

Synthesis and Characterization of Copolymers of Methyl Methacrylate with *N*-arylitaconimides via AGET-ATRP

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ABSTRACT

*This study presents the synthesis of copolymers of methyl methacrylate (MMA) with *N*-arylitaconimides (NAIs) [such as *N*-(4-chlorophenyl)itaconimide, *N*-phenylitaconimide, *N*-(4-methylphenyl)itaconimide and *N*-(4-methoxyphenyl)itaconimide] with architecture Poly(NAI-*ran*-MMA)-*b*-poly(NAI) via activators generated by electron transfer-atom transfer radical polymerization process. The structural characterization of these copolymers was carried out using IR, ¹H-NMR spectroscopy and elemental analysis. The molecular characterization was carried out using gel permeation chromatography and showed increased molecular weight of block copolymers as compared to the macroinitiator used for its synthesis. The thermal characterization was carried out using differential scanning calorimetry and thermogravimetric analysis. An increase in the molecular weight and T_g of Poly(NAI) block was observed as the electron releasing capacity of the substituent on aromatic ring of the pendant group is increased.*

KEYWORDS: *N*-arylitaconimides; Block copolymers; AGET-ATRP.

1. INTRODUCTION

The polymer materials obtained from renewable resources are of interest because of the environmental issues such as global warming and sustainability.^[1] The “itaconimides” are the

members of imide family with reactive exocyclic double bond and are obtained from the renewable resource *i.e.* D-glucose.^[2-3] The homopolymerization of *N*-arylitaconimide (NAI) monomers have been attempted *via* conventional free radical polymerization (FRP) methods

using 2,2'-azobisisobutyronitrile as an initiator. The homopolymers of NAI monomers showed high glass transition temperature (T_g) (250–300°C).^[4–5] To exploit the effect of imide functionality responsible for the high T_g of the resulting polymers, the NAI monomers have been copolymerized with monomers such as methyl methacrylate (MMA) but *via* conventional FRP methods. For the obtained copolymers an enhancement in T_g and thermal stability was observed which increased with increasing the NAI component in the polymer backbone. But the copolymers so obtained were of low molecular weights (< 5000 gmol⁻¹) with high polydispersity index (PDI) (1.5–3.5).^[6–7] This could be due to the fast termination process. The reactivity ratios determined for NAI and MMA were in the range of 1.28–1.34 and 0.24–0.35, respectively, thus limiting the architecture of copolymers *via* conventional FRP to “random” only.^[4–7] These limitations can be overcome by using controlled radical polymerizations (CRP) techniques such as activator generated by electron transfer-atom transfer radical polymerization (AGET-ATRP) process.^[8] AGET-ATRP is commonly used CRP technique, based on establishing a rapid dynamic equilibrium between the minute amount of growing free radicals ($R\cdot$) and large majority of the deactivators ($X-Cu^{II}Y/L_m$). In AGET-ATRP, the activators (Cu^IY/L_m) are formed *in situ* by the reduction of deactivators with reducing agent such as tin(II) 2-ethylhexanoate [$Sn(EH)_2$]. This then leads to normal initiation with the added alkyl halide ($R-X$) initiator.^[9–10]

There are handful reports available on MMA-NAI copolymer systems reporting architecture

other than random copolymers. The block copolymers of *N*-phenylitaconimide and its chloro derivatives with MMA were synthesized *via* reverse ATRP with long reaction duration (7 days) and low molecular weight (< 3000 gmol⁻¹).^[11] Hence, it was of interest to synthesize the copolymers of MMA and NAI monomers with higher incorporation of NAI in the polymer backbone as well as with improved molecular weight to give the polymers suitable for its applications at high temperature.

In this study, we report the synthesis of living copolymers of MMA and NAI monomers with architecture *i.e.* Poly(NAI-*ran*-MMA)-*b*-poly(NAI) *via* AGET-ATRP process. In the resulting copolymers '*N*-arylimide' was obtained as a pendant group. The effect of this pendant group on the properties of copolymers has also been investigated systematically by varying the substituent on the aromatic ring from strongly activating $-OCH_3$ to weakly deactivating $-Cl$ group. For this purpose, four NAI monomers *i.e.* *N*-(4-chlorophenyl)itaconimide (CPI), *N*-phenylitaconimide (PI), *N*-(4-methylphenyl)itaconimide (MPI), and *N*-(4-methoxyphenyl)itaconimide (MOPI) have been used.

EXPERIMENTAL

Materials

Itaconic acid (99.0%), phosphorus pentoxide (95.0%), *p*-toluidine (98.0%), *p*-anisidine (98.0%), *p*-chloroaniline (95.0%), 2,2'-bipyridine (Bpy) (99.5%) and silica gel (60–120 mesh) for column chromatography were used as supplied. Chloroform (99.7%), acetic anhydride (98.0%) and aniline (99.5%) were distilled prior to use. Acetone (99.0%) was dried overnight using potassium carbonate followed by distillation. Anhydrous sodium acetate (99.5%) was obtained by fusion. All the above chemicals were obtained from S. D. Fine Chem Limited,

