



Free Radical Polymerization of Methyl Methacrylate Using Anthracene Iodine Charge Transfer Complex as Novel Chain Transfer Agent

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Free radical polymerization of methyl methacrylate initiated by α, α' -azobisisobutyronitrile and anthracene iodine charge transfer complex as novel chain transfer agent was studied in DMSO at 60 ± 0.1 °C for 2 h under oxygen free condition. The system followed ideal kinetics. The overall activation energy is 43.5 kJ/mol. The average molecular weight is in between 32608-62662. The FTIR spectra shows band at 3020 and 1725 cm^{-1} due to phenyl protons of anthracene charge transfer complex and ester stretching of methyl methacrylate, respectively. The ^1H NMR spectra confirms the methoxy protons at 3.7 δ ppm. Thermogravimetric analysis shows the stability of polymer upto 230 °C.

Key Words: Kinetics, Mechanism, Free radical polymerization, Chain transfer agent.

INTRODUCTION

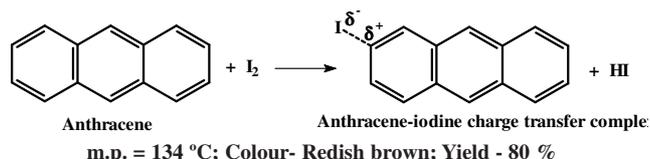
The literature survey reveals that the literature is almost devoid of radical polymerization of vinyl monomers using charge transfer complex as a chain transfer agent. The search reveals that few complexes have been reported as chain transfer agents in homo polymerization of methyl methacrylate¹, methyl acrylate², 2-vinyl pyridine³, styrene⁴ copolymerization^{5,6} and terpolymerization⁷. Hence it is worthwhile to study the application of anthracene iodine charge transfer complex in the domain of polymer science. The present articles report the synthesis of poly methyl methacrylate in dimethyl sulphoxide using AIBN as an initiator and anthracene-iodine charge transfer complex as a chain transfer agent.

Matsuzaki *et al.*⁸, reported polymerization of acrylate using free radical and γ -radiation process. Recently, Luo and Sen⁹ worked on rate enhancement in controlled radical polymerization of acrylates using recyclable heterogenous Lewis acid. Liu and Mishra¹⁰ studied atom transfer radical polymerization of methyl acrylate using 1-phenyl ethyl bromide or ethyl 2-bromopropionate as initiators. Srivastava *et al.*¹¹ have reported the photopolymerization of *n*-butyl methacrylate in solutions initiated by diphenyl ditelluride and the system followed non-ideal kinetics.

EXPERIMENTAL

Methyl methacrylate (Merck) were washed with 4 % alkali solution and distilled under reduced pressure. The solvent were purified as per standard procedures¹².

Preparation of anthracene iodine charge transfer complex [A-I.C.T.C.] was prepared by method reported in literature¹³. Iodine and anthracene were mixed in 1:1 molar ratio in the solid state in mortar and dissolved in ether which on evaporation the charge transfer complex was formed.



Polymerization procedure: A solution containing methyl methacrylate (MMA) with anthracene 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 2 h at 65 °C under an inert atmosphere of nitrogen. The polymer was precipitated with methanol and was dried to constant weight. Rate of polymerization was calculated by the method given in the literature¹⁴.

Viscosity average molecular weight (\bar{M}_v) of the polymer was determined in benzene at 30 ± 1 °C with an Ubbelohde viscometer with the values of Mark-Houwink constant¹⁵ using:

$$(\eta) = k[(\bar{M}_v)^\alpha \text{ where, } k = 5.2 \times 10^{-3} \text{ and } \alpha = 0.76].$$

Characterization: The polymers were characterized by FTIR, ^1H NMR and thermogravimetric analysis (TGA). FTIR was recorded with a Perkin-Elmer 59913 in dichloromethane.

