



Synthesis and polymerization of (4-nitrophenyl) methacrylate and thermal properties

Roghayeh SOLTANMORADI^{1,*}, Mohammad Hossein NASİRTABRİZİ²

¹ MSc, Department of Chemistry, Payame Noor University, Ardabil, Iran

² Faculty Member, Department of Chemistry, Ardabil branch, Islamic Azad University, Ardabil, Iran

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Abstract. The monomer 4-nitrophenyl methacrylate (NPMA) is synthesized by reaction 4-nitrophenol and methacryloyl chloride. After characterization of this monomer, by IR and ¹HNMR spectroscopic technique. The homo-and copolymers of 4-nitrophenyl methacrylate were synthesized with methyl methacrylate (MMA) and styrene (ST) by free radical polymerization using dimethyl formamide (DMF) as a solvent and azobis isobutyronitrile (AIBN) as an initiator at 70±1°C. The resulting homopolymer and copolymers were characterized by using IR and ¹HNMR spectroscopy. The solubility of the polymers was tested in various polar and non-polar solvents. The thermal behaviour of the present compounds has been determined by means of differential thermal analysis (DTA) and thermogravimetry (TGA) techniques. The glass transition temperature of the poly(NPMA) increase with increase in NPMA content. Thus the thermal stability of the polymers increase with NPMA content.

Keywords: 4-Nitrophenyl methacrylate, radical Polymerization, Thermogravimetric Analysis (TGA)

1. INTRODUCTION

The use of homopolymers and copolymers especially designed with functional active groups as lateral substituents of the main chain is a topic increasing and interest. Copolymerization is the most successful method adopted for the preparation of materials with tailor made properties[1-2]. These kinds of macromolecules possess significant importance from both a fundamental and an applied point of view. Polymers aromatic acrylates and methacrylates are highly reactive monomers due to the presence of the aromatic ring and thus form an interesting class of polymers. Phenyl methacrylates find application in the preparation of many polymeric reagents and as electro - active polymers[3-4]. Photoluminescent behavior was observed for copolymers of phenyl methacrylate with methyl methacrylate [5]. Phenyl methacrylate with activating substituents find application in peptide synthesis [6]. Copolymers of phenyl methacrylates possess thermotropic liquid crystalline properties [7]. Adhesives based on methacrylic copolymers are widely used in wood composites and in the leather industry. Phenyl nitromethacrylates find application in the manufacture of garment leathers the presence of nitro groups in poly(phenyl acrylate) may be expected to affect thermal behavior of these polymers. Poly (phenyl methacrylates) generally possesses high tensile strength, high thermal stability and their glass transition temperature is higher than their corresponding acrylate polymers due to the presence of the α -methyl group on their main chain. So they find widespread application in the preparation of materials such as photo luminescent [8] photo resist [9], adhesives for leather[10], photosensitive[11], biomaterials[12], optical telecommunication materials [13]. Thus copolymerization of 4-nitrophenyl methacrylate(NPMA) with other monomers may also lead to copolymers of quite different thermal behavior. The present work deals with the

*Corresponding author. Email address: Roghayehmoradi220@yahoo.com

synthesis, characterization and determination for the homopolymerization and copolymerization of NPMA with MMA and styrene.

2. EXPERIMENTAL

2.1. Materials

4-nitrophenol obtained from Merck chemical company. The radical initiator of azobis(isobutyronitrile) (AIBN) was purchased from Merck and purified by recrystallization from absolute ethanol. Methyl methacrylate (MMA) and Styrene(ST) were obtained from aldrich and distilled under reduced pressure to remove inhibitors before use. Tetrahydrofuran(THF) was distilled over sodium/ benzophenone. IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer. The NMR spectra were recorded on Bruker AVANCE DMX400 spectrometer, operating at 400 MHz (¹HNMR) and all chemical shifts were reported in ppm relative to tetramethylsilane.