Mumbai, India. Ethyl- α -bromoisobutyrate (EBiB) (98.0%), CuBr₂ (99.9%), and [Sn(EH)₂] (95.0%) were used as supplied after obtaining from Sigma-Aldrich Chemical Pvt. Ltd. Bangalore, India. MMA (99.0%, S. D. Fine Chem Limited, Mumbai, India) was purified by washing with 5% NaOH solution to remove the inhibitor followed by repeated washing with distilled water until the filtrate became neutral. To remove the traces of water, it was then kept in anhydrous magnesium sulfate followed by vacuum distillation with calcium hydride. CuBr (99.9%, Sigma-Aldrich Chemical Pvt. Ltd. Bangalore, India) was purified by stirring overnight in glacial acetic acid and washing with absolute ethanol and diethyl ether, followed by drying under vacuum. Anisole (99.0%, SRL Private limited, Mumbai, India) was purified by washing with 5% NaOH solution and then by distilled water. It was then kept on anhydrous potassium carbonate followed by vacuum distillation over sodium benzophenone to remove the traces of water. Four different NAI monomers *i.e.* CPI, PI, MPI and MOPI were synthesized in laboratory using procedure reported in our previous publication.^[12]

Methods

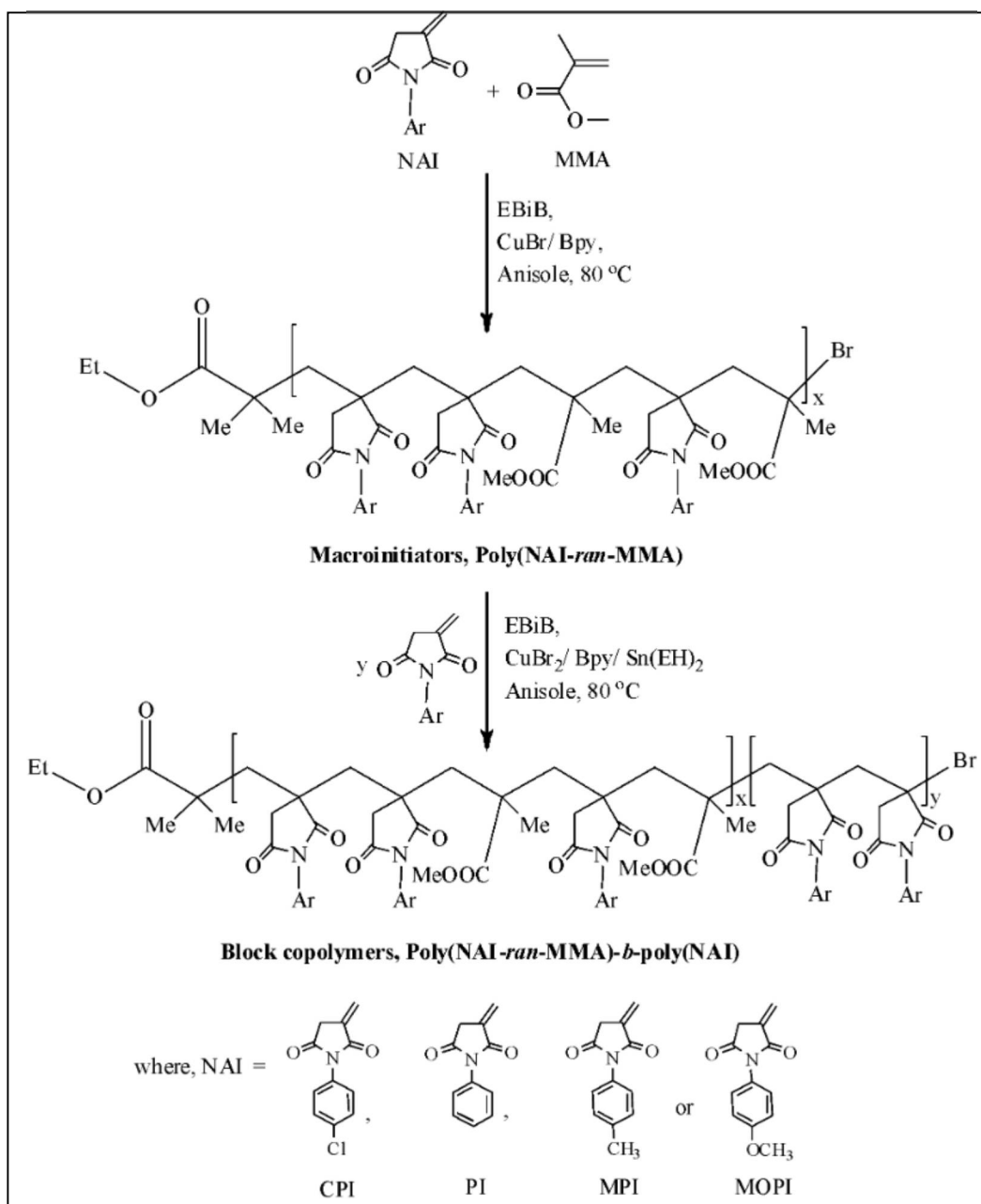
The IR spectra were recorded on Shimadzu DR-8031 FT-IR spectrophotometer in the region 4000 to 400 cm⁻¹ using KBr pellet method. ¹H-NMR spectra were recorded on Bruker AV III with an operating frequency of 500 MHz. Chemical shifts of protons are reported (in ppm) relative to tetramethylsilane in deuterated chloroform. The elemental analysis (CHN) of copolymers was performed using Vario Micro Cube elemental analyzer. Molecular-mass characteristics of the copolymers were determined by gel permeation chromatography (GPC) in THF as an eluent at flow rate of 0.75 mLmin⁻¹ and column temperature of 25 °C with an Agilent 1260 HPLC-GPC system equipped with column: PL gel 5 micron Mixed D: 300 mm × 7.5 mm with a differential refractometer. Polystyrene standards with molecular weight of 10³-10⁵ g mol⁻¹ were used for calibration. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were done using TGA/ DTA analyzer from TA instruments, model: SDT Q600, at heating rate of 10 °C per minute in nitrogen atmosphere (flow rate = 50 cm³min⁻¹).

