

STUDY ON THERMAL DEGRADATION BEHAVIOUR OF POLY (N-(META-CHLOROPHENYL) MALEIMIDE) AND ITS COPOLYMER OF METHYL METHACRYLATE

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Abstract:

Homopolymerization and copolymerization of (N-(*meta*-chlorophenyl) maleimide) monomer (N-MCPMI) was carried out at 70°C in DMF using AIBN as a free radical initiator for 16h and 24h, respectively. The average molecular weight of homopolymer (H-MCPMI) and copolymer (C-MCPMI) with methyl methacrylate (MMA) by GPC were found to be 8590 g/mol and 13745 g/mol with PDI 1.17 & 1.19, respectively. Very good control of PDI by conventional free radical polymerization was achieved. The result of thermal analysis reveals that H-MCPMI and C-MCPMI followed two-step degradation and multistep degradation process, respectively. The activation energy (ΔE^*), the entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and Gibbs free energy (ΔG^*) increases gradually with increase in the heating rate for both during thermal degradation study.

Keywords: N-phenylmaleimide; methyl methacrylate; thermal degradation; kinetics.

Introduction

The conventional free radical polymerization (FRP) process has been used to prepare about fifty percent vinyl polymers which is a robust and clean methodology. One of the major advantages of FRP is the robustness to vinyl monomers and fewer impurities in reaction media as compared to other methodologies. The FRP can be carried out in the eco-friendly environment, which reduces the production cost. Further uniqueness of this process is, it can be applied to a wide range of vinyl monomers, and also extended to thermally stable polymers. Amongst them, polymers of aromatic polyimides group were considered to have thermally stable [1-2], heat and chemical resistant and good electrical properties [3], and have other applications [4-5]. Other processes like condensation polymerization, ATRP, RAFT have several disadvantages like difficulty insolubility, infusibility, which can be easily modified by applying FRP process on functionalized alkene containing monomers [6]. FRP brings toughness/hardness in the polymers [7-10] and it provides thermoxidative property in aromatic polyimides such as well as a chemical insulator.

Therefore, it was thought to be worthwhile to synthesize the polymer of chlorosubstituted of N-phenylmaleimide monomer using AIBN as a free radical

initiator. In spite of other applications of these polymers, they can be environmentally resistant due to the presence of the aromatic ring in the repeating unit and can be modified further into polymeric self-assemblies. To achieve new properties in maleimide polymer one has to choose thermally stable homopolymer or copolymer. Recently, few studies on the thermal degradation behaviour of polymers [17-21] were carried out but this procedure does not apply to construct the self-assembly having thermal stability. But in our opinion, the thermal analysis could help to choose the thermally stable self-assemblies.

In view of the above, a study of the thermal degradation of a homopolymer of maleimide and its copolymer with MMA was attempted. Herein, in the present study, the kinetics of thermal degradation behavior of H-MCPMI and C-MCPMI have been studied. This outcome of this study could be applied to choose the thermally stable polymeric self-assemblies with improving the product applicability.

Results and discussion

Thermal analysis and Evaluation of Thermodynamic Parameters:

The thermodynamic activation parameters of decomposition processes for polymers such as activation energy (E^*), the entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and Gibbs free energy (ΔG^*), were calculated with the help of DTA and TGA curves for polymers by using Kissinger method[22-25].

The kinetic data processing was performed by applying the Kissinger method which explains the influence of the heating speed and the dependence of activation energy on conversion degree[25]. The method proposed by Kissinger is based on functional dependence of the heating rate (β) and variation of TG and DTA peak temperature (T_{max}) is in proportion to the maximum rate of reaction and equation:

$$\log \frac{\beta}{T_{max}^2} = \log \frac{AR}{E_a} - \frac{E_a}{2.302 \times RT_{max}} \quad \text{eq(1)}$$

