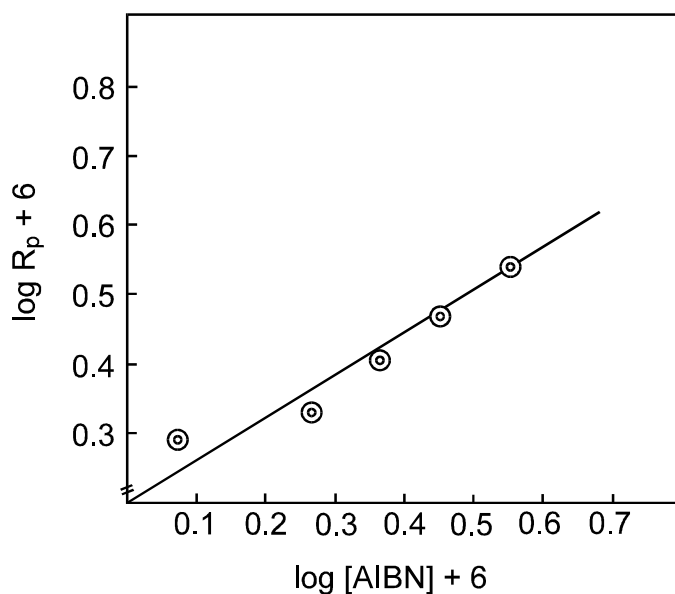


Fig.2 : Relationship between  $\log R_p$  versus  $\log [AIBN]$

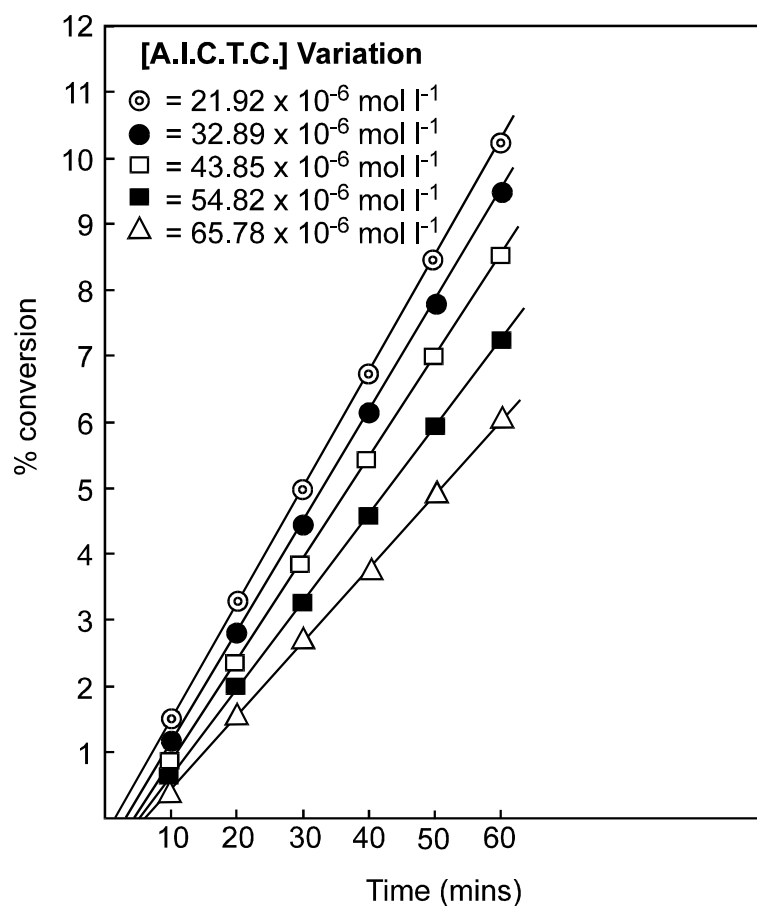


Fig.3 : Percentage conversion versus time plot for polymerization of ethyl acrylate.

$$[AIBN] = 2.43 \times 10^{-2} \text{ mol l}^{-1}$$

$$[EA] = 2.45 \text{ mol l}^{-1}$$

Polymerization time = 60 mins.

Polymerization temp. =  $60 \pm 0.1^\circ\text{C}$ .