Synthesis of Macroinitiator

In a three way round bottom flask equipped with reflux condenser and magnetic bead, NAI (0.01 mol) and MMA (0.04 mol) were dissolved in 10 mL of dry anisole. To this solution CuBr (0.25 mmol) and Bpy (0.75 mmol) were added. The resultant reaction mixture was subjected to freeze-vacuum-thaw cycle twice. The initiator EBiB (0.25 mmol) dissolved in 4 mL of dry anisole was separately degassed using freeze-vacuum-thaw cycle twice, and then charged to the reaction flask through a nitrogen-purged syringe. The whole reaction mixture was again subjected to freeze-vacuum-thaw cycle. The temperature of the reaction flask was raised to 80°C and maintained for 45h. The termination of polymerization reaction was done by the addition of methanol in excess, to the reaction mixture. The precipitated out copolymer was filtered and washed with hot methanol to remove the unreacted monomers. For removal of the copper catalyst, the copolymer was dissolved in acetone and the resultant solution was passed through the alumina bed. The filtrate was concentrated using rotary evaporator, reprecipitated with hot methanol, filtered and dried under vacuum. The percentage yield of the copolymers, determined using gravimetric method was found to be in the range of 40-50%.

Synthesis of Block Copolymers

In a three way round bottom flask, NAI monomer (0.025 mol), CuBr₂ (0.125 mmol), Bpy (0.375 mmol), Sn(EH)₂ (0.063 μ mol) and Poly(NAI-*ran*-MMA) (0.125 mmol) were added to the 20 mL of dry anisole under nitrogen atmosphere. The reaction mixture was subjected to freeze-vacuum-thaw cycle thrice followed by continuous stirring under inert atmosphere for 24h at 80°C. The termination of polymerization reaction was carried out by the addition of excess of methanol, to the reaction mixture. The precipitated copolymer was purified using the similar procedure as reported for the purification of macroinitiator. The percentage yield of the block copolymers was obtained using gravimetric method and it was found to be in the range of 50-60%.



Scheme 1: Reaction scheme for the synthesis of macroinitiators and block copolymers.

RESULTS AND DISCUSSION

The copolymers were characterized using IR, $^1\text{H-NMR}$ spectroscopy and elemental analysis. The molecular and thermal characterization was carried out using GPC, DSC and TGA, respectively.

IR Analysis

The IR spectra of copolymers Poly(NAI-*ran*-MMA) and Poly(NAI-*ran*-MMA)-*b*-poly(NAI), show characteristic absorption bands of $>\text{C}=\text{O}$ of imide group in the regions $1796\text{--}1785\text{ cm}^{-1}$ and $1754\text{--}1714\text{ cm}^{-1}$, respectively. The $>\text{C}=\text{O}$ peaks of MMA merged with the $>\text{C}=\text{O}$ peaks of imide group in the region $1754\text{--}1714\text{ cm}^{-1}$.

The $>\text{C}=\text{C}<$ stretching frequencies of phenyl ring of NAI were observed in the regions $1609\text{--}1593\text{ cm}^{-1}$, $1516\text{--}1500\text{ cm}^{-1}$ and $1485\text{--}1538\text{ cm}^{-1}$, respectively. The peaks observed in the region $618\text{--}600\text{ cm}^{-1}$ were assigned to C-Br stretches.

In the comparative IR spectra of macroinitiator, Poly(MOPI-*ran*-MMA) and block copolymer, Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI) (Figure 1), the C-H stretch peaks corresponding to $-\text{CH}_3$ (of MMA) and the C-H stretch peaks corresponding to aromatic ring (of MOPI) were observed in the regions $2853\text{--}2845\text{ cm}^{-1}$ and $3020\text{--}3000\text{ cm}^{-1}$, respectively. Due to the incorporation of Poly(MOPI) block, the relative