Plotting the left side of this equation against $1/T_{max}$ should give a straight line of the slope $-E_a/(2.303 \times R)$ and intercept $\log AR/E_a$ [25]. By applying this method several thermal kinetic analysis of the same substance at different heating rate was performed, while, other non-isothermal parameters[25] are calculated using the following equation:

$$E^* = -\text{slope} (2.303 R); \Delta S^* = 2.303[\log(Ah/kT)]R; \Delta H^* = E^* - RT;$$

$$\Delta G^* = \Delta H^* - T\Delta S^*;$$

where,

T_{\max} is the peak temperature,

H = Planck's constant (6.626×10^{-36} J-s),

k = Boltzmann constant = 1.38×10^{-26} J K⁻¹ mol⁻¹,

R = Gas constant = 8.314, JK⁻¹ mol

A = Arrhenius factor

Thermal degradation of homopolymer and its Kinetics

About 2.1 % mass loss for **H-MCPMI** was observed up to 160°C at a heating rate of **5°C/min**. The degradation was a single step process; majorly it was a gradual loss of fragments from the polymeric chain (Figure S-4a). Almost 50% polymer was degraded up to 307°C and 69% mass loss was observed up to 435°C, while up to 600°C almost 90% mass loss was observed. About 6.3 % char yield was obtained at 640°C. DTA curve clearly shows an endothermic peak at 157°C (Figure S-1a).

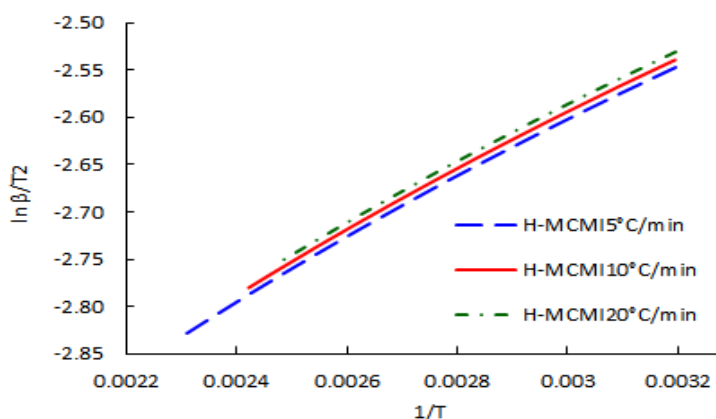


Fig. 1A The kinetics of first stage degradation of H-MCPMI at a different heating rate

The activation energy value shows the decomposition proceeds with an exothermic process and the activation energy was -6102 Jmol⁻¹ at a heating rate of **5°C/min** in the range of 40-160°C of decomposition temperature (fig.1 A). This value decreases to -9198 KJmol⁻¹ as temperature increases gradually in the range of 160- 440°C. The entropy of transition state was found negative in both steps. But entropy between 40-160°C and 160-440°C was -1.4017 Jmol⁻¹ and -1.3628 Jmol⁻¹, respectively. The entropy of transition state between 160-440°C was found to be increased (fig 1B). The ΔH^* values were found to be -9785 & -15126 Jmol⁻¹ between 40-160°C and 160-440°C, respectively. The decrease in enthalpy value may be due to weak bond breaking between 160-440

$^{\circ}\text{C}$ than $40\text{-}160^{\circ}\text{C}$. The ΔG^* values were found to be -9164 and -14155 Jmol^{-1} for $40\text{-}160^{\circ}\text{C}$ and $160\text{-}440^{\circ}\text{C}$, respectively.

About 3.3 % mass loss for **H-MCPMI** was observed 135°C at a heating rate 10°C/min . At this heating rate still it is a single step degradation process and almost 50% mass loss was observed up to 273°C and 68 % mass loss was observed upto 415°C , while up to 610°C about 90% mass loss was observed from the polymer (Figure S-1b). The whole degradation process shows again the gradual loss of mass from the polymer. 5.3 % char yield was obtained at 640°C . At this heating rate, the loss of mass was observed more than the mass loss occurred on heating rate 5°C/min , degradation process shows again the gradual loss of mass from a polymer, which clearly indicates, on increasing the heating rate the loss of mass from the polymeric substance increases rapidly. In this case, the DTA curve clearly shows an endothermic peak at 168°C (Figure S-4b).