^1H NMR spectra were recorded with Varian 100 HA JOEL LA 400 spectrometer using CDCl_3 as solvent and tetramethylsilane as internal reference. The thermogravimetric analysis runs were carried out using V 5.1 Dupont 2100 analyzer sample weight 10 mg and heating rate $10\text{ }^\circ\text{C}$ per min.

RESULTS AND DISCUSSION

No polymer was obtained when polymerized below $50\text{ }^\circ\text{C}$. The polymerization runs were associated with an induction period of about 2-16 min. The kinetic studies have been carried out by varying the concentration of initiator (AIBN), chain transfer agent (anthracene iodine charge transfer complex), monomer (methyl methacrylate) and temperature. The results are summarized in Tables 1 to 3 and Figs. 1 to 3.

Effect of [AIBN]: The effect of concentration of [AIBN] on the rate of polymerization was studied by varying the concentration from $1.21 \times 10^{-2}\text{ mol L}^{-1}$ to $3.65 \times 10^{-2}\text{ mol L}^{-1}$ and keeping the [A-I.C.T.C.], [MMA] constant at $43.85 \times 10^{-6}\text{ mol L}^{-1}$, 2.50 mol L^{-1} respectively (Fig. 1 and Table-1). The initiator exponent value, calculated from the slope of the plot of $\log R_p$ versus $\log [\text{AIBN}]$ was found to be 0.5 (Fig. 2). The percentage conversion also increases with the increase in concentration of AIBN. The average molecular weight also increases with increase in the concentration of AIBN. The induction period of 2-14 min.

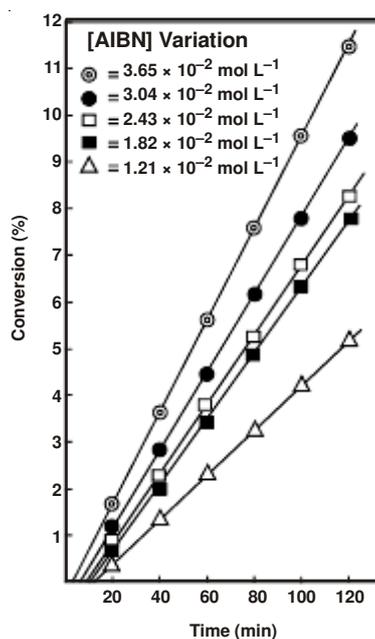


Fig. 1. Percentage conversion versus time plots for polymerization of methyl methacrylate; [A-I.C.T.C.] = $43.85 \times 10^{-6}\text{ mol L}^{-1}$; [MMA] = 2.50 mol L^{-1} ; polymerization temp. = $60 \pm 0.1\text{ }^\circ\text{C}$; polymerization time = 2 h

Effect of concentration of anthracene iodine charge transfer complex: The effect of concentration of [A-I.C.T.C.] on the rate polymerization was studied by varying the concentration from 21.92×10^{-6} to $65.78 \times 10^{-6}\text{ mol L}^{-1}$ keeping the [AIBN] and [MMA] constant at $2.43 \times 10^{-2}\text{ mol L}^{-1}$ and 2.50 mol L^{-1} respectively (Fig. 3 and Table-2). It was observed that with the increase in concentration of [A-I.C.T.C.] the percentage conversion as well as the rate of polymerization decreases from

3.33×10^{-6} to 2.08×10^{-6} . The induction period is 6-18 min. This indicates that anthracene iodine charge transfer complex acts as a chain transfer agent in the polymerization reaction. This effect may be attributed to the decrease in rate initiation and rate of propagation and increase in the rate of termination¹⁶. The plot between $1/\log R_p$ and $\log [\text{A-I.C.T.C.}]$ (Fig. 4) is linear. The exponent value is 0.6. The average molecular weight \bar{M}_v decrease with the increases in concentration of anthracene iodine charge transfer complex.