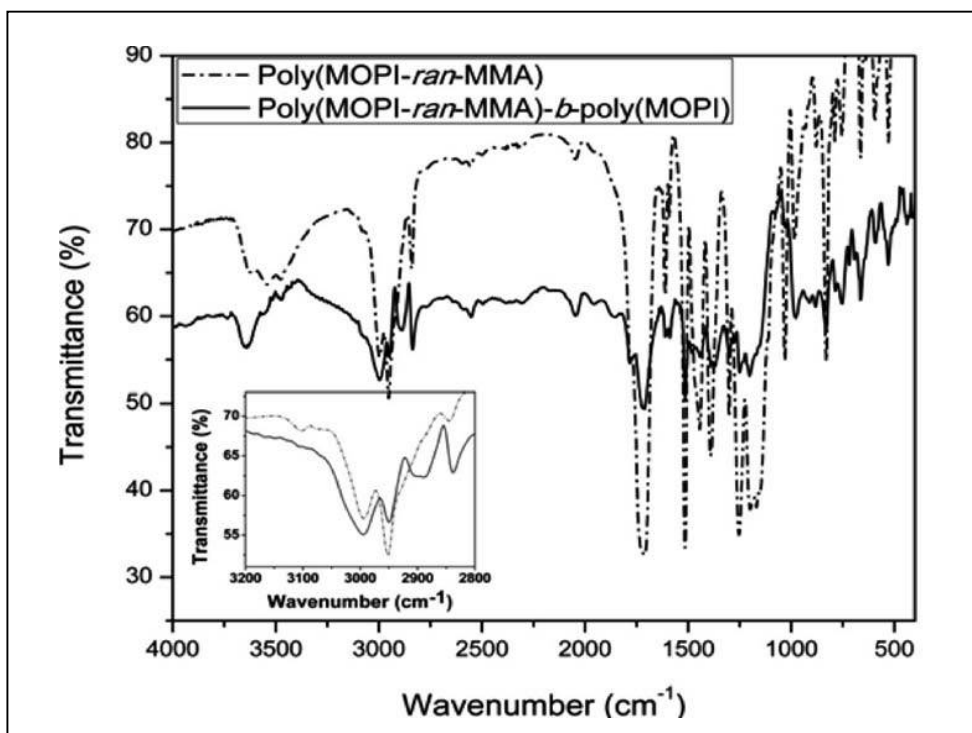


Figure 1: Comparative IR spectra of Poly(MOPI-*ran*-MMA) and Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI).

peak intensity of C-H stretch peaks due to aromatic ring, in the region $3020\text{--}3000\text{ cm}^{-1}$ were increased for block copolymers as compared to the macroinitiator. Similar results were obtained for Poly(CPI-*ran*-MMA)-*b*-poly(CPI), Poly(PI-*ran*-MMA)-*b*-poly(PI) and Poly(MPI-*ran*-MMA)-*b*-poly(MPI) block copolymers.

¹H-NMR Analysis

The ¹H-NMR spectra of copolymers Poly(NAI-*ran*-MMA) and Poly(NAI-*ran*-MMA)-*b*-poly(NAI), show peaks due to the phenyl ring of NAI in region $\delta = 7.6\text{--}7.2$ ppm. The peaks of --OCH_3 of MMA and --CH_2 (adjacent to the carbonyl group) were observed, at $\delta = 3.6 \pm 0.10$ ppm and $\delta = 3.5 \pm 0.12$ ppm, respectively. The peaks of --CH_2 and --CH_3 of the side chain were observed

in the regions $\delta = 2.9\text{--}1.6$ ppm and $\delta = 1.5\text{--}0.9$ ppm, respectively. For Poly(MPI-*ran*-MMA)-*b*-poly(MPI), the peaks of --CH_3 substituted on aromatic ring was observed at $\delta = 2.4$ ppm. Similarly, for Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI), the peaks of --OCH_3 substituted on aromatic ring was observed at $\delta = 3.8$ ppm.

In the comparative ¹H-NMR spectra of macroinitiator, Poly(MOPI-*ran*-MMA) and block copolymer, Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI) (Figure 2), due to the incorporation of Poly(MOPI) block, the relative peak intensity of --OCH_3 of MOPI ($\delta = 3.8$ ppm) increased as compared to the peak intensity of --OCH_3 of MMA ($\delta = 3.6$ ppm), as expected. Similarly, for Poly(CPI-*ran*-MMA)-*b*-poly(CPI), Poly(PI-*ran*-

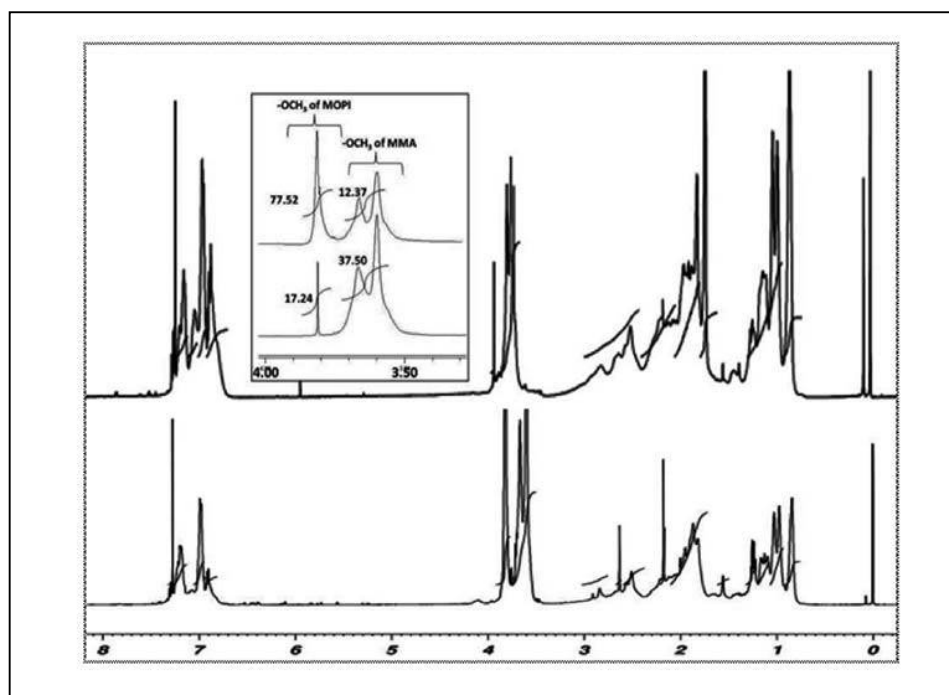


Fig. 2. Comparative ¹H-NMR spectra of Poly(MOPI-*ran*-MMA) and Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI).