2.2. Synthesis of 4-nitrophenyl methacrylate (NPMA)

For the synthesis of 4-nitrophenyl methacrylate, 4-nitrophenol (1.17g ,0.008mol) and triethylamine (1.02ml ,0.008mol) was added to round-bottom flask containing 2-butanone(10ml). The mixture was heated under reflux for 30 min. Then methacryloyl chloride (1.1ml ,0.01mol) was added drop wise into the flask in such a way that the temperature was maintained around 0°C. The reaction was allowed to proceed for 1 h at 0°C with constant stirring. Then the ice bath was removed and the reaction mixture was stirred at room temperature for a further period of 3 h. The product obtained was filtered, washed with water , %5 NaOH and finally with water. The organic layer was separated and dried over anhydrous Na₂SO₄ .The pure monomer was obtained by recrystallization from methanol. The reaction scheme for the synthesis of NPMA is show in (**Figure 1**).

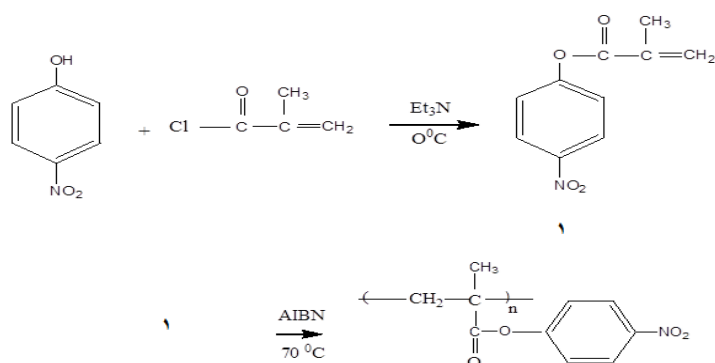


Figure 1. Synthesis of Monomer (NPMA) and Homopolymer.

2.3. Homopolymerization of NPMA

In two-round bottom flask, a mixture of 1.2g (0.0006 mol) of NPMA, 0.01g(0.3×10^{-4} mol) of AIBN was dissolved in 15ml of dried DMF, respectively. The reaction mixture was thoroughly degassed by bubbling N₂ through the solution for 30 minutes. The reaction was carried out at

70°C for 48 hours and methanol was added in excess to precipitate the product. The resulting polymer solution was slowly poured in a large volume of methanol with stirring where the polymer was precipitated out, filtered and washed with methanol. The product was finally dried under vacuum. Figure 1.

3. SYNTHESIS OF COPOLYMERS

3.1. Synthesis of copolymer of poly(NPMA-co-MMA)

In two-round bottom flask, 0.34g (0.002 mol) of NPMA, 0.01g(0.03×10^{-4} mol) of AIBN, 0.5 ml (0.004 mol) MMA was dissolved in 10 ml of dried DMF, respectively. The mixture were thoroughly degassed, sealed under vacuum, maintained at 70°C and shaken by a shaker machine for about 48 h. After this time, the viscous solution were separately poured from the flask into 150 ml of suitable non-solvent. The precipitates were collected, washed with methanol for several times and dried under vacuum at room temperature. **Figure 2.**

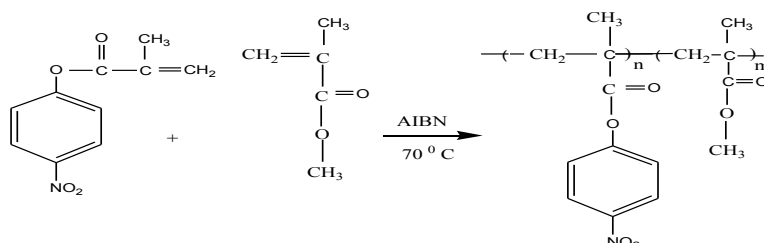


Figure 2. Synthesis of Poly(NPMA-co-MMA)

3.2. Synthesis of copolymer of poly(NPMA-co-ST)

In two-round bottom flask, 0.34g (0.002 mol) of NPMA, 0.01g (0.03×10^{-4} mol) of AIBN, 0.5 ml (0.003 mol) styren was dissolved in 10 ml of dried DMF, respectively. The mixture were thoroughly degassed, sealed under vacuum, maintained at 70°C and shaken by a shaker machine for about 48 h. After this time, the viscous solution were separately poured from the flask into 150 ml of suitable non-solvent. The precipitates were collected, washed with methanol for several times and dried under vacuum at room temperature. Figure 3.