TABLE-1
EFFECT OF AIBN ON THE RATE OF POLYMERIZATION OF METHYL METHACRYLATE

Runs No.	AIBN $\times 10^{-2}$	Conversion (%)	$R_p \times 10^{-6}$	\bar{M}_v
1.	1.21	5.1	1.82	69,929
2.	1.82	6.7	2.08	81,174
3.	2.43	8.3	2.42	88,888
4.	3.04	8.6	2.91	1,00,764
5.	3.65	11.3	3.64	1,08,875

[MMA] = 2.50 mol L^{-1} ; [A-I.C.T.C.] = $43.85 \times 10^{-6}\text{ mol L}^{-1}$;
Polymerization time = 2 h; polymerization temp. = $60 \pm 0.1\text{ }^\circ\text{C}$

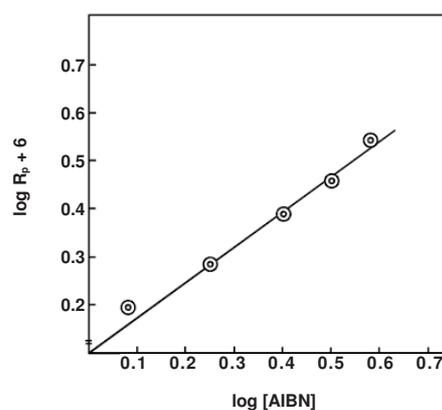


Fig. 2. Relationship between $\log R_p$ versus $\log [\text{AIBN}]$

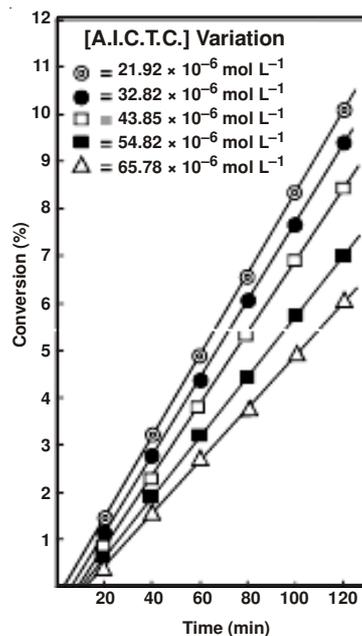


Fig. 3. Percentage conversion versus time plot for polymerization of methyl methacrylate; [AIBN] = $2.43 \times 10^{-2}\text{ mol L}^{-1}$; [MMA] = 2.50 mol L^{-1} ; Polymerization temp. = $60 \pm 0.1\text{ }^\circ\text{C}$; Polymerization time = 2 h

TABLE-2
EFFECT OF ANTHRACENE IODINE CHARGE TRANSFER
COMPLEX ON THE RATE OF POLYMERIZATION OF
METHYL METHACRYLATE

Runs No.	A-I. C.T.C. $\times 10^{-6}$	Conversion (%)	$R_p \times 10^{-6}$	\bar{M}_v
1.	21.92	10.0	3.33	62662
2.	32.82	9.4	2.75	52136
3.	43.85	8.3	2.58	42099
4.	54.62	6.9	2.50	38871
5.	65.78	6.1	2.08	32608

[MMA] = 2.50 mol L⁻¹; [AIBN] = 2.43 $\times 10^{-2}$ mol L⁻¹; Polymerization time = 2 h; polymerization temp. = 60 \pm 0.1 $^{\circ}$ C

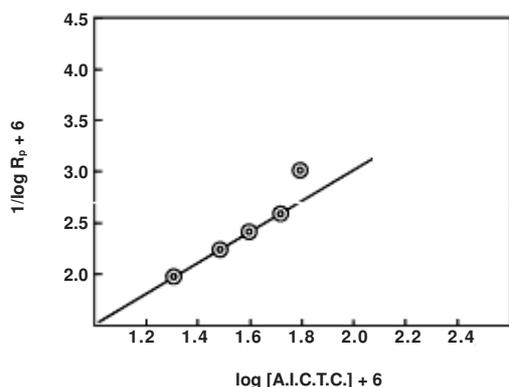


Fig. 4. Relationship between $1/\log R_p$ versus $\log [A-I.C.T.C.]$

Effect of concentration of methyl methacrylate [MMA]:

The effect of methyl methacrylate concentration on the rate of solution polymerization (R_p) has been studied by varying the MMA concentration from 1.25 to 3.76 mol L⁻¹, keeping the [AIBN] and [A-I.C.T.C.] constant at 2.43 $\times 10^{-2}$ and 43.85 $\times 10^{-6}$ mol L⁻¹ in DMSO respectively (Fig. 5). It is observed from Table-3 that R_p is a direct function of methyl methacrylate concentration. The exponent value, calculated from the slope of $\log R_p$ versus $\log [MMA]$ is unity (Fig. 6) *i.e.*, $R_p \propto [MMA]^1$

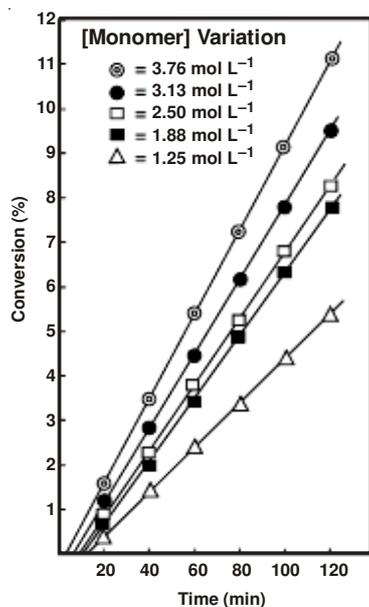


Fig. 5. Percentage conversion versus time plot for polymerization of methyl methacrylate; [A-I.C.T.C.] = 43.85 $\times 10^{-6}$ mol L⁻¹; [AIBN] = 2.43 $\times 10^{-2}$ mol L⁻¹; [MMA] = 2.50 mol L⁻¹; Polymerization temp. = 60 \pm 0.1 $^{\circ}$ C; Polymerization time = 2 h

TABLE-3
EFFECT OF METHYL METHACRYLATE ON
THE RATE OF POLYMERIZATION

Runs No.	MMA mol L ⁻¹	Conversion (%)	$R_p \times 10^{-6}$	\bar{M}_v
1.	1.25	5.6	1.04	29574
2.	1.88	7.9	1.88	35696
3.	2.50	8.3	2.58	42099
4.	3.13	9.5	3.91	59102
5.	3.76	10.9	5.64	66272

[AIBN] = 2.43 $\times 10^{-2}$ mol L⁻¹; [A-I.C.T.C.] = 43.85 $\times 10^{-6}$ mol L⁻¹
Polymerization time = 2 h; polymerization temp. = 60 \pm 0.1 $^{\circ}$ C

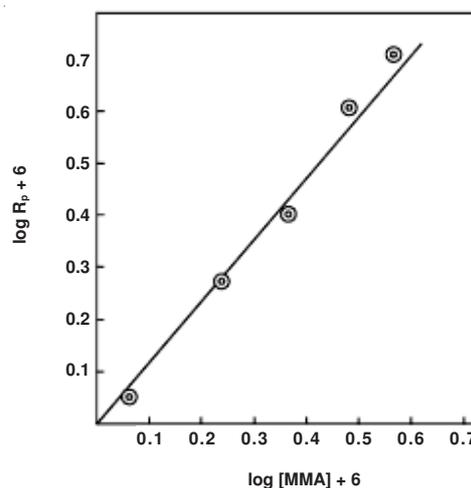


Fig. 6. Relationship between $\log R_p$ versus $\log [MMA]$

Effect of temperature: Polymerization runs were carried out at 50, 55, 60, 65 and 70 $^{\circ}$ C (Fig. 7). The rate of polymerization increases with increase in temperature. The value of activation energy was computed from the Arrhenius plot (Fig. 8) is 43.5 kJmol L⁻¹, which supports a radical mode of polymerization.