MMA)-*b*-poly(PI) and Poly(MPI-*ran*-MMA)-*b*-poly(MPI) copolymers, the peak intensity of aromatic protons of NAI ($\delta = 7.6$ - 7.2 ppm) and the peak intensity of $-\text{OCH}_3$ protons of MMA ($\delta = 3.6 \pm 0.2$ ppm) were compared with

corresponding macroinitiators and an increase in the relative peak intensity of aromatic protons of NAI as compared to the peak intensity of $-\text{OCH}_3$ protons of MMA was observed as shown in Figure 3.

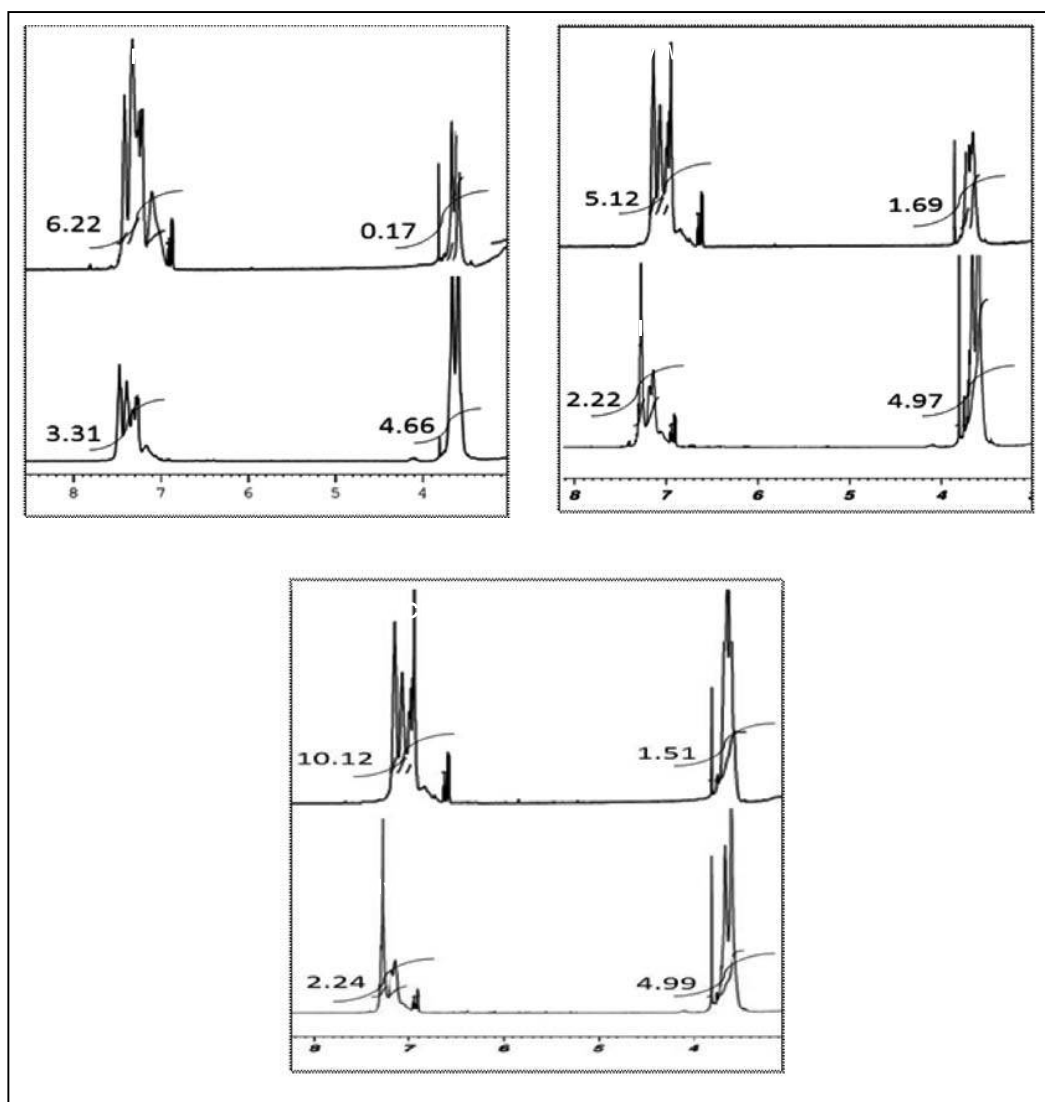


Fig. 3. Comparative ^1H -NMR spectra of macroinitiators and block copolymers.

Elemental Analysis

A good agreement was observed between the experimentally found and theoretically

calculated values¹³ of carbon, hydrogen and nitrogen. The detail of the elemental analysis is given in **Table 1**.