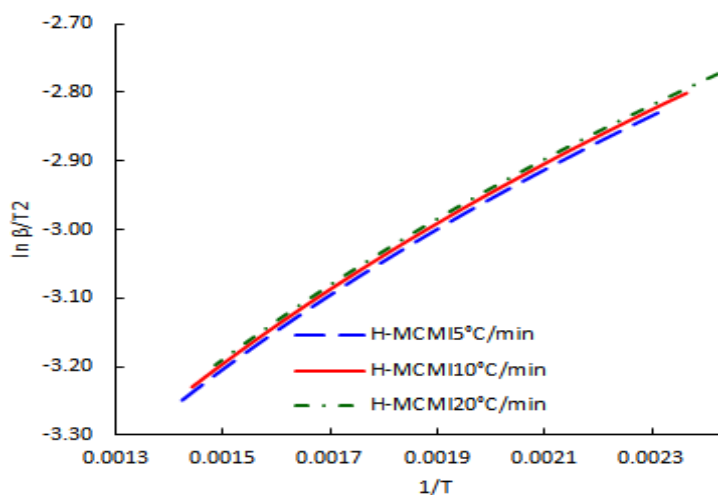


Fig. 1B The kinetics of second stage degradation of H-MCPMI at a different heating rate

The activation energy value shows the decomposition proceeds with an exothermic process and activation energy was -5964 KJmol^{-1} at a heating rate of 10°C/min in the range of $40\text{-}140^{\circ}\text{C}$ of decomposition temperature this value decreases to -8965 KJmol^{-1} as temperature increases gradually in the range of $140\text{-}430^{\circ}\text{C}$ (fig.1A). The entropy of transition state was found negative in both steps. But entropy between $40\text{-}140^{\circ}\text{C}$ and $140\text{-}430^{\circ}\text{C}$ was $-1.4068 \text{ KJmol}^{-1}$ and $-1.3875 \text{ KJmol}^{-1}$, respectively. The entropy of transition state between $140\text{-}430^{\circ}\text{C}$ was found to be increased. The ΔH^* values were found to be -9398 & $-14726 \text{ KJmol}^{-1}$ between $40\text{-}140^{\circ}\text{C}$ and $140\text{-}430^{\circ}\text{C}$, respectively. The decrease in enthalpy value may be due to weak bond breaking between $140\text{-}430^{\circ}\text{C}$ (fig.2B)

than 40-140°C. The ΔG^* values were found to be -8817 and -13780 KJmol^{-1} for 40-140°C and 140-430°C, respectively.

About 4.6 % mass loss for **H-MCPMI** was observed up to 132°C at a heating rate of **20°C/min** and almost 50% polymer was degraded upto 277°C and 68 % mass loss was observed up to 400°C, while up to 612°C about 90 % mass loss was observed (figure S-1c). The whole degradation process shows again a single step and gradual mass loss of polymeric chain arisen. 0.3 % char yield was obtained at 640°C. The change in heating rate clearly indicated the mass loss occurred faster at a higher heating rate than slow heating rate, but the amount of char yield is more in higher heating rate than slower heating rate. In this case, the DTA curve clearly shows an endothermic peak at 174°C with more area under endothermic peak than above two heating rates (figure S-1c).

The activation energy value shows the decomposition starts with an exothermic process and the activation energy was -5893 Jmol^{-1} at a heating rate of **20 °C/min** in the range of 40-130°C of decomposition temperature this value decreases as temperature increases gradually in next step to -8729 Jmol^{-1} between 130- 410°C. The entropy of transition state was found negative in both steps. But entropy between 40-130°C and 130-410°C was -0.5657 Jmol^{-1} and -1.3962 Jmol^{-1} , respectively. The entropy of transition state between 130-410°C was found to be decreased, which is just opposite to slow heating rate process. The ΔH^* values were found to be -6974 & -14407 Jmol^{-1} between 40-130°C and 130-410°C, respectively. The decrease in enthalpy value may be due to weak bond breaking between 130-410 °C than 40-130°C. The ΔG^* values were found to be -6900 and -13454 Jmol^{-1} for 40-130 and 130-410°C, respectively.