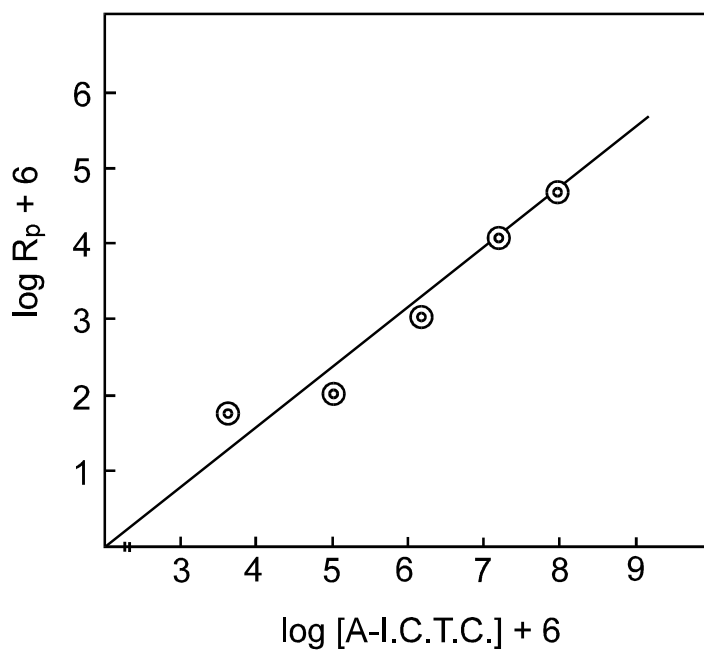


Fig.4 : Relationship between  $\log R_p$  versus  $\log [A-I.C.T.C.]$

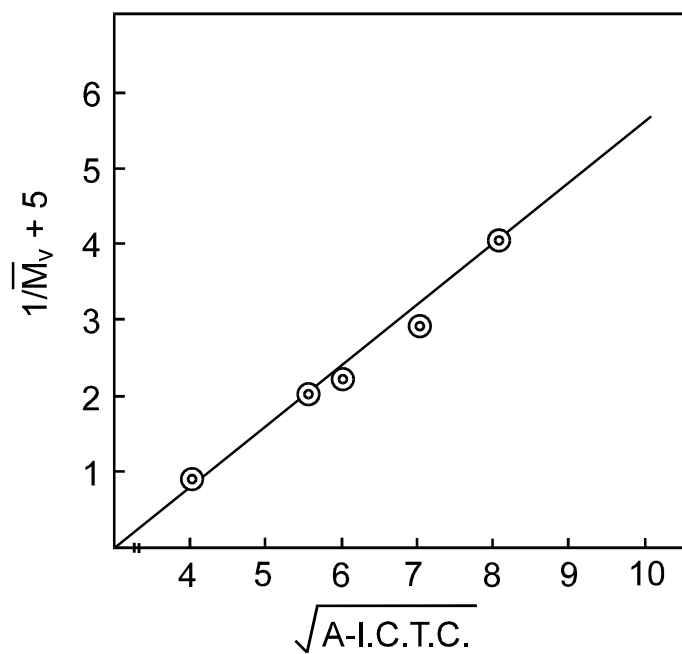


Fig.5 : Relationship between  $1/\bar{M}_v$  versus  $\log [A-I.C.T.C.]$

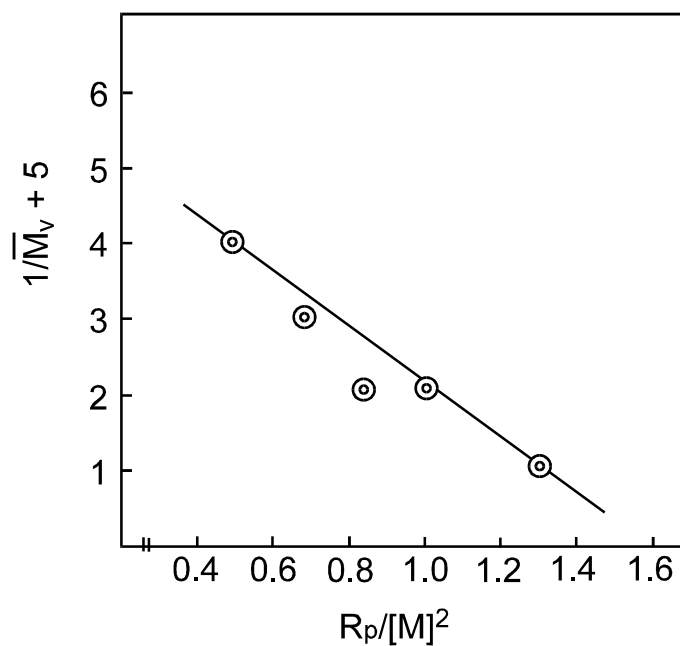
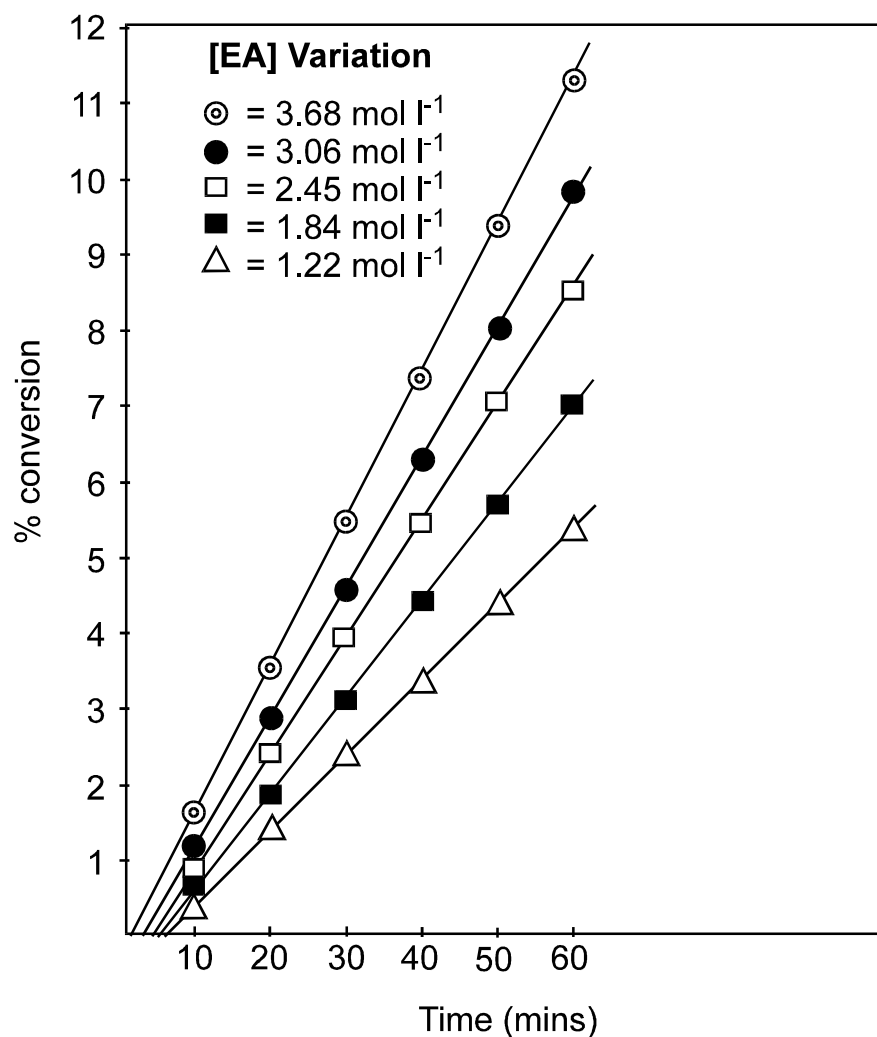
Fig.6 : Relationship between  $1/\bar{M}_v$  versus  $R_p/[M]^2$ 