Table 1. Percentage yield and elemental analysis of macroinitiators and block copolymers.

Copolymer Designation	Yield(%)	Experimental			Theoretical		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
Poly(CPI- <i>ran</i> -MMA)	40	65.54	6.91	2.31	65.35	6.82	2.13
Poly(PI- <i>ran</i> -MMA)	45	63.84	7.17	2.39	64.10	7.07	2.45
Poly(MPI- <i>ran</i> -MMA)	48	63.61	6.92	2.98	63.54	6.74	3.02
Poly(MOPI- <i>ran</i> -MMA)	50	59.92	5.77	3.12	60.10	5.68	3.21
Poly(CPI- <i>ran</i> -MMA)- <i>b</i> -poly(CPI)	49	66.01	6.56	4.44	66.41	6.39	4.79
Poly(PI- <i>ran</i> -MMA)- <i>b</i> -poly(PI)	54	58.75	6.40	4.09	54.47	6.61	3.83
Poly(MPI- <i>ran</i> -MMA)- <i>b</i> -poly(MPI)	58	63.02	5.78	4.78	63.99	5.85	4.65
Poly(MOPI- <i>ran</i> -MMA)- <i>b</i> -poly(MOPI)	61	59.31	5.85	3.42	60.42	6.05	3.30

Molecular Weights of Copolymers

The number average molecular weight (\bar{M}_n) in (gmol^{-1}) of the block copolymers *i.e.* Poly(CPI-*ran*-MMA)-*b*-poly(CPI), Poly(PI-*ran*-MMA)-*b*-poly(PI), Poly(MPI-*ran*-MMA)-*b*-poly(MPI), and Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI) were obtained as, 8.0×10^4 , 9.3×10^4 , 9.6×10^4 , and 1.0×10^5 , respectively with PDI ~ 1.2 - 1.4 , as compared to the corresponding macroinitiators *i.e.* Poly(CPI-*ran*-MMA), Poly(PI-*ran*-MMA), Poly(MPI-*ran*-MMA) and Poly(MOPI-*ran*-MMA) for which \bar{M}_n in (gmol^{-1}) were obtained as, 4.1×10^3 , 4.2×10^3 , 4.9×10^3 and 5.7×10^3 , respectively with PDI ~ 1.3 - 1.4 . This increase in the \bar{M}_n of the block copolymer as compared to the corresponding macroinitiator was in concordance with the theoretically calculated values in (gmol^{-1} using the literature based formula^[14]) *i.e.* 8.1×10^4 , 9.4×10^4 , 9.7×10^4 , and

1.0×10^5 for Poly(CPI-*ran*-MMA)-*b*-poly(CPI), Poly(PI-*ran*-MMA)-*b*-poly(PI), Poly(MPI-*ran*-MMA)-*b*-poly(MPI), and Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI), respectively. From Scheme 1 we can infer that the propagating polymer chain for the block copolymer will have a terminal *N*-arylimide substituted free radical. This radical is stabilized when **X** on aromatic ring is an electron releasing group. For different **X** in *N*-arylimide substituted free radicals, the stability increases in the order, $-\text{Cl}$ ($-I$, inductive effect) $< -\text{H}$ $< -\text{CH}_3$ ($+I$, inductive effect) $< -\text{OCH}_3$ ($+M$, mesomeric effect). The increase in the stability of free radical increases the selectivity of growing polymer chain and reduces the loss of growing radical due to side reactions such as termination or chain transfer. This explains the increase in \bar{M}_n of the copolymers in the order,

\bar{M}_n

Poly(CPI-*ran*-MMA)-*b*-poly(CPI) < Poly(PI-*ran*-MMA)-*b*-poly(PI) < Poly(MPI-*ran*-MMA)-*b*-poly(MPI) < Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI)..

Thermal Characterization of Copolymers

The DSC scans of all the copolymers show shift in the base line corresponding to the T_g .

For macroinitiators the T_g was observed in the range of 160-180 °C (**Figure 4a**). For block copolymers well separated T_g s were observed corresponding to the two blocks indicating the phase separation between them (**Figure 4b**). The T_g in the temperature range of 179-182 °C was attributed to Poly(NAI-*ran*-MMA) block and for Poly(NAI) block the T_g was observed in the