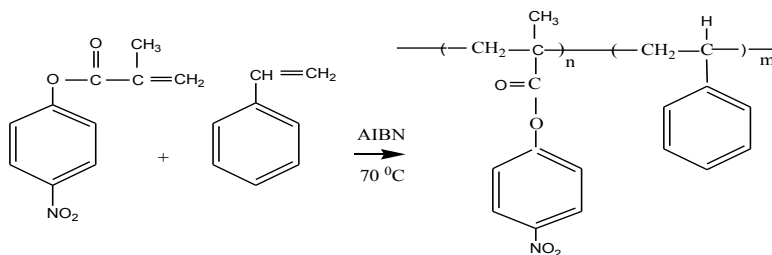


Figure 3. Synthesis of Poly(NPMA-co-ST)

4. RESULTS AND DISCUSSION

4.1. Solubility studies

The solubility of the polymers was tested in various polar and non-polar solvents. About 1-2 mg of the polymer was added to about 2 ml of different solvents in a test tube and the solubility of the polymers was noted after 24 h. The copolymers and homopolymer was soluble in THF, DMF, CHCl_3 but insoluble in hydroxylic solvents ethanol, n-hexen, and water. (**Table 1**)

Table 1. Solubility test of Poly(Npma-co-MMA), Poly(Npma-co-ST) and Homo polymer(Npma) .

Compound	poly(Npma -co - MMA)	poly(Npma-co- ST)	Homo polymer(Npma)
THF	++	++	++
CHCl_3	++	++	++
Ethanol			
DMSO	++	++	++
n-hexene			
Methanol			

4.2. Characterization of Homopolymer

4.2.1. Infrared spectra

The IR spectrum of poly(NPMA) is shown in **Figure 4**. The spectrum shows a peak at 3070 cm^{-1} due to the C-H stretching of the aromatic ring. The peaks at 2900 , 2938 , 2911 and 2177 cm^{-1} are attributed to the asymmetrical and symmetrical C-H stretching of the methylene and methyl groups. The ester carbonyl stretching occurs at 1759 cm^{-1} . The peaks at 1205 and 1012 cm^{-1} are due to the C-O stretching. The aromatic C=C stretching was observed at 1500 and 1452 cm^{-1} . The peaks at 1346 and 1523 cm^{-1} are due to the N=O stretching.

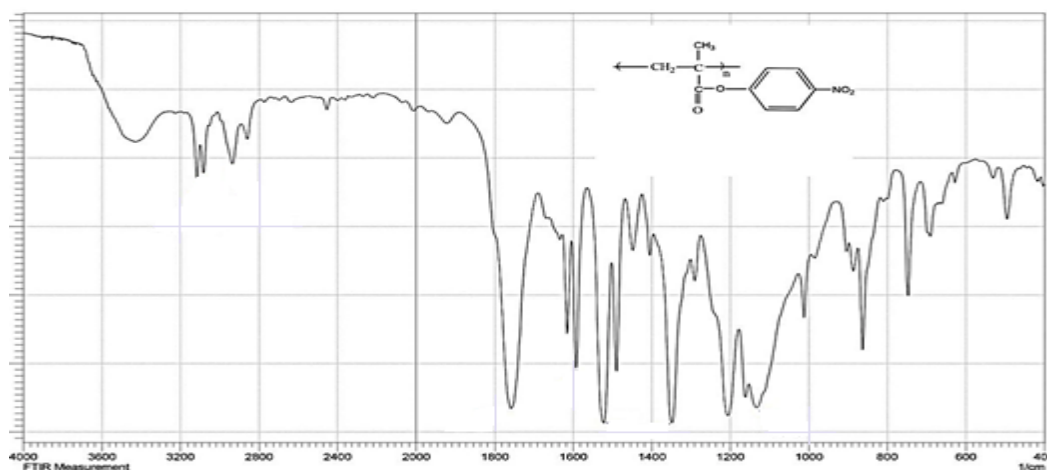


Figure 4. FT-IR spectrum of poly(NPMA)