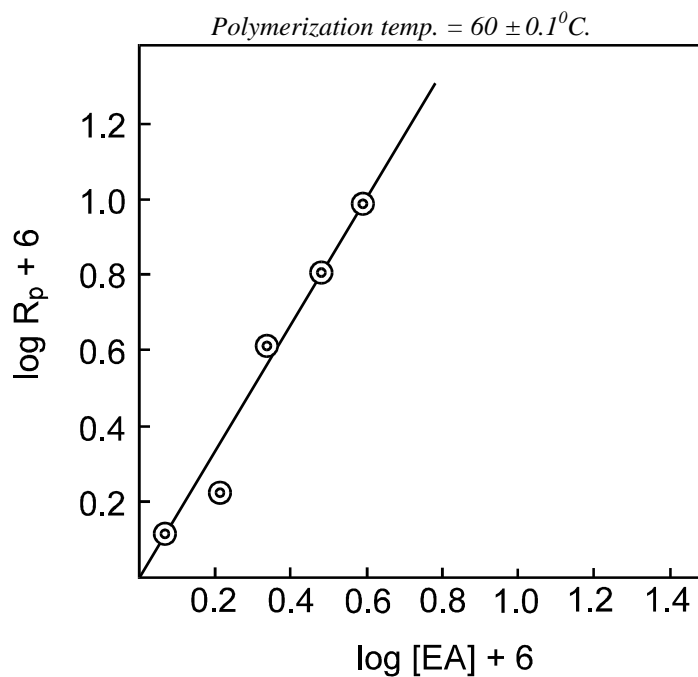
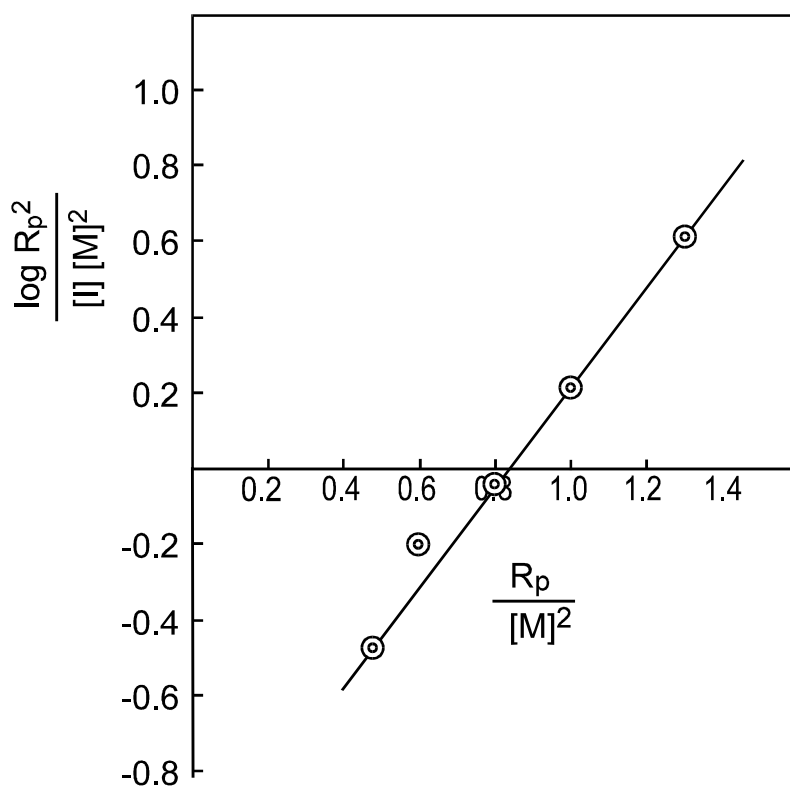
Fig.7 : Percentage conversion versus time plot for polymerization of ethyl acrylate.

$[AIBN] = 2.43 \times 10^{-2} \text{ mol l}^{-1}$

$[A-I.C.T.C.] = 43.85 \times 10^{-6} \text{ mol l}^{-1}$

Polymerization time = 60 mins.



Fig.8 : Relationship between  $\log R_p$  versus  $\log [EA]$ .Fig.9 : Relationship between  $\log R_p^2/[I][M]^2$  versus  $R_p/[M]^2$