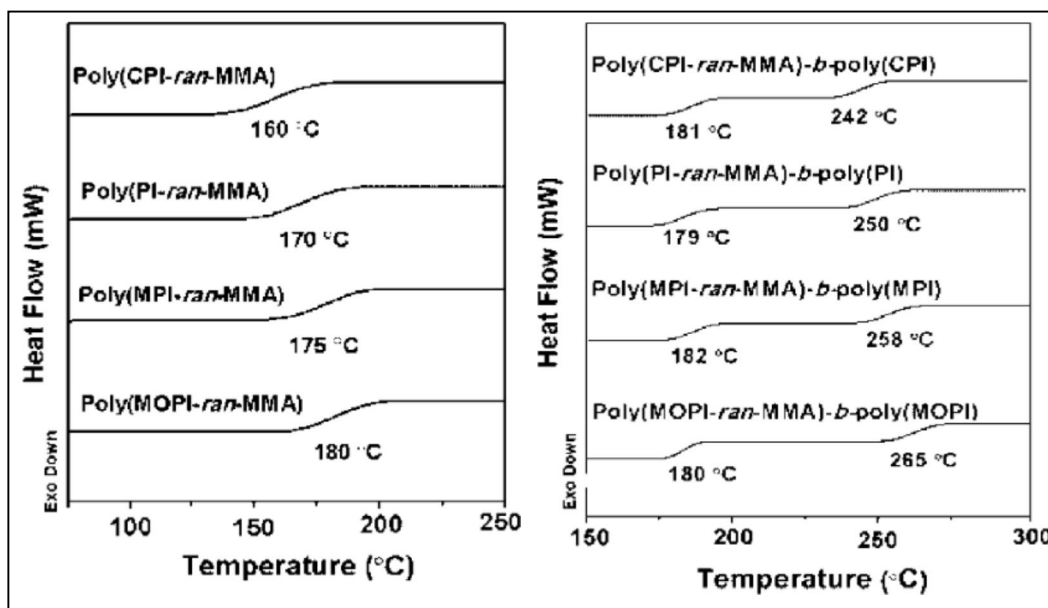


Figure 4: DSC scans of (a) macroinitiators and (b) block copolymers.

temperature range of 242-265 °C. In literature the T_g reported for the homopolymers, Poly(CPI), Poly(PI), Poly(MPI) and Poly(MOPI) are 238 °C, 220 °C, 232 °C, and 220 °C, respectively.⁴ The detail of T_g s for the copolymers is given in **Table 2**. The T_g of the copolymers increased in the order, Poly(CPI-*ran*-MMA)-*b*-poly(CPI) < Poly(PI-*ran*-MMA)-*b*-poly(PI) < Poly(MPI-*ran*-MMA)-*b*-poly(MPI) < Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI). This can be attributed to the increase in the polarity and

rigidity of the pendant group with increase in electron releasing capacity of the substituent on the aromatic ring of NAI.

For Poly(methyl methacrylate) (PMMA) a three-step degradation has been reported.^[15-16] The degradation is attributed to head-to-head linkages in first step (150-250 °C), end unsaturation in second step (250-350 °C) and random chain scission in third step (350-500 °C). In contrast to virgin PMMA, Katiyar et al. have

Table 2. The T_g s observed in the DSC scans of the macroinitiators and block copolymers.

Copolymer Designation	First block			Second block		
	T_o (°C)	T_g (°C)	T_e (°C)	T_o (°C)	T_g (°C)	T_e (°C)
Poly(CPI- <i>ran</i> -MMA)	141	160	182	-	-	-
Poly(PI- <i>ran</i> -MMA)	152	170	192	-	-	-
Poly(MPI- <i>ran</i> -MMA)	156	175	194	-	-	-
Poly(MOPI- <i>ran</i> -MMA)	160	180	199	-	-	-
Poly(CPI- <i>ran</i> -MMA)- <i>b</i> -poly(CPI)	162	181	198	221	242	265
Poly(PI- <i>ran</i> -MMA)- <i>b</i> -poly(PI)	160	179	190	229	250	269
Poly(MPI- <i>ran</i> -MMA)- <i>b</i> -poly(MPI)	163	182	195	240	258	271
Poly(MOPI- <i>ran</i> -MMA)- <i>b</i> -poly(MOPI)	165	180	200	246	265	286

T_o = onset temperature and T_e = endset temperature

reported the two-step degradation of fullerene containing PMMA. The first stage degradation is attributed to end chain scission (300-380 °C) and the second step degradation is associated with random chain scission (380-500 °C).^[17] The thermogravimetric scans for macroinitiators and block copolymers are given in **Figures 5a** and **5b**, respectively. The macroinitiators, Poly(NAI-*ran*-MMA) were stable up to 300 °C and degraded in single step due to random chain scission in the temperature range of 300-450 °C. The 7-8% weight loss in the temperature range of 200-250 °C was due to the loss of solvent trapped in copolymer. The block copolymers, Poly(NAI-*ran*-MMA)-*b*-poly(NAI) were stable up to 330 °C and showed two steps degradation in the temperature ranges 330-410 °C and 410-500 °C, respectively. The weight loss (22-28%) in the region 330-410 °C could be due to the scissions of small groups at the end of polymer chain such as methoxycarbonyl side groups. The major weight loss (48-55%) in the region

410-450 °C is attributed to the random scissions of main chains which leads to the formation of macroradicals which further undergo unzipping to give the monomers as reported by Katiyar et al.^[17] The random chain scission for the block copolymers (410 °C) starts at a temperature which is 60 °C higher than virgin PMMA. This may be due to the formation of N-arylimide substituted free radical as an intermediate in this step which is more stable as compared to the methyl carboxylate substituted free radical obtained as an intermediate in the random chain scission of virgin PMMA. Due to the higher incorporation of aromatic ring the char yield was found to be higher (~ 15-22% at 600 °C) for block copolymers as compared to the macroinitiators (~ 9-17% at 600 °C) used for its synthesis and follows the order, Poly(CPI-*ran*-MMA)-*b*-poly(CPI) < Poly(PI-*ran*-MMA)-*b*-poly(PI) < Poly(MOPI-*ran*-MMA)-*b*-poly(MOPI) < Poly(MPI-*ran*-MMA)-*b*-poly(MPI).