4.2.2. ^1H NMR spectrum

The ^1H NMR of Poly(NPMA) is shown in **Figure 5**. The spectrum show resonance signals at 7 and 8.03 ppm due to the aromatic protons. The resonance signal 1.60 ppm is due to the backbone methylene protons. The α -methyl protons show resonance signal 1.2 ppm.

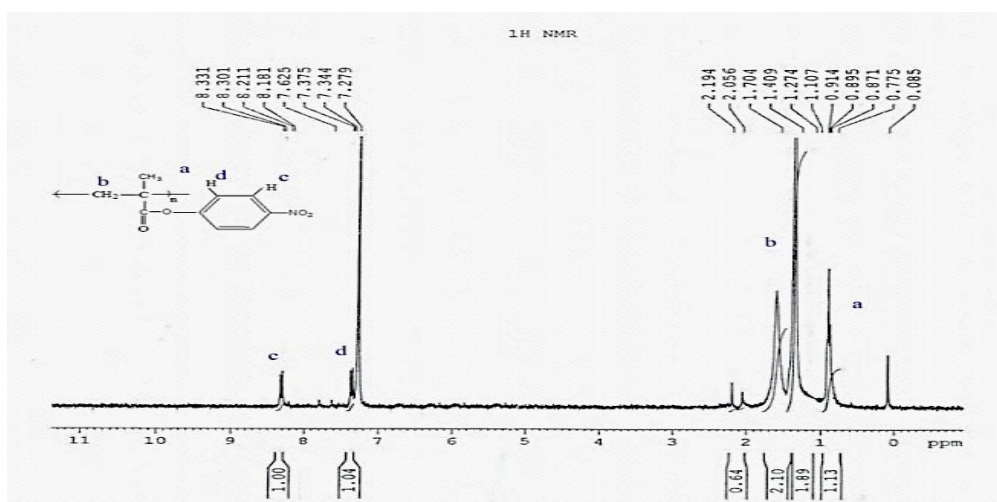


Figure 5. ^1H NMR spectrum of poly(NPMA).

4.3. Characterization of the copolymers

4.2.1. Infrared spectra

The IR spectrum of poly(NPMA-co-MMA) is shown in Figure 6. The peak at 1728 cm^{-1} is attributed to the ester carbonyl. The peaks at 1348 and 1528 cm^{-1} are due to the $\text{N}=\text{O}$ stretching. The bands at 1112 and 1205 cm^{-1} which may be due to $\text{C}-\text{O}$ stretching vibration of ester group. bands at 1490 and 1595 cm^{-1} correspond to aromatic $\text{C}=\text{C}$ stretching. The spectrum show a peak at 3082 cm^{-1} due to the $\text{C}-\text{H}$ stretching of the aromatic ring. The peaks at 2995 and 2177 cm^{-1} are attributed to symmetrical $\text{C}-\text{H}$ stretching of the methylene and methyl groups.

The IR spectrum of poly(NPMA-co-ST) is shown in Figure 7. The aromatic($=\text{C}-\text{H}$) stretching was observed at 3082 cm^{-1} . The $\text{C}-\text{H}$ stretching due to the methyl and methylene groups were observed at 2927 cm^{-1} and 2950 cm^{-1} . The carbonyl stretching due to the ester group was observed at 1759 cm^{-1} . The aromatic $\text{C}=\text{C}$ stretching were observed at 1593 and 1490 cm^{-1} . The $\text{C}-\text{O}$ stretching due to the ester group was observed at 1013 and 1205 cm^{-1} .

