Naphthalene-iodine charge transfer complex as a degradative chain transfer agent in polymerization of methyl methacrylate*

A. Varshney*, K. Prajapati and N. Jain

D. G. College, Kanpur (India)

ABSTRACT

$\alpha-\alpha'$azobisisobutyronitrile initiated radical polymerization of MMA in presence of naphthalene-iodine charge transfer complex in DMSO at 65 ± 0.1^0C for 2 hours under a nitrogen blanket, follows ideal kinetics. Dilatometric technique is used to prepare the polymer. The overall activation energy and average value of k_p^2/k_t are 32.37 kJ and 1.14×10^{-2} l $mol^{-1}s^{-1}$ respectively. The polymer has a viscosity -average molecular weight between 23741-65285.The FTIR spectrum of the polymer shows the presence of band at 3010 cm^{-1} and 1735 cm^{-1} for the phenyl group of the complex and ester stretchings of MMA respectively. ^{1}H-NMR spectrum shows the peak at 7.8 δ ppm and 3.7 δ ppm due to phenyl protons and ester group of MMA respectively. The thermal properties of the polymer were investigated by TGA technique. The TGA spectrum shows the stability of polymer upto 250^0C.

Keywords: Kinetics, naphthalene-iodine charge transfer complex (N-I.CTC), methyl methacrylate(MMA), mechanism.

INTRODUCTION

Polymer chemistry, a significant branch of organic chemistry is expanding vigorously because of unique properties of polymers such as being light weight having an advantage of rigidity, impact strength high temperature resistance etc. A search of literature reveals that a number of initiators[1-3] retarders[4], chain transfer agent[5,6] have been used in polymerization of methyl methacrylate.Block Polymers[7],Coordination Polymers[8],and Grafted Polymers [9]have been synthesized and the kinetics has been studied.Very recently Ashrafi etal[10] have studied the kinetics of 2-propanol by using nano catalyst. Allen *et al*[11]reported dihydromyrcene and isopropylbenzene as degradative transfer agents for polymerization of vinyl acetate. Ferington and Tobolsky[12] used disulphides and Harward & Simpson[13] used diazoaminobenzene as initiators and degradative transfer agent. Sriavastava *et al* [14] reported β-picolinium-p-chlorophenacylide as initiator and degradative transfer agent for polymerization of methyl methacrylate. However, the reports regarding the use of charge transfer complexes as retarders/chain transfer agents are still scarce.

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An important trend now a days in polymer chemistry is to synthesize the polymers with controlled molecular weight. Present article is an out come of such efforts in this direction to synthesis the polymer of MMA in presence of AIBN and [N-I.C.T.C.] acting as initiator and chain transfer agent respectively.

MATERIALS AND METHODS

Methyl methacrylate was washed with 4% NaOH solution followed by distilled water and then distilled by vacuum before polymerization. The solvents were purified by usual methods[15]. The initiator α,α'−azobisisobutyronitrile (AIBN) was recrystallised twice from methanol (m.p.–102ºC) followed by drying under vacuum were used.

The charge transfer complex of naphthalene and iodine was prepared[16] by dissolving 0.005 moles of naphthalene and 0.005 moles of iodine in minimum amount of ether. On evaporation the complex was formed.
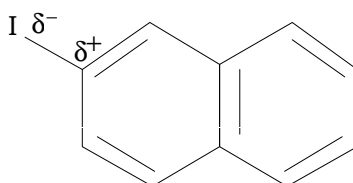
Naphthalene iodine charge transfer complex

M. P. = 64.5^{0}C
Colour = Dark brown
Yield = 84%

Polymerization Procedure

A solution containing MMA with naphthalene iodine charge transfer complex in the presence of AIBN was carried out in a dilatometric apparatus (Capillary diameter 3 mm; Capillary length 6 cm and bulb capacity 3 ml). The polymerization runs were carried out for 120 mins at 65ºC under an inert atmosphere of nitrogen. The polymer was precipitated with methanol, and was dried to constant weight. Rate of polymerization was calculated from the slope of linear plot of percent conversion versus time[17].

Measurements: Viscosity average molecular weight (M_v) of the polymer was determined in benzene at 30 + 1ºC with an Ubbelohde viscometer with the values of Mark–Houwink constant[18] using :

$$(\underline{\eta}) = k[(M_v)^{\alpha} \text{ where } k = 5.2 \times 10^{-3} \text{ and } \alpha = 0.76].$$

Characterization

The polymers were characterized by FTIR, ^{1}H-NMR and thermo gravimetric analysis (TGA). FTIR was recorded with a Perkin-Elmer 59913 in dichloromethane. ^{1}H-NMR spectra were recorded with Varian 100 HA JOEL LA 400 spectrometer using CDCl$_3$ as solvent and tetramethylsilane as internal reference. The TGA runs were carried out using V 5.1 DuPont 2100 analyzer sample weight 10 mg and heating rate 10ºC per minute.

Kinetics of homopolymerization:

The polymerization of MMA was performed in a dilatometric apparatus (capillary diameter, 2 mm, capillary length 8 cm, bulb capacity 3 ml) in dimethyl sulphoxide at 65^{0}C for 120 mins

under the atmosphere of nitrogen. The progress of the polymerization reaction was monitored as meniscus movement per unit volume per unit time by a Cathetometer. The volume contraction data was converted to percent conversion by master graph. The homopolymer were precipitated with methanol and dried to constant weight.

Kinetics of free radical polymerization has been studied by varying the concentration of (N-I.C.T.C.), (AIBN) initiator(s), (MMA) monomer(s) and temperature. The results are illustrated in Table–I - III and Figs.1 to 14.

TABLE-I: Effect of [AIBN] on homopolymerization of MMA in presence of [N-I.C.T.C.].

Run No.	AIBN x 10^{-2} (mol l^{-1})	(%) conversion	R_p x 10^6 (mol $l^{-1}s^{-1}$)	M_v
1.	1.21	3.6	1.95	39625
2.	1.82	4.5	2.23	45286
3.	2.43	5.8	2.60	72129
4.	3.04	6.2	3.13	86233
5.	3.65	8.0	3.91	91654

[MMA] = 3.13 mol l^{-1}
[N-I.C.T.C.] = 52.49 x 10^{-6} mol l^{-1}
Polymerization time = 2 hrs
Polymerization Temp. = 65 ±0.1ºC

TABLE-II: Effect of [N-I.C.T.C.] on homopolymerization of MMA in presence of [AIBN].