Thus, the decrease in E^* , ΔH^* , ΔG^* (all non-isothermal parameters) and increase of ΔS^* at 5 and 10 °C /min heating, while decreases at 20°C/min between 130-600°C than 40-130°C, which suggest that the degradation between 130-600°C was more endothermic and weak bond breaking taken place as compared to the degradation between 40-140°C.

Thermal degradation of Copolymer and its Kinetics

About 1.5 % mass loss for C-MCPMI was observed up to 160°C at a heating rate of **5°C/min**. and almost 50% copolymer was degraded up to 330°C, and up to 520°C about 90 % mass loss was observed (figure S-2a). The thermal curve of the copolymer (C-MCPMI) shows a four-step degradation process with and gradual mass loss from the copolymer. The initial degradation was between 256-318°C with a maximum mass loss at 288°C, and stage degradation was between 339-423°C with a maximum mass loss at 402°C. About 3 % char yield was obtained at 500°C in case of the copolymer (C-MCPMI) (Figure S-2b).

The activation energy value shows the decomposition proceeds with an exothermic process and activation energy was -6102 Jmol^{-1} at a heating rate of 5°C/min at the range of $40\text{-}170^\circ\text{C}$ of decomposition temperature this value decreases as temperature increases gradually in every step to -12974 Jmol^{-1} at the range of $470\text{-}570^\circ\text{C}$ (fig 2A, 2B, 2C, 2D). The entropy was negative from range -1.4486 to $-1.3596 \text{ Jmol}^{-1}$. Here the negative value of entropy suggests the stability of the copolymer. The enthalpy and Gibbs free energy values were also negative in the range of -9702 to -19982 Jmol^{-1} and -9095 to -18836 Jmol^{-1} , respectively, (Table S1).

About 1.6 % mass loss for C-MCPMI was observed up to 160°C at a heating rate of 10°C/min . and almost 50 % copolymer was degraded up to 330°C , and up to 500°C about 90 % mass loss was observed (figure S-2b). The thermal curve of the copolymer (C-MCPMI) shows a four-step degradation process. The initial stage of degradation was between $273\text{-}350^\circ\text{C}$ with a maximum mass loss at 316°C , and another stage degradation was between $358\text{-}441^\circ\text{C}$ with a maximum mass loss at 405°C . About 3 % char yield was obtained at 600°C in case of the copolymer (C-MCPMI) (figure S-2b).

The activation energy value shows the decomposition proceeds with an exothermic process and activation energy was -6095 Jmol^{-1} at a heating rate of 10°C/min at the range of $40\text{-}150^\circ\text{C}$ of decomposition temperature this value decreases as temperature increases gradually in every step to -12939 Jmol^{-1} at the range of $450\text{-}580^\circ\text{C}$ (Table S1). The entropy was negative from the range of -1.4026 to $-1.1773 \text{ Jmol}^{-1}$. Here the negative value of entropy suggests the stability of the copolymer and enthalpy and Gibbs free energy values were also negative in the range of -9777 to -20114 Jmol^{-1} and -9156 to -19098 Jmol^{-1} (table S1) (fig 2A, 2B, 2C, 2D).

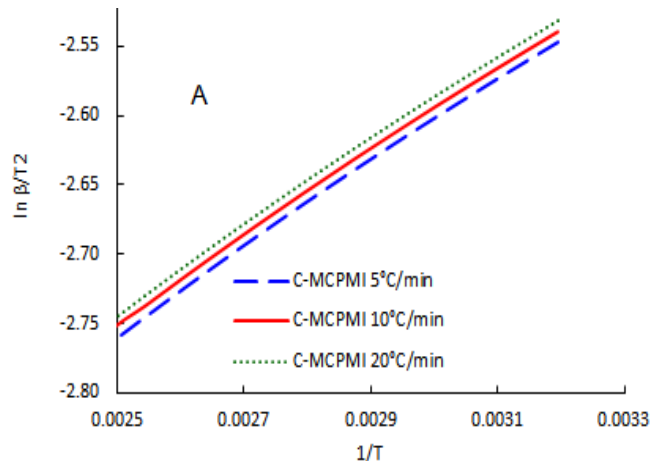


Fig. 2A The kinetics of C-MCPMI degradation on stage-I at different heating rate i.e. 5°C , 10°C and 20°C/min .