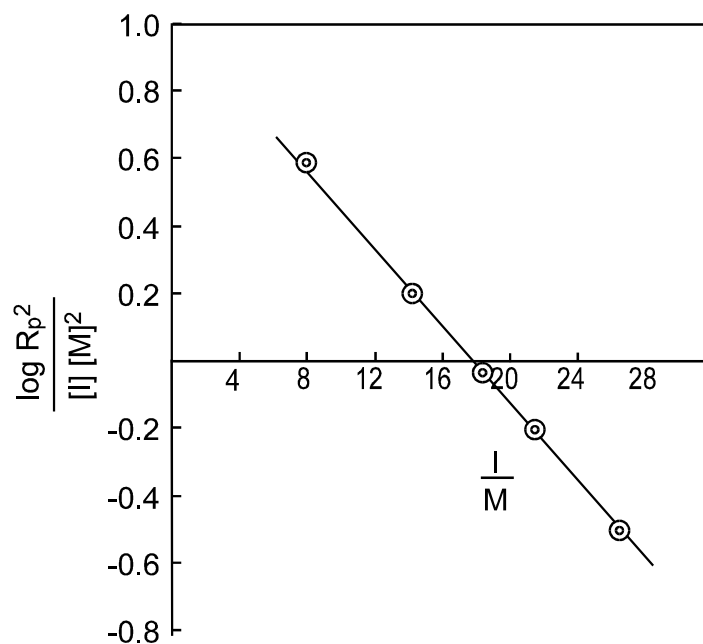


Fig.10 : Relationship between  $\log R_p^2/[I][M]^2$  versus  $I/M$

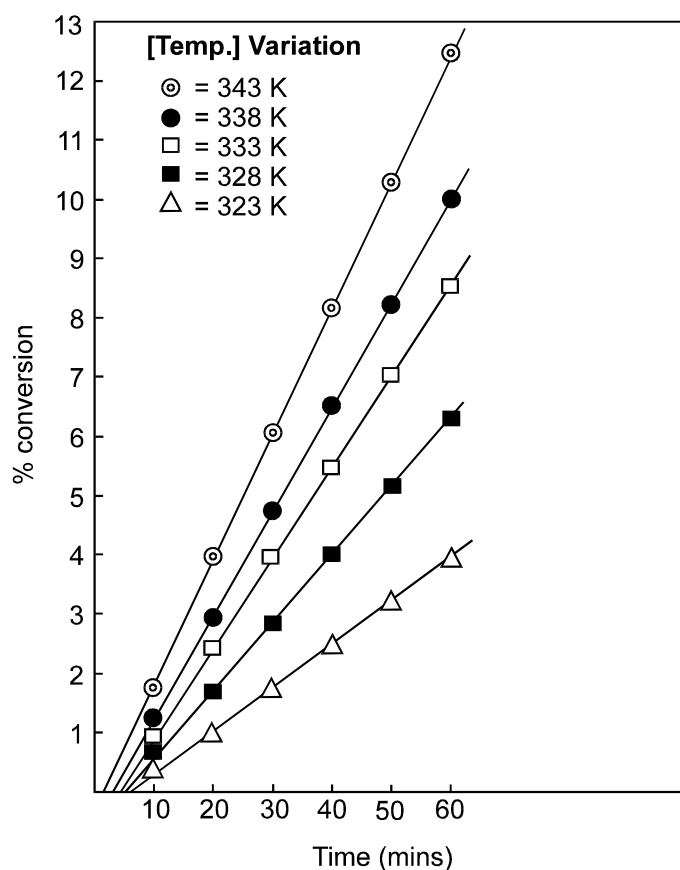


Fig.11: Percentage conversion versus time plot for polymerization of ethyl acrylate.

$[AIBN] = 2.43 \times 10^{-2} \text{ mol l}^{-1}$   
 $[A-I.C.T.C.] = 43.85 \times 10^{-6} \text{ mol l}^{-1}$   
 $[EA] = 2.45 \text{ mol l}^{-1}$   
 Polymerization time = 60 mins.