Run No.	[N–I.C.T.C.] x 10^{-6} (mol l^{-1})	(%) conversion	R_p x 10^{-6} (mol l^{-1})	M_v
1.	26.24	9.2	3.65	65283
2.	39.37	8.6	3.13	54523
3.	52.49	6.2	2.34	41650
4.	65.61	5.4	2.08	32721
5.	78.74	3.6	1.56	28560

[MMA] = 3.13 mol l^{-1}
[AIBN] = 2.43 x 10^{-2} mol l^{-1}
Polymerization time = 2 hrs,
Polymerization Temp. = 65 ±0.1ºC

TABLE-III: Effect of [MMA] on homopolymerization of MMA in presence of [AIBN] and [N-I.C.T.C.]

Run No.	MMA moles	(%) conversion	R_p x 10^{-6} (mol l^{-1} s^{-1})	M_v
1.	1.88	4.6	0.94	23741
2.	2.50	5.1	1.66	29574
3.	3.13	6.2	2.60	35696
4.	3.76	7.6	3.76	45350
5.	4.38	9.3	5.84	52136

[AIBN] = 2.43 x 10^{-2} mol l^{-1}
[N-I.C.T.C.] = 52.49 x 10^{-6} mol l^{-1}
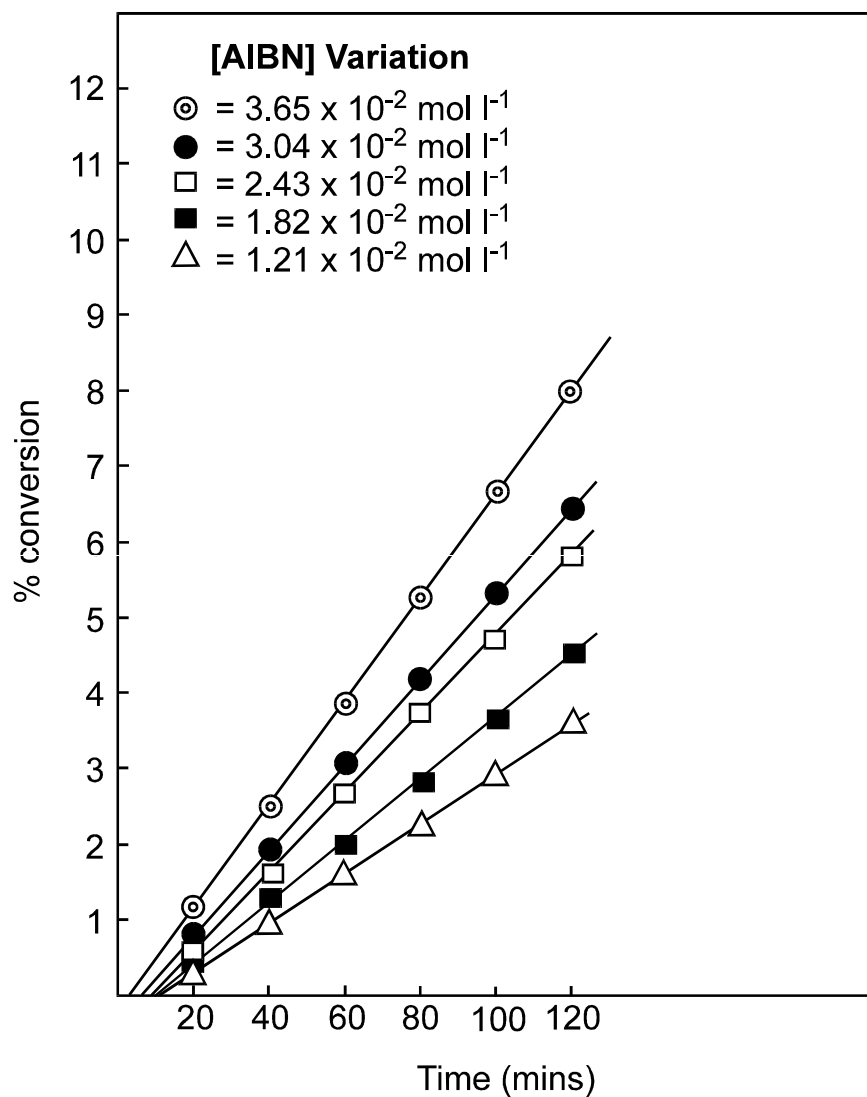*Polymerization time = 2 hrs*
Polymerization temp. = 65 ±0.1ºC

Fig.1: Percentage conversion versus time plots for homopolymerization of methyl methacrylate.
[N-I.C.T.C.] = 52.49 x 10⁻⁶ mol l⁻¹
[MMA] = 3.13 mol l⁻¹
Polymerization temp. = 65 ± 0.1⁰C
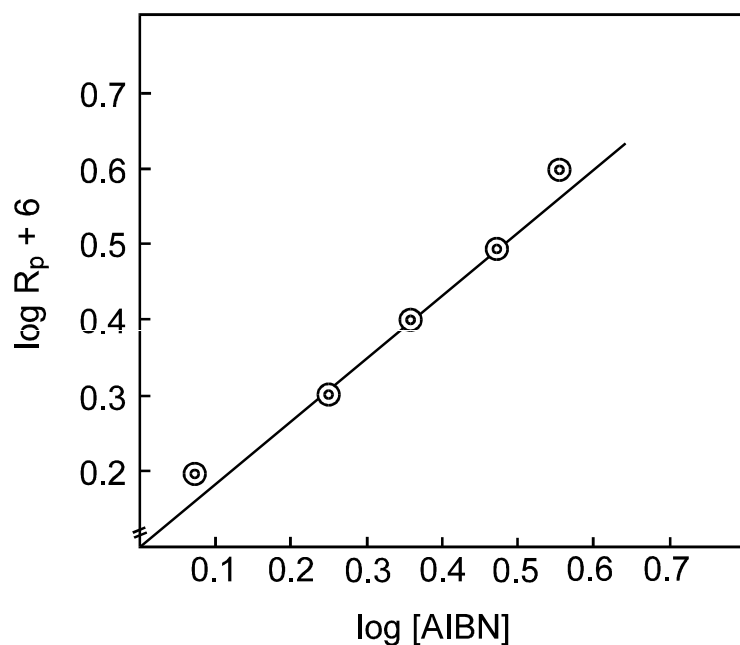*Polymerization time = 120 mins.*