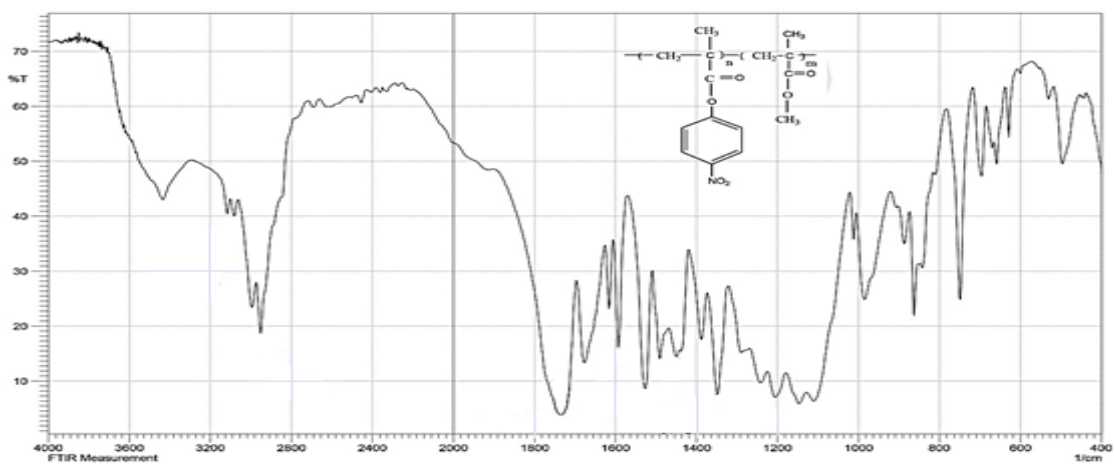


Figure 6. FT-IR spectrum of poly(NPMA-co-MMA).

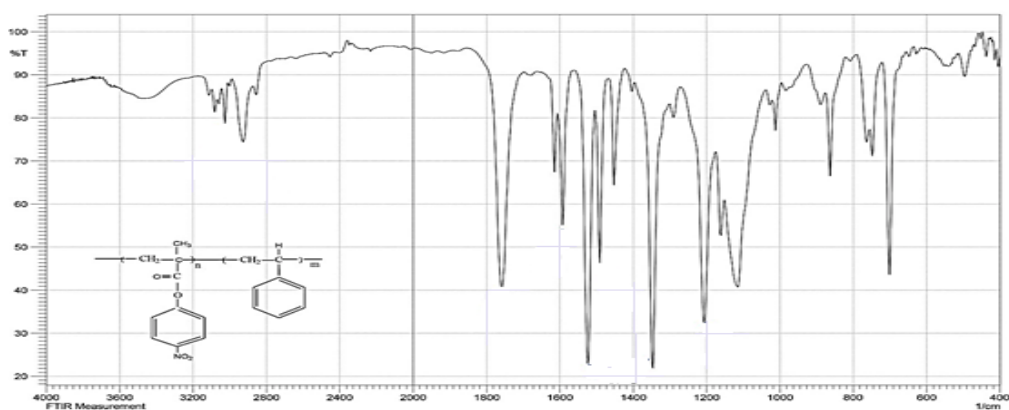


Figure 7. FT-IR spectrum of poly(NPMA-co-ST).

4.2.2. ^1H NMR spectrum

The ^1H NMR of Poly(NPMA-co-MMA) is shown in Figure 7. The spectrum shows resonance signals at 7 and 8.4 ppm due to the aromatic protons. The resonance signal at 2 ppm is due to the backbone methylene protons. The α -methyl protons show resonance signal 1.02ppm. The resonance signal at 3.60 ppm was attributed to three methyl protons of $-\text{COOCH}_3$ in copolymers and MMA.

The ^1H NMR of Poly(NPMA-co-ST) is shown in Figure 8. The spectrum shows resonance signals at 7 and 8.42 ppm due to the aromatic protons. The resonance signal at 1.35 and 2.20 ppm are due to the backbone methylene protons. The α -methyl protons show resonance signal 1.04ppm.