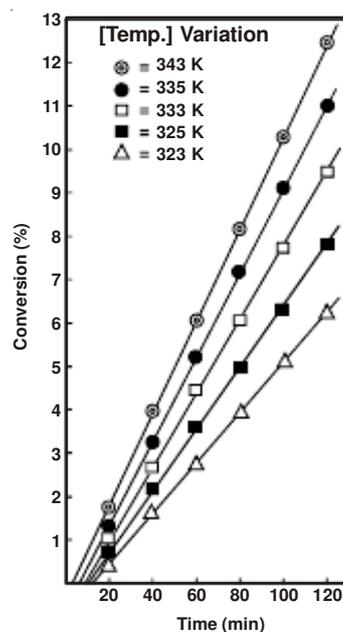
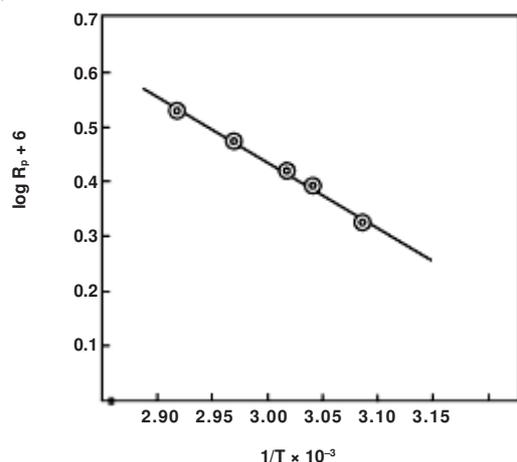


Fig. 7. Percentage conversion versus time plot for polymerization of methyl methacrylate; [A-I.C.T.C.] = 43.85 $\times 10^{-6}$ mol L⁻¹; [AIBN] = 2.43 $\times 10^{-2}$ mol L⁻¹; [MMA] = 2.50 mol L⁻¹; Polymerization temp. = 60 \pm 0.1 $^{\circ}$ C; Polymerization time = 2 h

Fig. 8. Relationship between $\log R_p$ versus $\log 1/T$

Characterization of polymers

Fourier transform infrared spectroscopy: The polymer obtained was characterized by FTIR¹⁷. The spectra shows the band (Fig. 9) of C-H stretching vibration of methyl and methylene group at 2950 and 3000 cm^{-1} respectively. The $>C=O$ stretching range shows ester carbonyl band at 1730 cm^{-1} . The C-H deformation range shows bands in the region of 1450-1380 cm^{-1} .

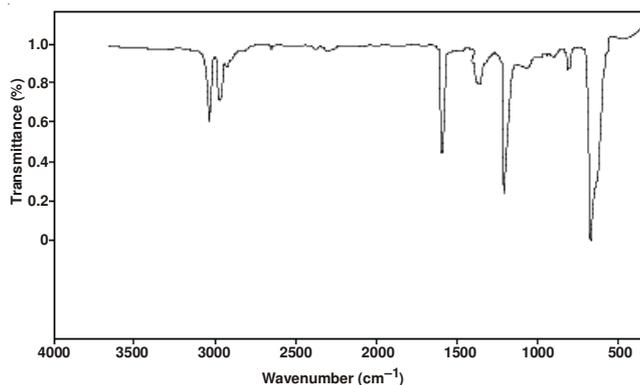


Fig. 9. FTIR spectrum of poly(methyl methacrylate) (Run No. 3)

¹H NMR: The ¹H NMR spectra of the polymer shows (Fig. 10) the following peaks^{18,19} and confirm the structure of the polymer. The methyl proton signals are assigned in the range of 0.8 to 1.1 δ ppm. The signal in the range 1.3 can be assigned to the hydrogen in the polymer backbone. Signals at 3.7 δ ppm, a 7.6 δ ppm correspond to the ester group ($-\text{OCH}_3$) of methyl methacrylate and phenyl protons of the complex, respectively.