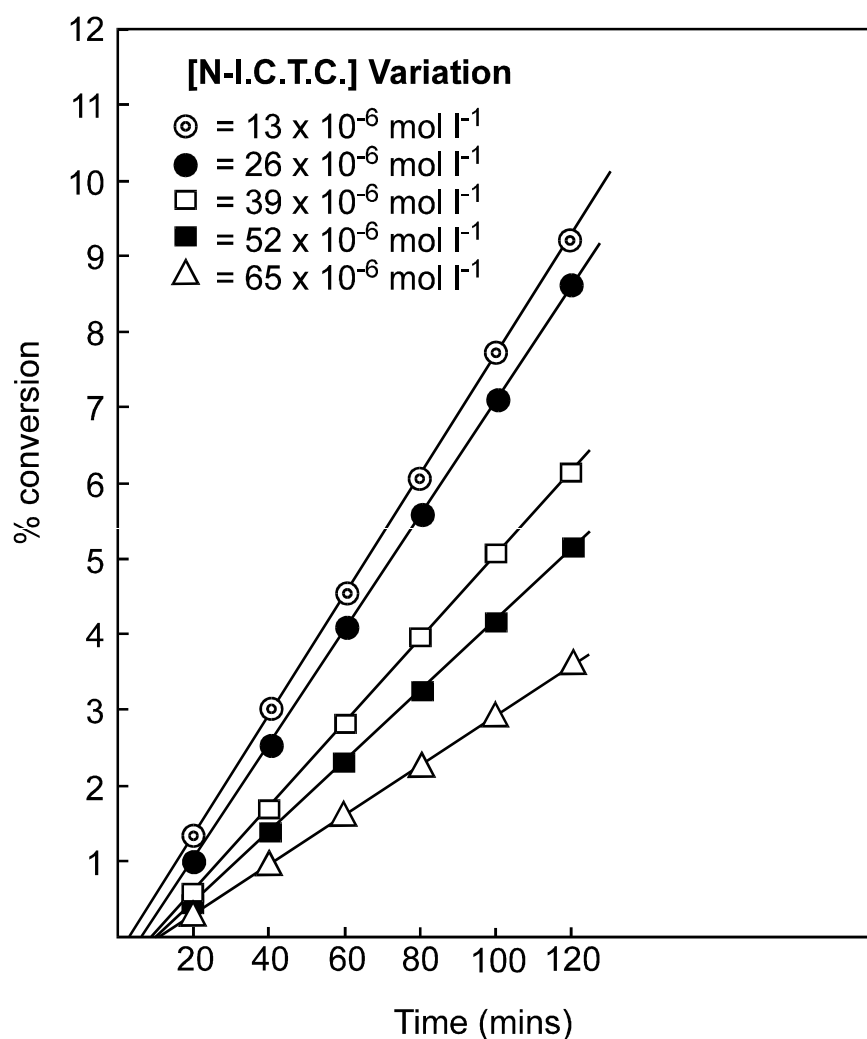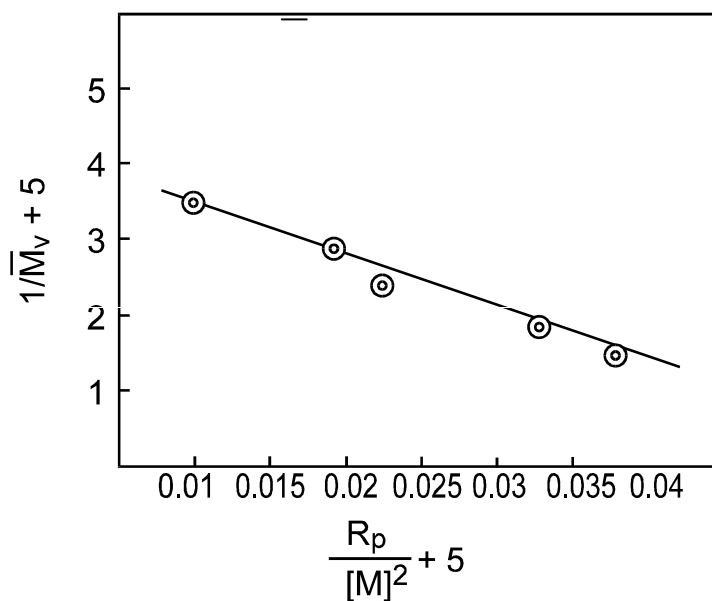**Fig.2: Relationship between log R_p and log [AIBN] for polymerization of MMA.**

Fig.3:   Percentage conversion versus time plots for polymerization of methyl methacrylate.
[MMA] = 3.13 mol l⁻¹

[AIBN] = 2.43 x 10⁻² mol l⁻¹
Polymerization temp. = 65 ± 0.1⁰C
Polymerization time = 120 mins.
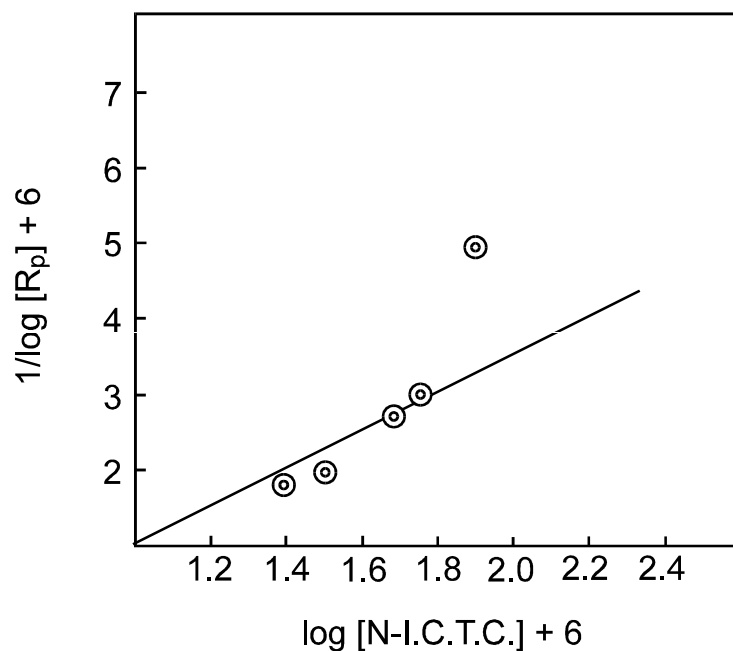
Fig.4: Relationship between 1/log R_p and log [N-I.C.T.C.].