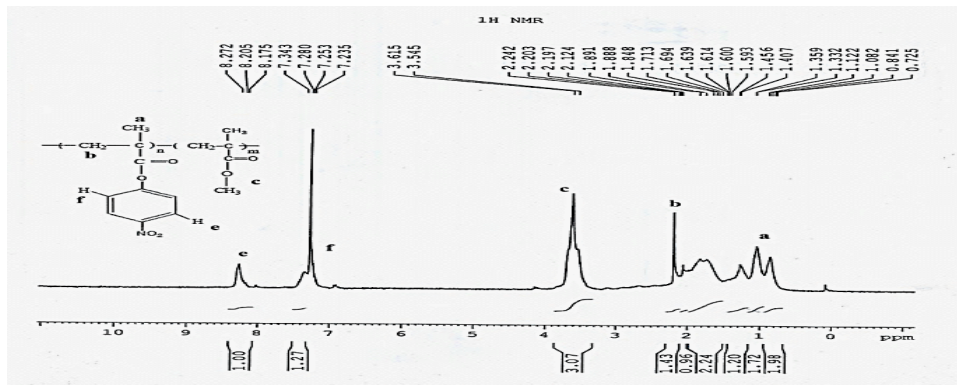


Figure 8. ¹H NMR spectrum of poly(NPMA-co-MMA)

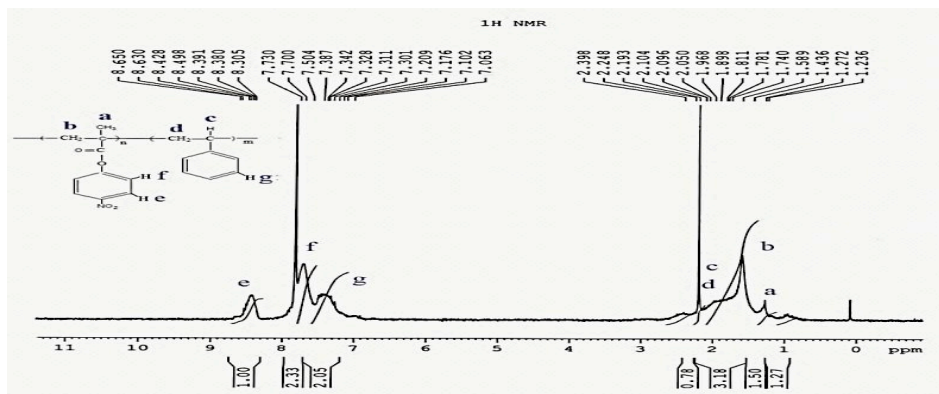


Figure 9. ¹H NMR spectrum of poly(NPMA-co-ST)

5. GLASS TRANSITION TEMPERATURES

The glass transition temperature (T_g) of the homopolymer and copolymers was determined by DTA are shown in Figure 9. The T_g of poly(NPMA) is 195°C and that of poly (NPMA-co-MMA) is 175°C and of poly(NPMA-co-ST) is 123°C. Results clearly indicate that the thermal stability of the poly(NPMA) increases with rising NPMA content in the polymer. Study of DTA of copolymers indicated that the presence of bulky nitrophenol in polymer structure increases the polymers rigidity with increasing glass transition temperature and creates polymers with vast applications industry. The T_g and TGA polymers are given in table 1.