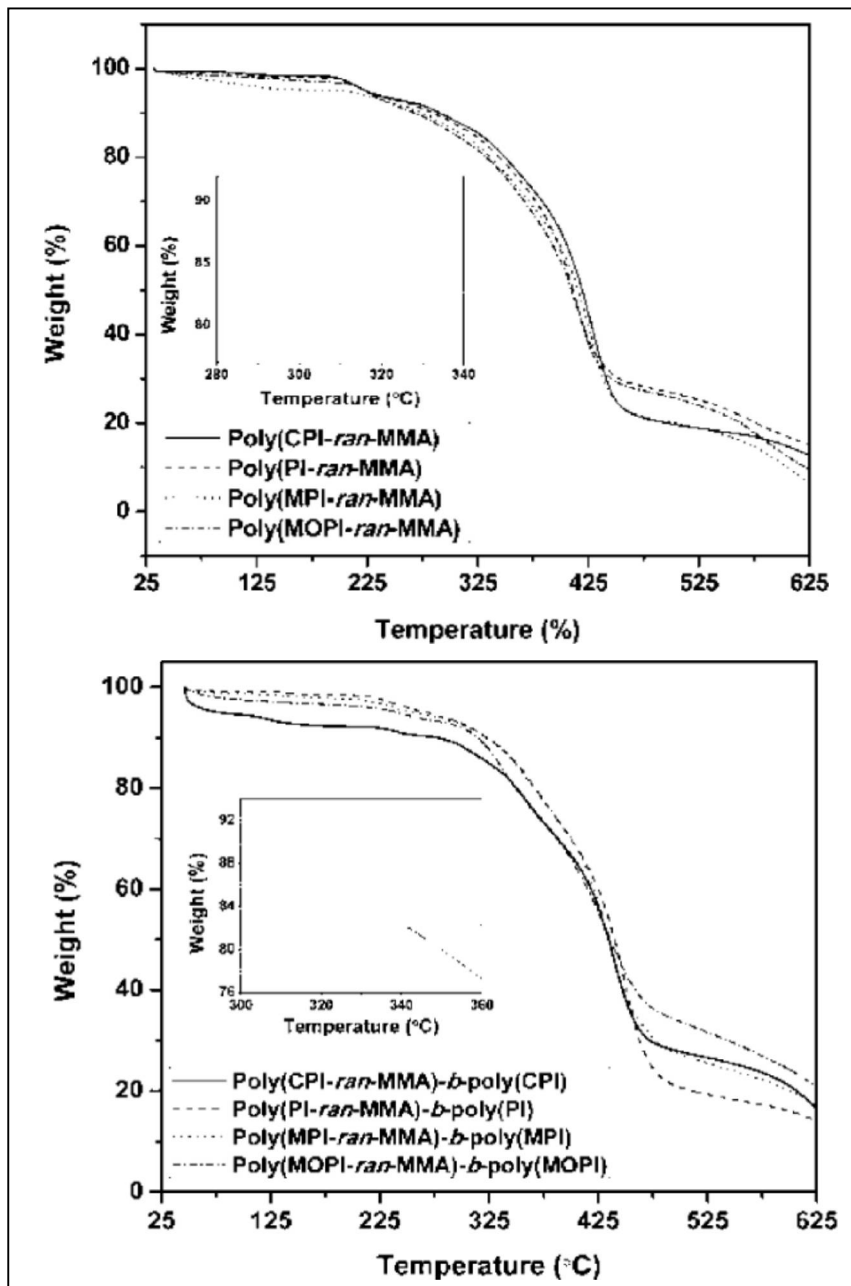


Figure 5: TGA scans of (a) macroinitiators and (b) block copolymers.

CONCLUSION

The copolymers of MMA and NAI monomers with architecture *i.e.* Poly(NAI-*ran*-MMA)-*b*-poly(NAI) have been synthesized using corresponding Poly(NAI-*ran*-MMA) as macroinitiator *via* AGET-ATRP process and characterized. To investigate the effect of pendant groups on the properties of copolymers four different NAI monomers were selected on the basis of electron releasing or electron withdrawing effect of the substituent on aromatic ring. The IR and ¹H-NMR spectroscopy based data shows the incorporation of Poly(NAI) block. The block architecture was further confirmed by the increase in the molecular weight of block copolymers as compared to the corresponding macroinitiator. The experimentally obtained values of molecular weight agreed well with the theoretically calculated values. Both the molecular weights and T_g of copolymers Poly(NAI-*ran*-MMA) as well as Poly(NAI-*ran*-MMA)-*b*-poly(NAI) increased with an increase in the polarity of the pendant group. The polarity and rigidity of the pendant group increased with the increase in electron releasing nature of the substituent. The T_g corresponding to the two blocks *i.e.* Poly(NAI-*ran*-MMA) and Poly(NAI) were observed in the temperature range of 179-182 °C and 242-265 °C, respectively. This results in an overall higher T_g of copolymers synthesized in this study as compared to PMMA which has a softening temperature of ~105 °C. Thus, the living copolymers of NAI and MMA with block architecture were successfully synthesized and characterized. These copolymers with 20-40% increase in softening temperature and 15-20% increase in molecular weight as compared to previously reported copolymers of NAI and MMA may be

useful as 'thermoplastics' in the higher temperature range.

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