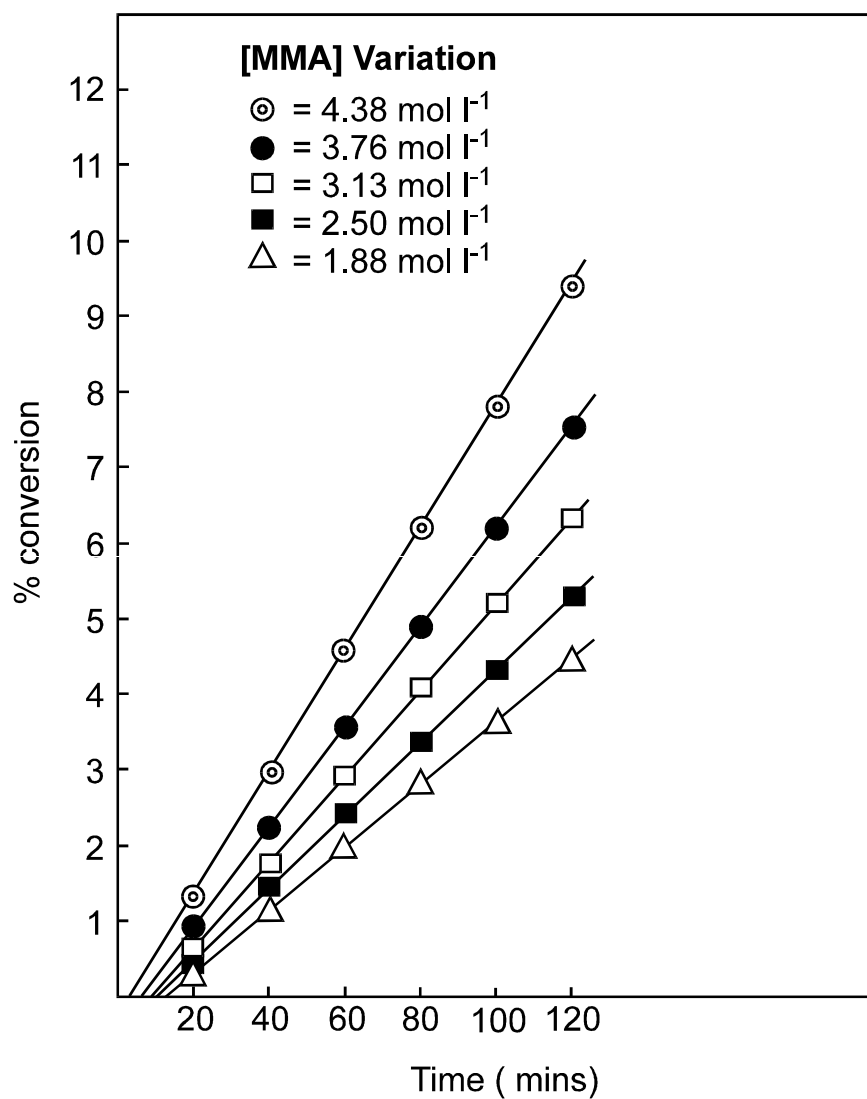**Fig.5: Relationship between 1/M$_v$ and $R_p/[M]^2$ for polymerization of   MMA.**

Fig.6:   **Percentage conversion versus time plot for polymerization of methyl methacrylate.**
[N-I.C.T.C.] = 52.49 x 10^{-6} mol l^{-1}
[AIBN] = 2.43 x 10^{-2} mol l^{-1}
Polymerization temp. = 65 ± $0.1^{0}C$
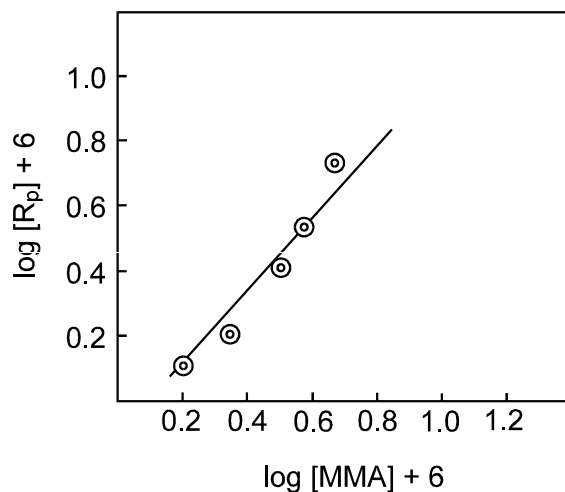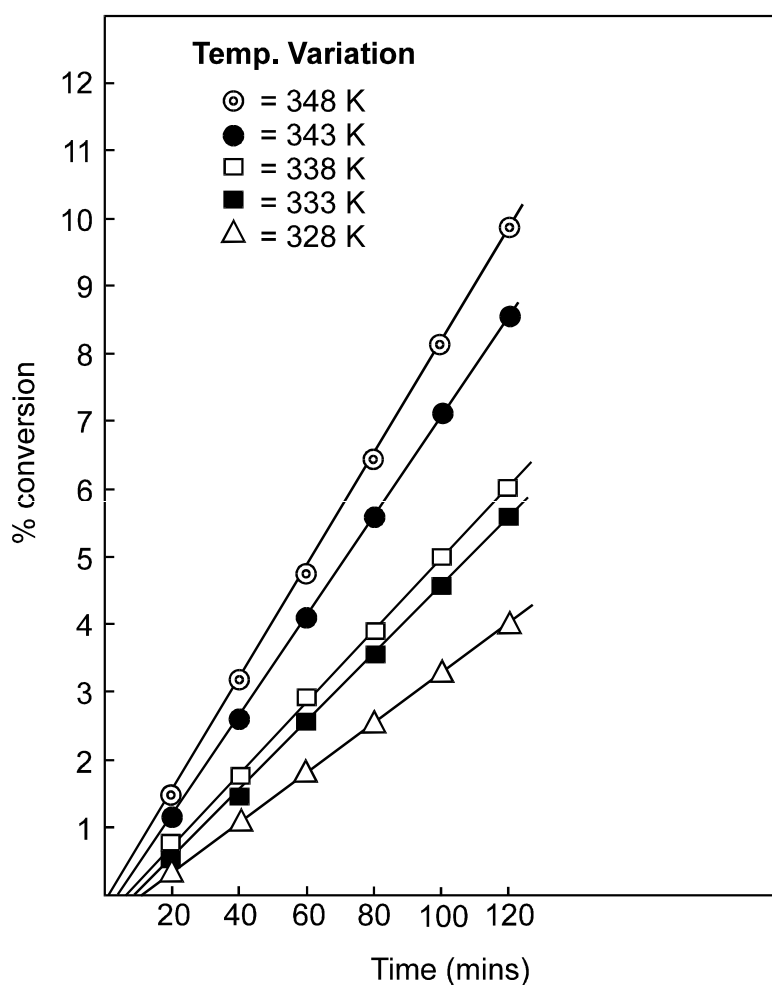*Polymerization time = 120 mins.*