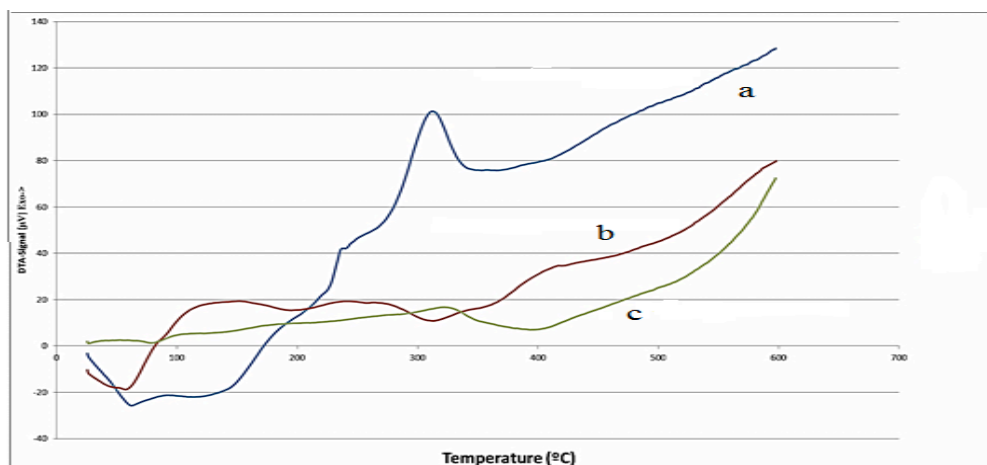


Figure 10. DTA curves (a)poly(NPMA);(b)poly(NPMA-co-MMA);(c)poly(NPMA-co-ST)

6. THERMOGRAVIMETRIC ANALYSIS

TGA curves for poly(NPMA), poly(NPMA-co-MMA) and poly(NPMA-co-ST) are shown in Figure 10. All the polymers reported here undergo decomposition in a two-stage process. The first stage of Poly(NPMA-co-MMA) occurred around 211°C with the onset temperature ($T_{5\%}$ temperature of 5% weight loss). After 4-nitrophenol was dissociated from the compound. The initial decomposition of poly(NPMA), poly(NPMA-co-MMA) and poly(NPMA-co-ST) are 190, 211 and 140°C.

Table 2. TGA and Tg data for poly(NPMA-co-MMA), Poly(NPMA-co-ST), and Homo polymer(NPMA)

Compound	T5	T10	Tmax	Tg
Poly(NPma-CO-MMA)	211	267	330	175
Poly(Npma-CO-ST)	140	251	355	123
Homo Polymer (Npma)	190	214	260	195

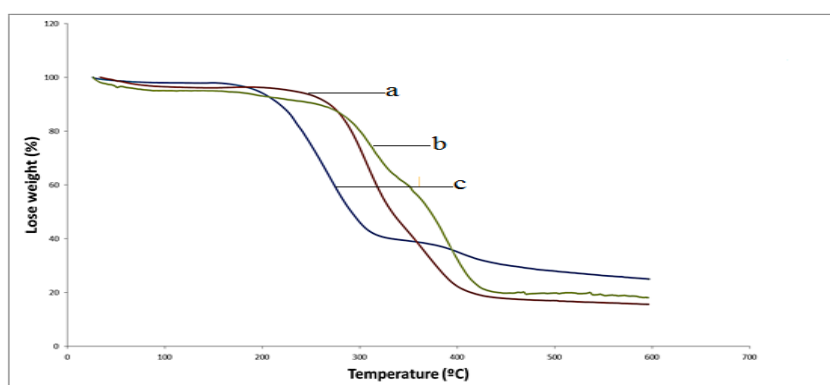


Figure 11. TGA curves(a)poly(NPMA-co-MMA);(b)poly(NPMA-co-ST);(c)poly(NPMA)

10. CONCLUSIONS

The copolymers of NPMA with MMA and ST and homopolymer NPMA were synthesized by free radical solution polymerization techniques. Characterization of poly (NPMA-co-MMA), poly (NPMA-co-ST) and Homopolymer were performed by FT-IR and ¹HNMR techniques. The homopolymer and copolymers are soluble in tetrahydrofuran, chloroform, dimethyl formamide and insoluble in n-hexene and hydroxyl-groups containing solvents such as methanol, ethanol and water. Thermogravimetric analysis indicated that the thermal stability of the polymers increases with the increase of NPMA units in the polymers. The glass transition temperature of the homopolymer increases with NPMA content.

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