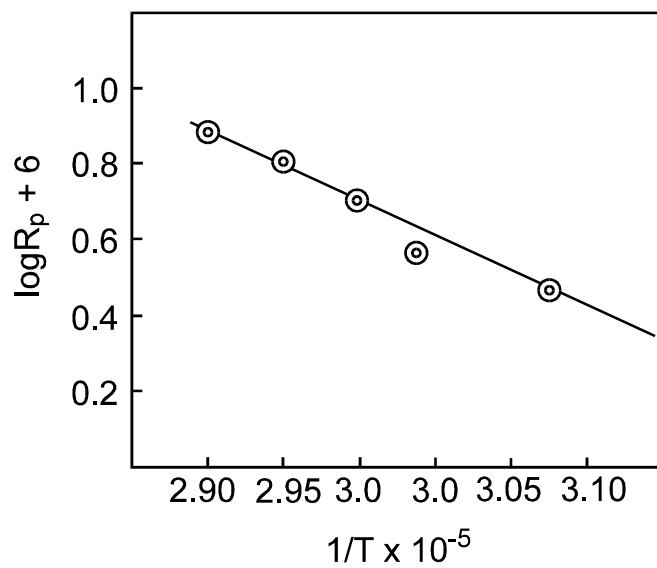


Fig.12 : Relationship between  $\log R_p$  versus  $1/T$

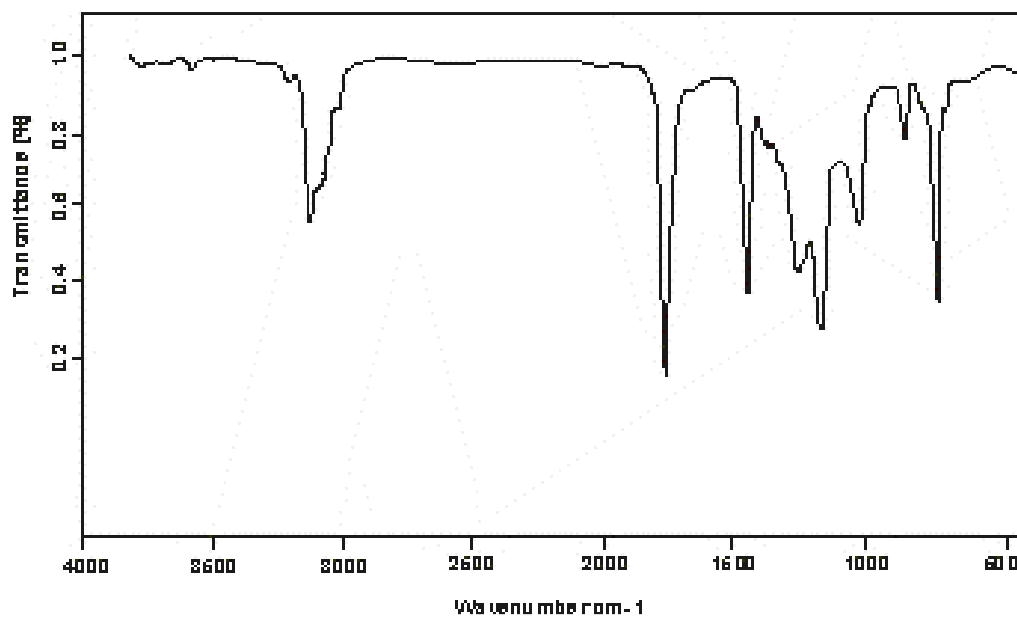


Fig.13 : FTIR spectrum of poly(ethyl acrylate).