Fig.7: Relationship between log R_p and log MMA.

  Fig.8:   Percentage conversion versus time plot for polymerization of methyl methacrylate.
[N-I.C.T.C.] = 52.49 x 10^{-6} mol l^{-1}
[AIBN] = 2.43 x 10^{-2} mol l^{-1}
[MMA] = 3.13 mol l^{-1}
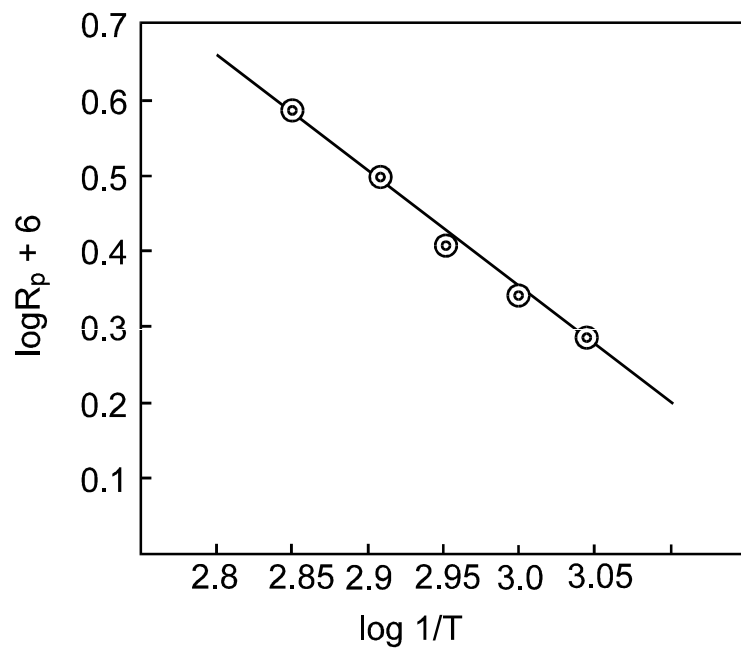*Polymerization time = 120 mins.*