Thermogravimetric analysis: Thermal degradation of polymers involves a large number of different lengths of polymer chains both of stable molecules and free radicals. Their interaction makes the degradation of polymers very complex. The thermogravimetric analysis curve (Fig. 11) exhibits weight loss with temperature^{20,21}. The decomposition of the polymer started from 130 $^{\circ}\text{C}$. The thermal behaviour data are as follows: (a) Onset of major weight loss 260 $^{\circ}\text{C}$, completion of major weight loss 400 $^{\circ}\text{C}$; (b) Total weight loss in the range 260-400 $^{\circ}\text{C}$; (c) Almost total volatilization of polymer occurred at 400 $^{\circ}\text{C}$.

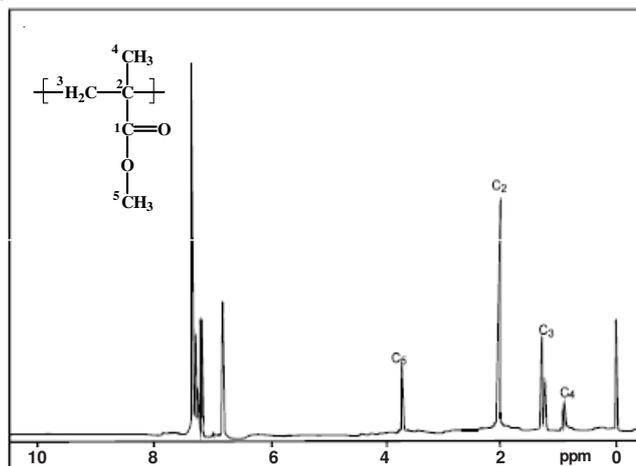
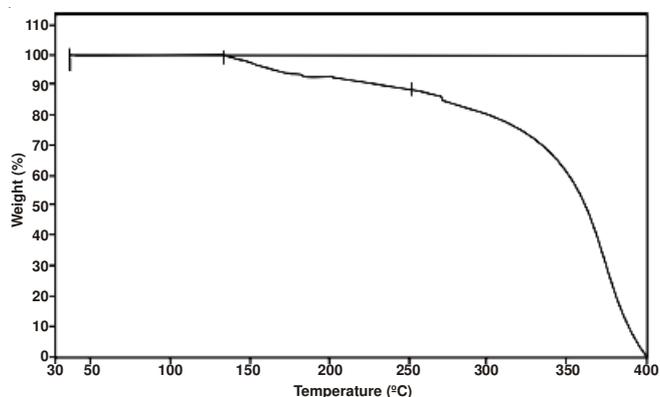
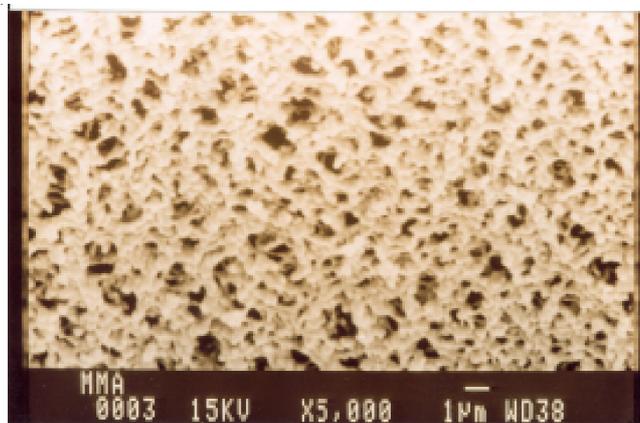
Fig. 10. ¹H NMR spectrum of poly(methyl methacrylate)

Fig. 11. Thermo gravimetric analysis curve of poly(methyl methacrylate)

The thermogravimetric analysis data show a weight loss of 15 % as the temperature increases to 260 $^{\circ}\text{C}$, which is attributed to the loss of absorbed water^{22,23}. The range of temperature above 260 $^{\circ}\text{C}$ are the regions of major weight loss and appear to be due to dehydration and to the extensive degradation of the polymer backbone chain.