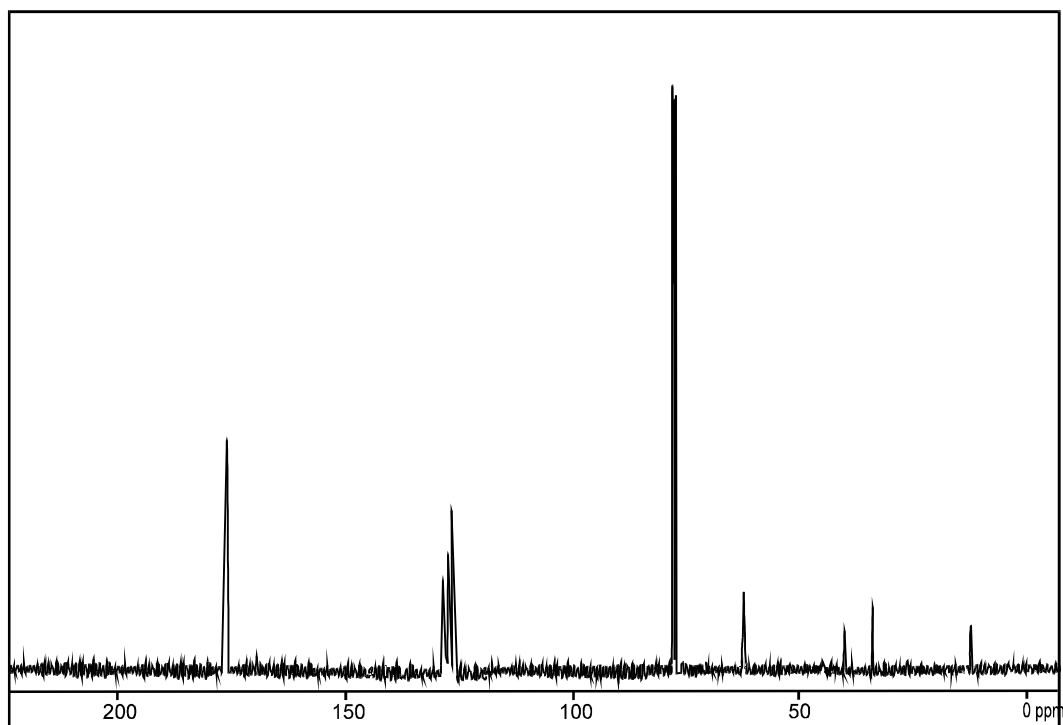


Fig.14 :  $^1\text{H}$ -NMR spectrum of poly(ethyl acrylate)