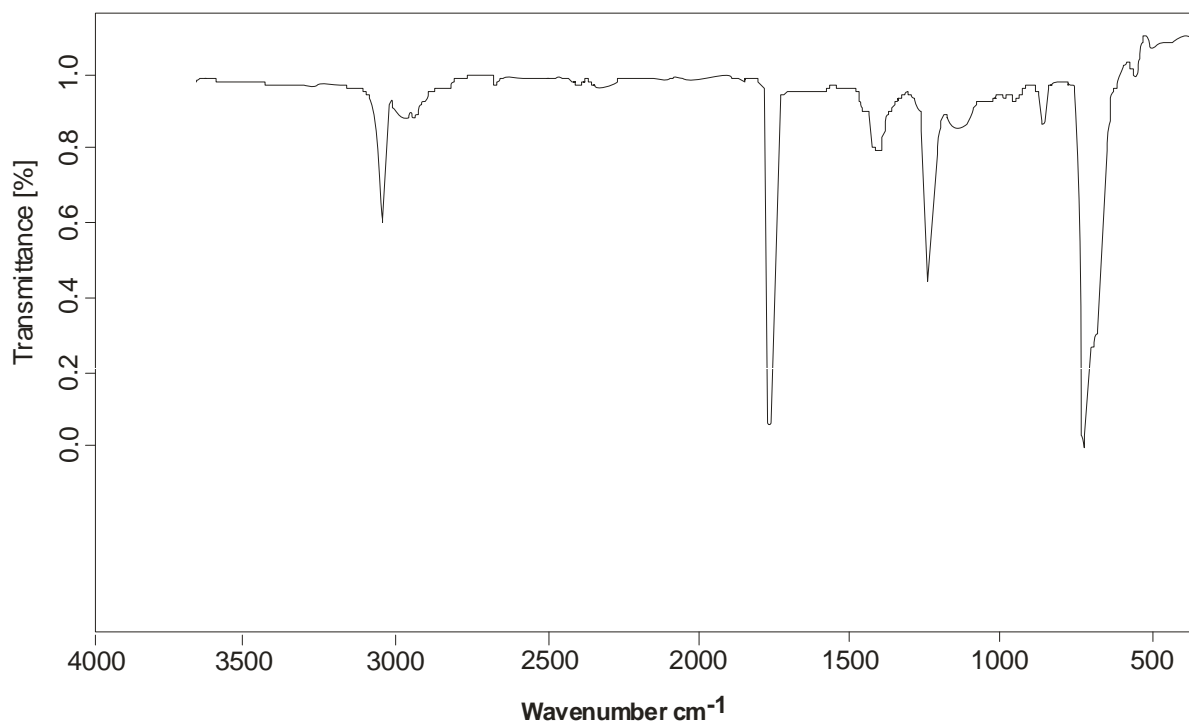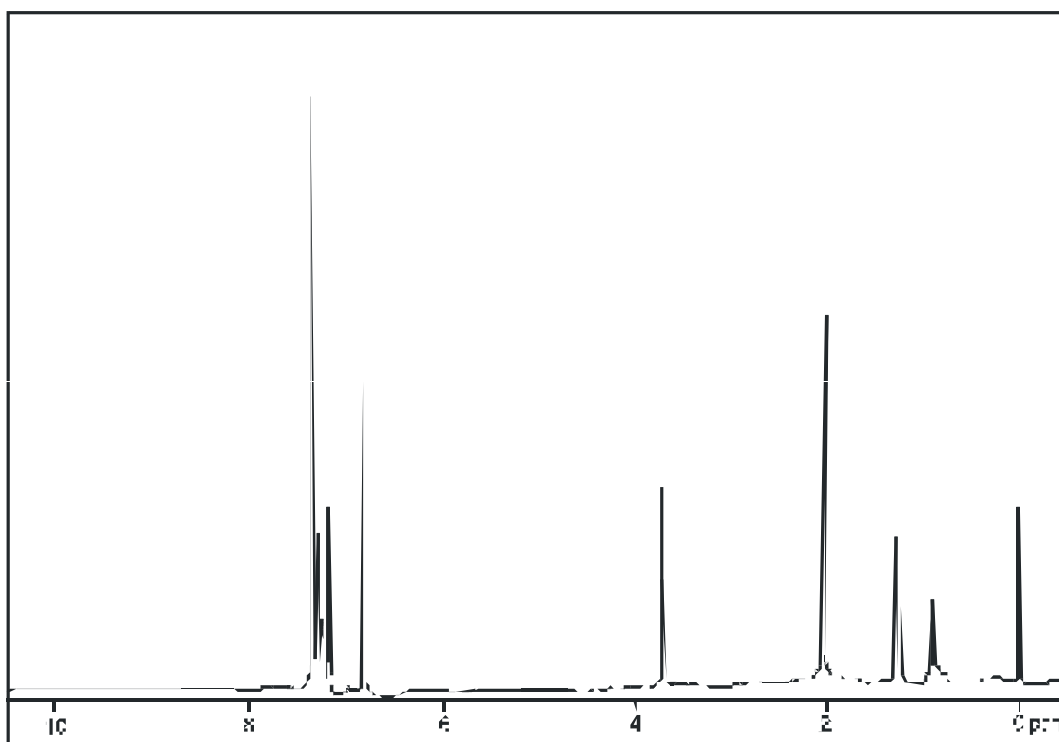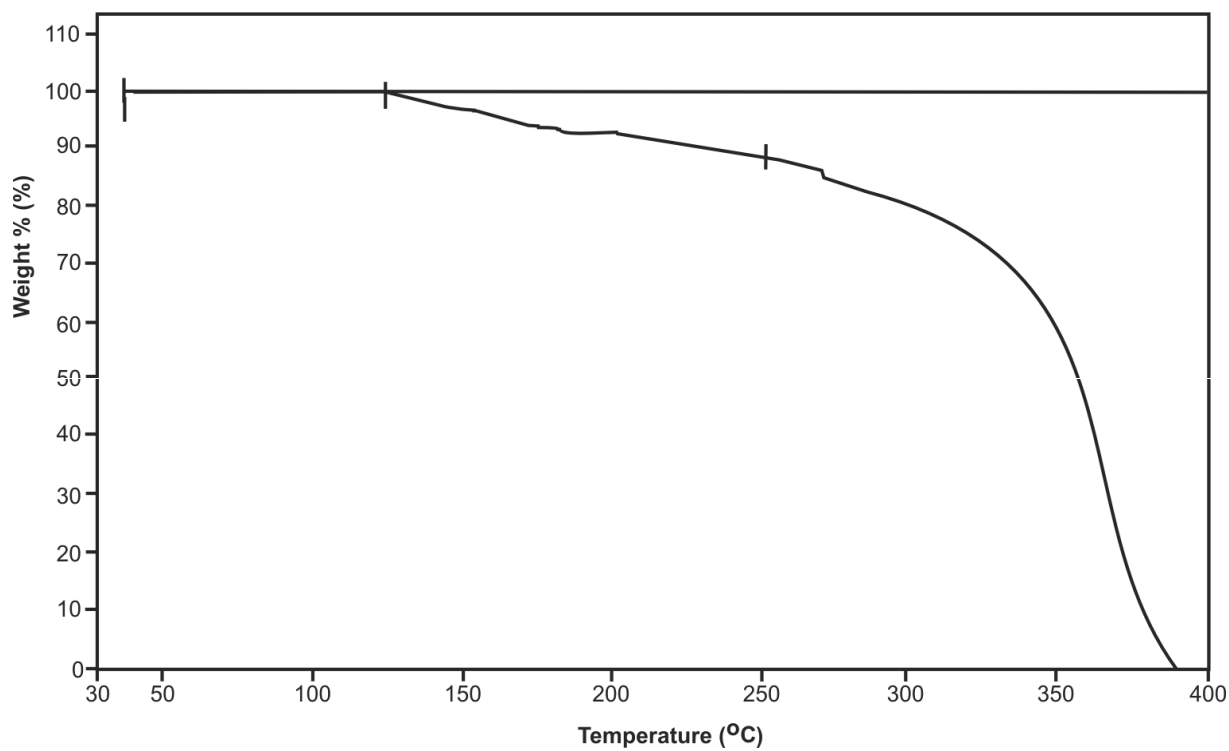**Fig.9:   Relationship between log R_p and log 1/T.**

Fig.10: FTIR spectrum of polyMMA (Run no. 3).