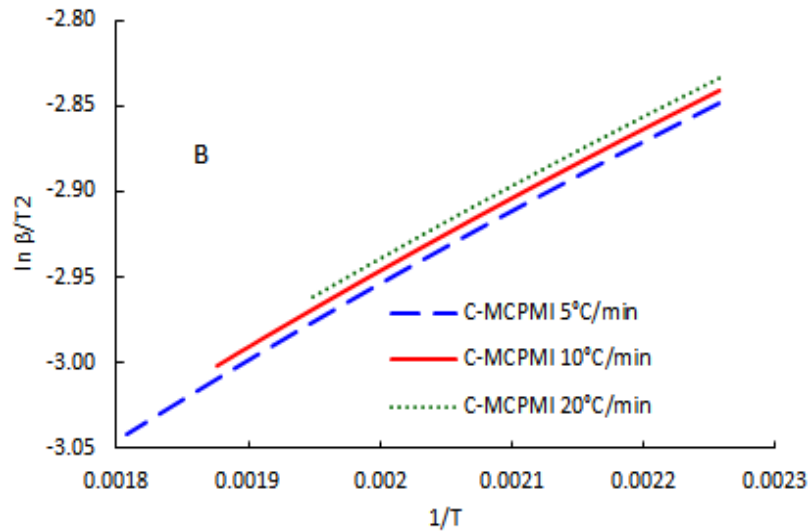


Fig. 2B The kinetics of C-MCPMI degradation on stage-II at different heating rate i.e. 5°C, 10°C and 20°C/min.

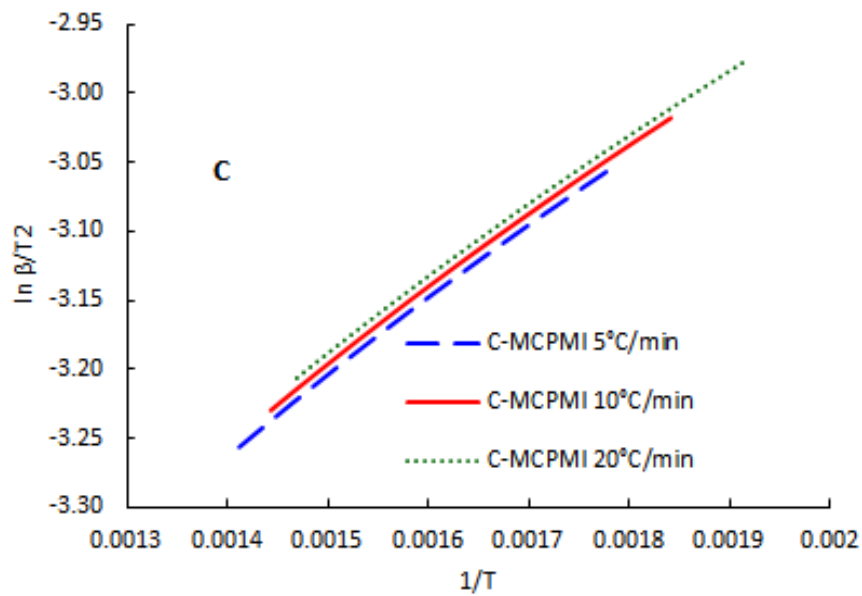


Fig. 2C The kinetics of C-MCPMI degradation on stage-III at different heating rate i.e. 5°C, 10°C and 20°C/min.