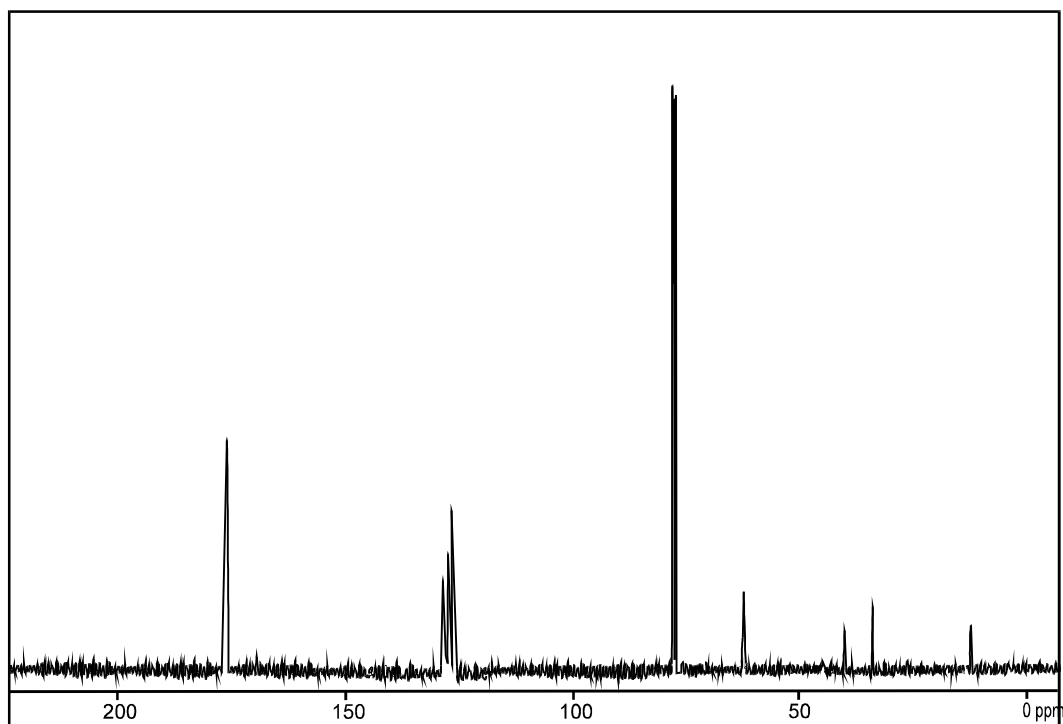
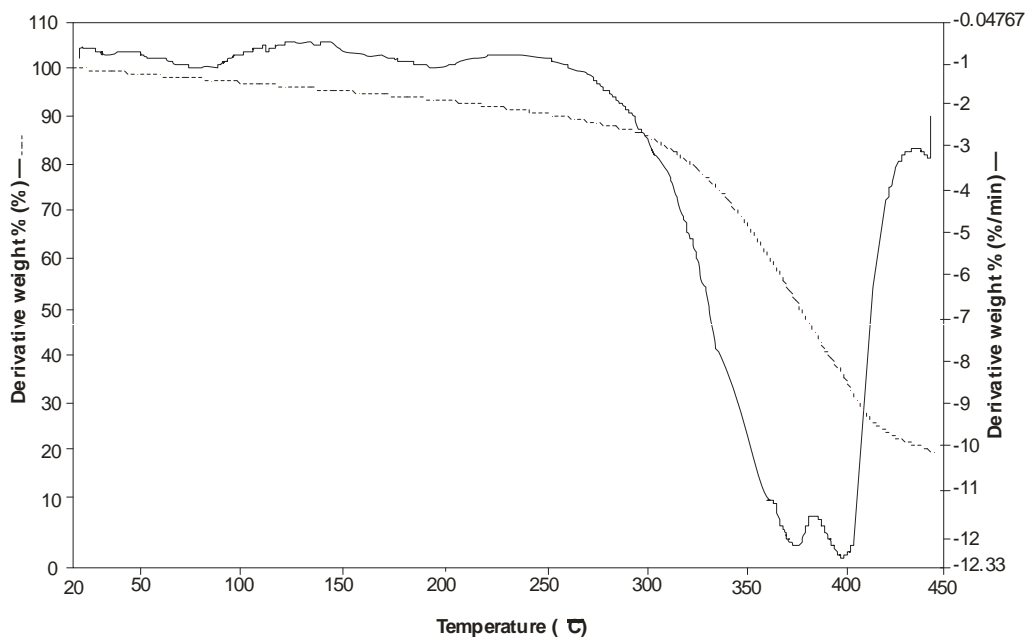
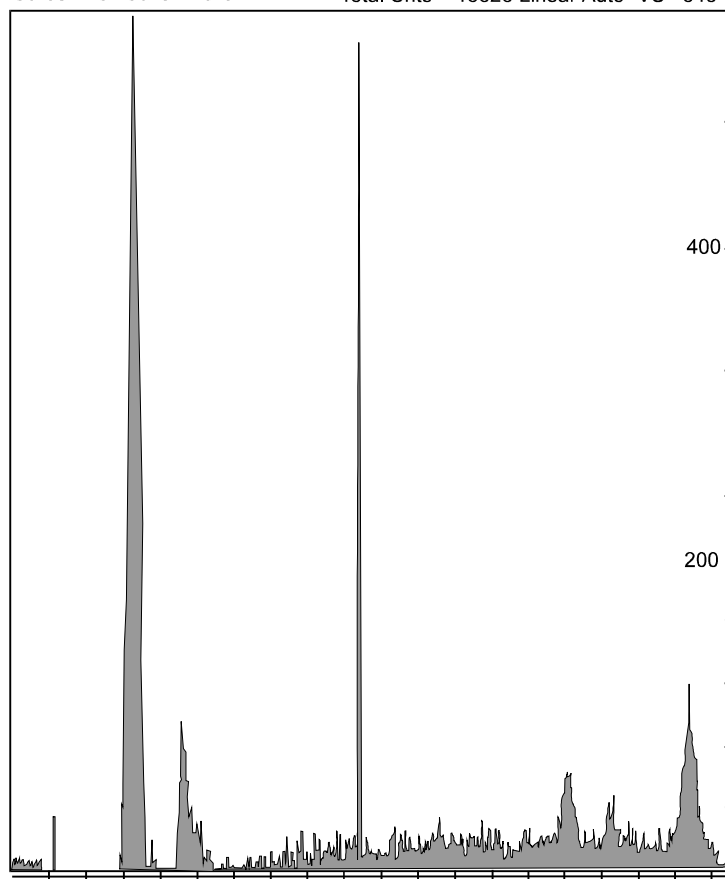


Fig.15 :  $^{13}\text{C}$ -NMR spectrum of poly(ethyl acrylate).

**Fig.16 : TGA curve of poly(ethyl acrylate).**

Spectrum: EA      Range : 10 kev  
Cursor = 5.230keV 4cnt      Total Cnts = 15828 Linear Auto- VS= 548

**Fig.17 : SEM analysis of poly(ethyl acrylate).**

## CONCLUSION

The polymerization of ethyl acrylate initiated by AIBN using A-I.C.T.C. follows a non ideal kinetics radical polymerization due to degradative initiator transfer with reinitiation. The activation energy is 42 kJ mol<sup>-1</sup>.

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