Fig.11: [1]**H-NMR spectrum of polyMMA (Run no. 3).**
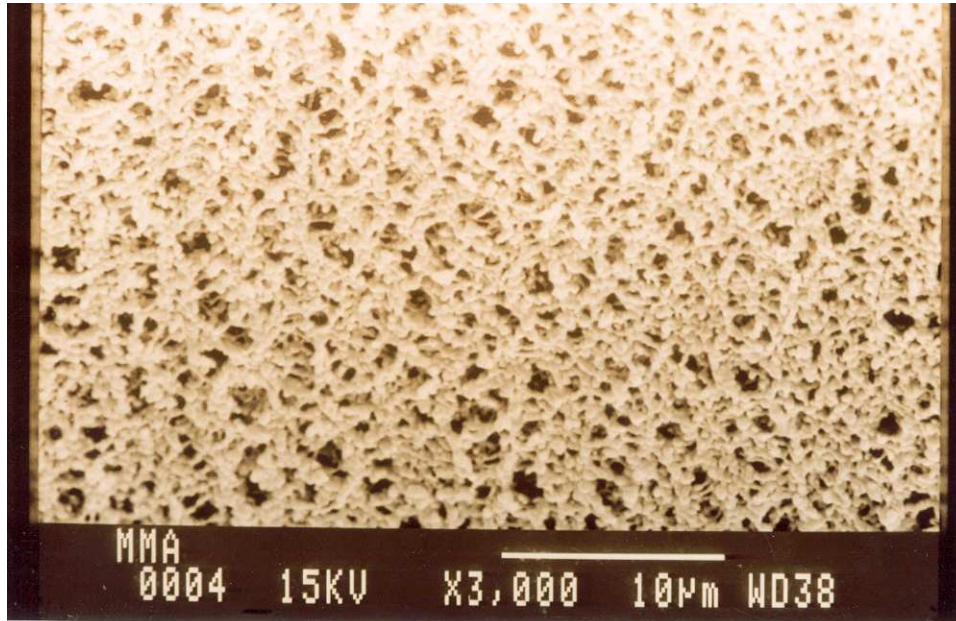

Fig.12: TGA curve of polyMMA (Run no. 3).

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Fig.13: SEM photograph of polyMMA run no. 3 at magnification x 3000.

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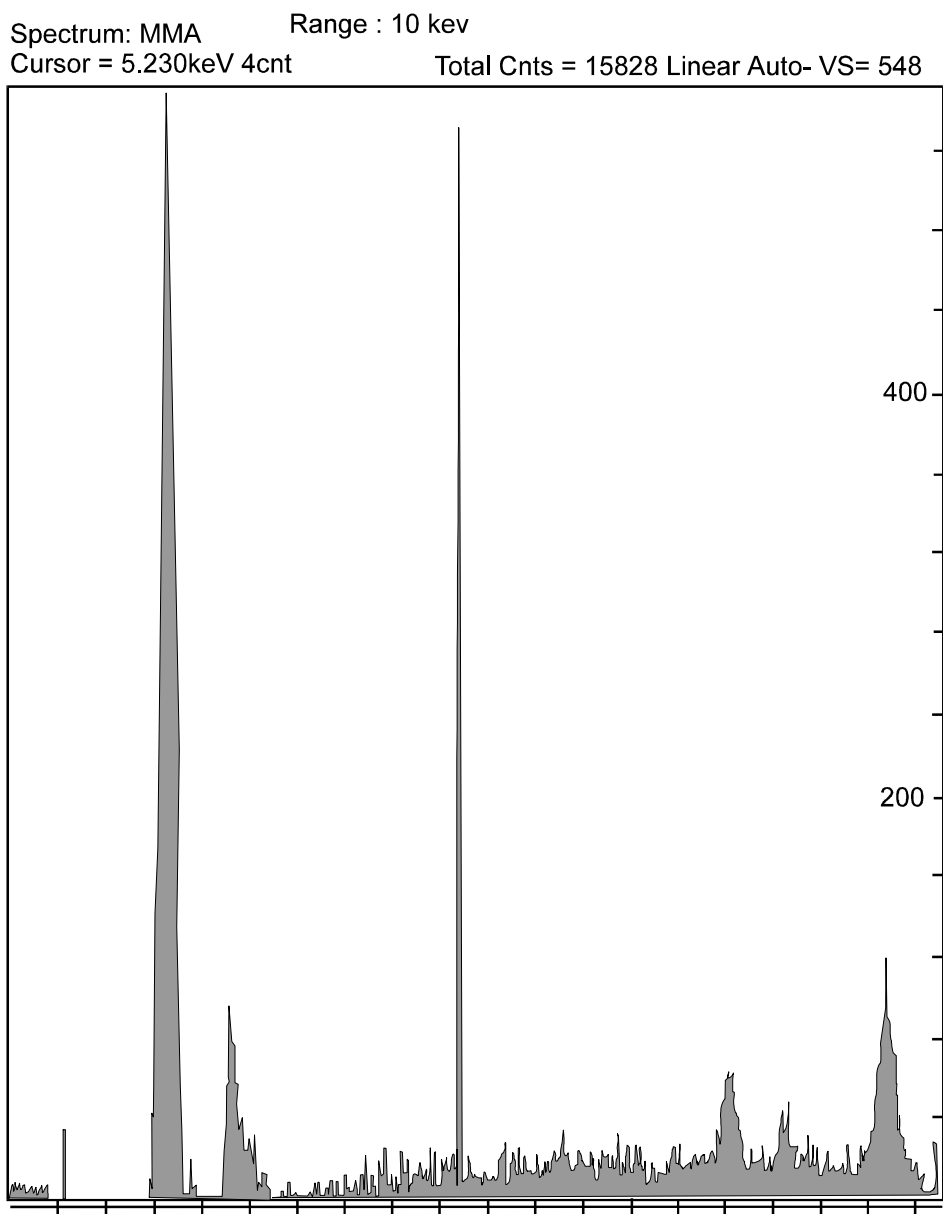

Fig.14:   SEM report of run no. 3.