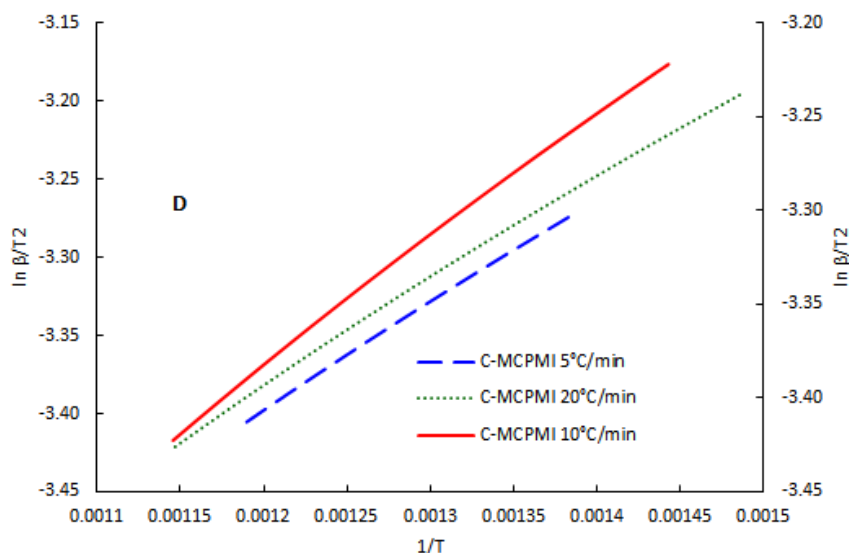


Fig. 2D The kinetics of C-MCPMI degradation on stage-IV at different heating rate i.e. 5°C, 10°C and 20°C/min.

About 1.3 % mass loss for C-MCPMI was observed up to 160°C at a heating rate of **20°C/min**. and almost 50 % copolymer was degraded up to 300°C, and up to 490°C about 90 % mass loss was observed (figure S-2c). The thermal curve of the copolymer (C-MCPMI) shows a four-step degradation process. The initial stage of degradation was between 248-356°C with a maximum mass loss at 316°C, and another stage degradation was between 378-459°C with a maximum mass loss at 415°C. About 4.5 % char yield was obtained at 568°C in case of the copolymer (C-MCPMI) (figure S-2c).

The activation energy value shows the decomposition proceeds with an exothermic process and activation energy was -6102 Jmol^{-1} at a heating rate of 20°C/min at the range of 40-160°C of decomposition temperature this value decreases as temperature increases gradually in every step to -12918 Jmol^{-1} at the range of 410-600°C. The entropy was negative from a range of -1.4043 to $-1.3425 \text{ Jmol}^{-1}$. Here the negative value of entropy suggests the stability of the copolymer. The enthalpy and Gibbs free energy values were also negative in the range of -9702 to -20177 Jmol^{-1} and -9094 to -19005 Jmol^{-1} , respectively, (table S1) (fig 2A, 2B, 2C, 2D).

So, by studying the degradation pattern for copolymer (C-MCPMI) at the different heating rate it was observed that degradation steps are almost the same in this case but their range of degradation is changing. On increasing the heating rate at 5°C/min to 20°C/min while activation energy value decreases at different

decomposition temperature range. On observing the change in the activation energy and other non-isothermal parameters of C-MCPMI with an increase in heating rate, it is concluded that increased heating rate does not affect the degradation of C-MCPMI to a large extent as the increase in activation energy is not much significant.

Experimental

Materials

The Maleic anhydride (SRL, Mumbai) recrystallized from chloroform and then further purified by sublimation at 54°C. AIBN (Avra, India) was recrystallized from ethanol. The other reagents like Phosphorus pentoxide (P₂O₅), Sulphuric acid, methanol, Acetone were purchased from Merck India and used as such without further purification.