Scanning electron microscopy: The picture (Fig. 12) shows single phase morphology. The SEM report (Fig. 13) indicates the absence of iodine in the polymer. The absence of iodine was also confirmed by a qualitative test²⁴.

Fig. 12. Scanning electron microscopy photograph of polyMMA run no. 3 at magnification $\times 5000$

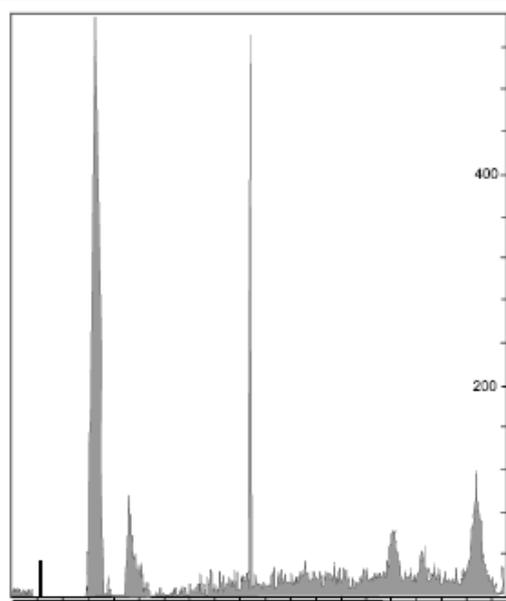
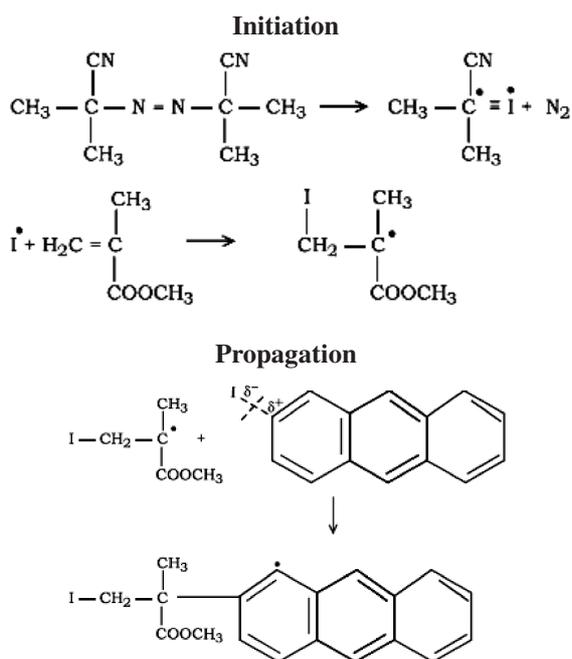


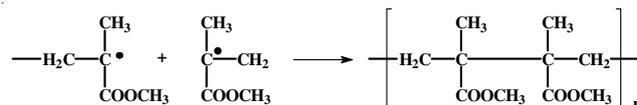
Fig. 13. Scanning electron microscopy report of run no. 3

Mechanism: The quantitative test of iodine in the polymer showed its absence. The FTIR spectrum also did not show bands at 500 cm^{-1} in the region due to iodine.

A comparison of the FTIR of the polymer with that prepared in the absence of charge transfer complex shows that the bands in the regions of 3000 cm^{-1} due to phenyl group is absent. The polymer prepared in the presence of charge transfer complex shows the bands in the region of 3000 cm^{-1} . Further, the peak area due to phenyl protons in $^1\text{H NMR}$ spectrum is also observed when prepared in the presence of charge transfer complex. From these observations we can conclude that anthracene has been incorporated in the polymer therefore the following mechanism has been proposed.



Termination



Conclusion

Poly(methyl methacrylate) has been synthesized *via* free radical solution polymerization by using AIBN/A-I.C.T.C. as initiator and chain transfer agent respectively. The polymer is thermally stable upto 260°C . The system follows ideal kinetics. The energy of activation is evaluated as 43.5 kJ mol^{-1} . The \bar{M}_v is in the range of 32608-62662.

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