Effect of AIBN:
The effect AIBN on rate of polymerization (R_p) is studied by varying its concentration from 1.21 x 10^{-2} to 3.65 x 10^{-2} mol l^{-1} keeping N-I.C.T.C, MMA and temperature constant at 52.49 x 10^{-6} mol l^{-1}, 3.13 moles and 65^0C respectively shown in Table-1 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 is 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 of AIBN.

$$R_p \; \alpha \; [AIBN]^{0.5}$$

Effect of [N-I.C.T.C.]:
The effect [N-I.C.T.C.] on rate of polymerization (R_p) is studied by varying [N-I.C.T.C.] from 26.24 x 10^{-6} mol l^{-1} to 78.74 x 10^{-6} mol l^{-1} (Fig.3) keeping the AIBN and MMA constant at 2.43 x

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10^{-2} mol l^{-1} and 3.13 moles respectively Table-IV.3.2. The order of reaction with respect to N-I.C.T.C. calculated from the slope of the plot 1/log R_p vs log [N-I.C.T.C.] is 0.8 (Fig.4). The plot obtained is linear. The exponent value obtained is fairly higher than 0.50 expected for a simple radical polymerization of mutual bimolecular termination[19]. It is observed that as the concentration of [N-I.C.T.C.] increases the percentage conversion and the rate of polymerization decrease. Further, the induction period is 4-16 mins. This indicates that the [N-I.C.T.C.] acts as a chain transfer agent. The average molecular weight (M_v) of the polymer also decreases gradually as the concentration [N–I.C.T.C.] increases. k_p^2/k_t calculated from the plot between $1/M_v$ against $R_p/[M]^2$ (Fig.5), is 1.12 x 10^{-2} mol l^{-1} s^{-1}.

Effect of MMA:
The effect of [MMA] on the rate of polymerization Table-3 has been studied by varying [MMA] from 1.88 to 4.38 mol l^{-1} keeping [AIBN] and [N-I.C.T.C.] constant at 2.43 x 10^{-2} mol l^{-1} and 52.49 x 10^{-6} mol l^{-1} (Fig.6), respectively. It is observed that with the increase in concentration of MMA the percentage conversion and the rate of polymerization increases. The induction period is 2 to 14 minutes. The average molecular weight also increases with the increase in concentration of methyl methacrylate. The plot between log R_p vs log [MMA] is unity (Fig.7).

$$R_p \, \alpha \, [MMA]^1$$

Effect of Temperature:
The polymerization runs were also carried out from 55°, 60°, 65°, 70° and 75°C to evaluate the energy of activation because no polymerization occurred below 55°C (Fig.8). The energy of activation calculated from the Arrhenius plot is 32.37 kJ (Fig.9).

Characterization of polymers:
The FTIR spectrum[20] of the polymer (Fig.10) shows bands at 3010 cm^{-1} for phenyl group of the complex. The ester stretching was observed at 1735 cm^{-1}. The C-H deformation band was observed in the region 1325–1450 cm^{-1} and C-O-C stretching band was observed in the region 1110–1270 cm^{-1}.

^{1}H-NMR spectrum[21,22] shows (Fig.11), the following peaks and confirms the structure of the polymer. We observed the methyl protons in the range of 0.8 to 1.00 ppm. The signals in 1.4 range can be assigned to the hydrogen in the polymer backbone. Signals at 3.9 δ ppm and 7.8 δ ppm correspond to the ester group (–OCH$_3$) of MMA and phenyl protons (– C$_6$H$_5$) respectively.

Thermogravimetric Analysis:
The TGA curve for the polymer (Fig.12) exhibits weight loss with temperature[23]. The stability of polymer is upto 250^0C. There are three distinct phases of weight loss.

1. The decomposition of the polymer started from 195°C.
2. The weight loss of about 11% was observed in the range 120-250°C. This may be attributed to the loss of absorbed water.
3. The weight loss of about 85% was in the range 250-390°C and appears to be due to extensive degradation of the polymer backbone chain.

Scanning Electron Microscopy:
The picture (Fig.13) shows single phase morphology. The SEM report (Fig.14) indicates the absence of iodine in the polymer. The absence of iodine was also confirmed by a qualitative test[24].

MECHANISM

The FTIR spectrum of the polymer shows no band in the region 500 cm^{-1} due to iodine confirming the absence of iodine in the polymer but confirming the band of phenyl group in the region 3000 cm^{-1} thus confirming the incorporation of phenyl group of naphthalene.

The above findings are also confirmed by the ^{1}H-NMR spectrum. Therefore the following mechanism has been proposed.
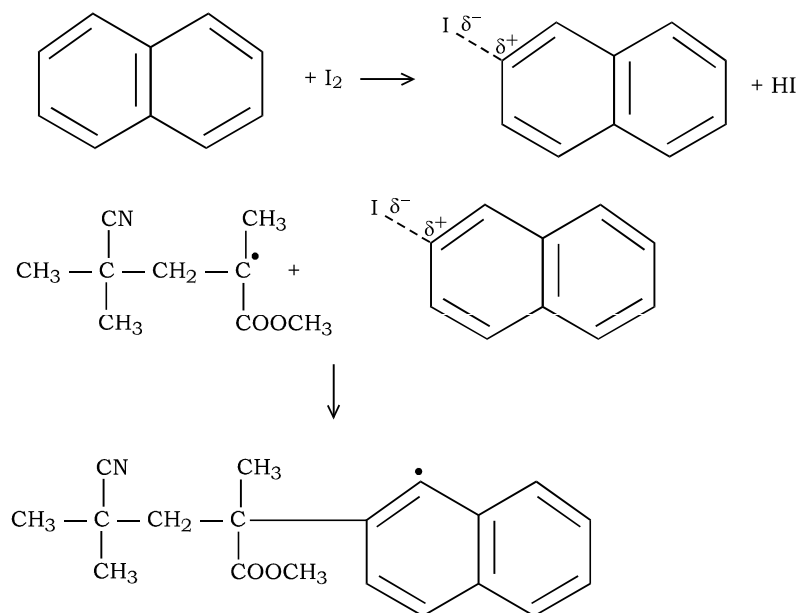
CONCLUSION

Polymethyl methacrylate has been synthesized via free radical solution polymerization using AIBN/N-I.C.T.C. observing naphthalene iodine charge transfer complex as a chain transfer agent. The molecular weight of the polymers are observed in the in the range 28560–65283. The mechanism was elucidated with the help of ^{1}H NMR and FTIR Spectrum. The thermal analysis showed the stability of polymer upto 250ºC.

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