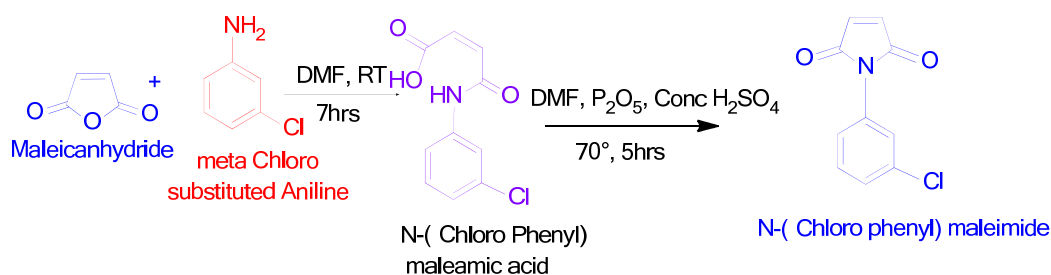
Instrumentation

The number average molecular weight and polydispersity index of the homopolymer and copolymers were determined using a Water gel permeation chromatography (GPC) system equipped with 13082008 MIX BEAD THF (30) sec (1000) sec columns. Thermograms in nitrogen were obtained on a Mettler TA-3000 system at the heating rate of 5°, 10°, & 20°C/min from 40°C onwards.

Synthesis of N-(*meta*-chlorophenyl) maleimide monomer

The N-MCPMI was synthesized from maleic anhydride (ME) with chlorine substituted at *meta* place of aniline in DMF as shown in scheme-1 with slight modification in the method of previously reported method [25].

In a round bottom flask 0.1 moles of *m*-chloro substituted aniline and 9.8 g of maleic anhydride (0.1 moles) in 40 ml DMF was added under stirring at room temperature for 7h, after completion of the reaction the reaction mixture was precipitated in ice-cold water, filtered, dried and then recrystallized from ethanol to obtain the functionalised intermediate.

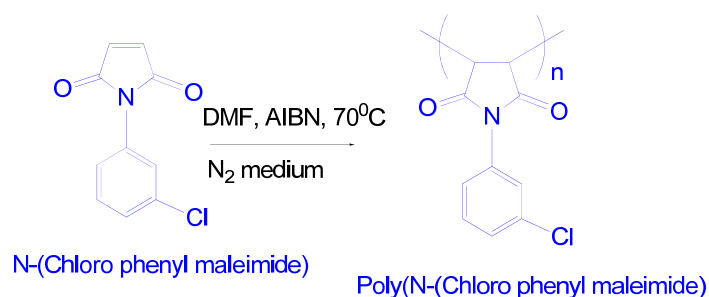


Scheme 1: The synthetic route N-(*meta*-chlorophenyl) maleimide

The intermediate was cyclised in DMF followed by addition of 6g P_2O_5 and 2 drops of conc. H_2SO_4 into it at $70^\circ C$, for 5h. After completion of the reaction, the mixture was precipitated in ice cold water. The crude monomer was filtered and washed with $NaHCO_3$ solution to remove any acid if formed. The product was filtered and dried in vacuum for 10h at $35^\circ C$. Yellow crystals of monomers are obtained. N-MCPMI: Yield: 86%, m.p. $114^\circ C$.

Homopolymerization of N-(*meta*-chloro-phenyl) maleimide

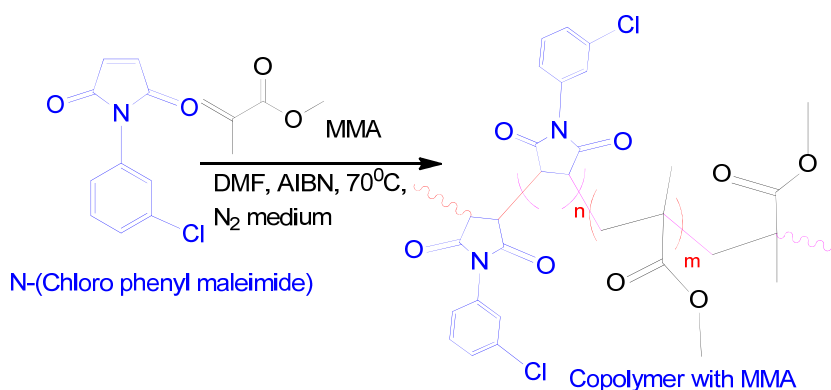
The *meta*-chloro substituted N-Phenylmaleimide (0.5 mol fraction) monomer was mixed well with 80 ml DMF in a round bottom flask. Then, a free radical initiator, AIBN (0.002 g) was added to initiate the reaction. The reaction mixture was refluxed at $70^\circ C$ for 16h under inert atmosphere (scheme-2).



Scheme 2: Homopolymerization procedure for N-(*meta*-chloro-phenyl) maleimide

The product of homopolymer was in a dissolved state in DMF. It was precipitated out in ice-cold water. It was then washed with 2-3 times methanol, dried at $60^\circ C$ under vacuum.

Copolymerization of N-(*meta*-chloro-phenyl)maleimide with MMA



Scheme 3: Copolymerization of m-(N-(Chlorophenylmaleimide)) and MMA monomer

The meta-chloro substituted N-Phenylmaleimide (0.5 mol fraction) monomer was mixed well with 80 ml DMF in a round bottom flask, then 1 ml of MMA was added into the flask at a low temperature. Then, free radical initiator (AIBN, 0.002 g) was added to the reaction mixture in an inert atmosphere. It was then refluxed using at 70°C for 24h (Scheme 3).

The product of copolymer was in a dissolved state in DMF. This copolymer product was precipitated out in 5% methanol-water mixture. It was then washed 2-3 times with methanol to purify and dried at 60°C under vacuum. The precipitate was brown in colour.

The FT-IR spectra of C-MCPMI (Figure S-5a) shown the following absorption frequencies (cm^{-1}) at 3077 are due to aromatic C-H stretching, while the peak at 3118 is due to -CH stretching for the heterocyclic ring, peak at 3121 is due to alkene C-H stretching. The bands at 1783 and 1720 cm^{-1} are assigned to C=O stretching for five-membered imide ring. The bands 1590, 1529 and 1487 cm^{-1} are attributed for aromatic C=C stretching, while aromatic C-N stretching was observed at 1442 cm^{-1} . The C-N-C stretching is observed at 1194 cm^{-1} . The peaks at 2962 and 2954 cm^{-1} are assigned due to C-H stretching of CH_3 & CH_2 of MMA.

^1H NMR (300 MHz, TMS, CDCl_3 , ppm) for C-MCPMI (Figure S-5b): δ 7.21-8.03 ppm (2d, 4H phenyl). δ 3.70-3.89 ppm appeared for (S, 2H -CH-CH-), δ 0.85-1.12 ppm (T, 3H CH_3), δ 1.89-2.04 ppm (2H, CH_2).

Gel permeation chromatography (GPC)

Molecular weight usually decreases while the polydispersity index increases with increasing the maleimide content indicating a higher rate of transfer to the maleimide monomer. GPC traces show (fig 3 and table-1) that the synthesized homopolymer and copolymer contain no impurities. The low PDI values indicate that the polymer show narrow molar mass distribution even synthesized by FRP, which is of rare occurrence. The copolymer is higher molecular weight polymer as compared to the homopolymer.

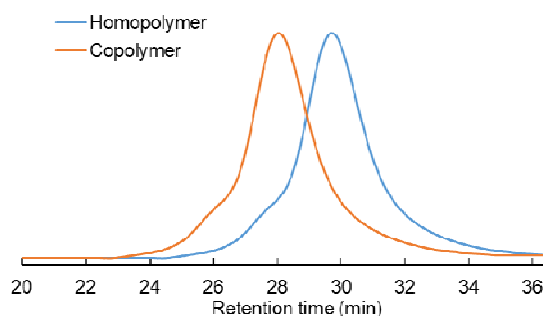


Fig 3 GPC traces of H-MCPMI and C-MCPMI

Table 1: Molecular weight and PDI of Homopolymer and Copolymer:

Polymers	H-MCPMI (g/mol)	C-MCPMI (g/mol)
Mw	8590	13745
PDI	1.17	1.19

Conclusions

The free radical polymerization methodology was applied for the synthesis of m-chloro substituted homopolymer of maleimide using AIBN as a free radical initiator and DMF as a solvent at 70°C for 16h was successful. The thermal degradation of homopolymer and copolymer was recorded at different heating rates and degradation kinetics were studied at various stages. The high activation energy explains the thermal stability of the polymers. The entropy of activation has a negative value, which explains the decomposition reaction proceeded at a lower rate. The thermal analyses reveal that the initial decomposition temperatures for homopolymer and copolymer are very close to each other at 5°C/min.

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