



## Synthesis, Homopolymerization and Copolymerization of 9-antril methyl metacrylate and $\beta$ -naphthyl metacrylate

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**Abstract.** 9-antril methyl metacrylate is synthesized by reaction of 9-anthracene methanol and methcryloyl chloride in the peresence of Et<sub>3</sub>N in THF as solvent. After characterization of this monomer, by IR and NMR spectroscopic technique, we report the homopolymerization and copolymerization 9-antril methyl metacrylate using the reaction of styrene in the presence of AIBN as initiator. The structure of all target compounds was characterized by spectral analyses. The thermal behavior of the polymers is studied by TGA.

**Keywords:** 9-anthracene methanol, methcryloyl chloride, Copolymerization,  $\beta$ -naphthol

### 1. INTRODUCTION

The use of homopolymers and copolymers particularly designed with functional groups as substituents of the main chain is a topic steadily increasing activity. Because of substitution of the methyl group the main chain restricts the degree of rotation and motion of the polymer backbone. Aromatic acrylates and methacrylates copolymers are widely used in various applied areas [1-8]

4-Nitrophenyl methacrylate family copolymers are versatile used in various applied areas [9-11] Such as paint materials [12] adhesives for leather [13], inhibition of corrosion metals in acidic medium [14, 15]. Methyl methacrylate containing copolymers exhibit interesting characteristics such as thermal stability [16], electroactive properties [17], Antimicrobial [18]. For example Glycidyl methacrylate (GMA) use in industrial such pharmaceutical usage in drug delivery [19]. Also phenyl acrylates reported glass top coats for automobile [20].

The present article describes the synthesis, characterization, and thermal properties of copolymers of 4-benzoylphenyl methacrylate with methyl methacrylate. Monomer reactivity ratios are very important parameters which can offer information about relative reactivity of monomer pairs, elucidation of copolymer structure, copolymer composition and monomer sequence distribution. The monomer reactivity ratios of the comonomers are also reported.

### 2. EXPERIMENTAL

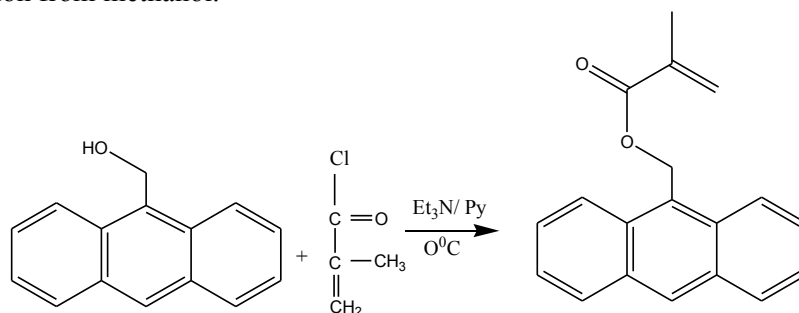
#### 2.1. Materials

Chemicals were purchased from Fluka, Merck and Aldrich Chemical companies. All commercially available chemicals and reagents were used without further purification. FT-IR spectra were recorded on a Shimadzu 8400S spectrophotometer. The NMR spectra were recorded on a Bruker AVANCE DMX400 spectrometer, operating at 400 MHz (<sup>1</sup>H NMR) and 100 MHz (<sup>13</sup>C NMR). The chemical shift values are expressed in ppm relative to TMS as an internal standard.

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## Synthesis of 9-anthryl methyl metacrylate monomer:

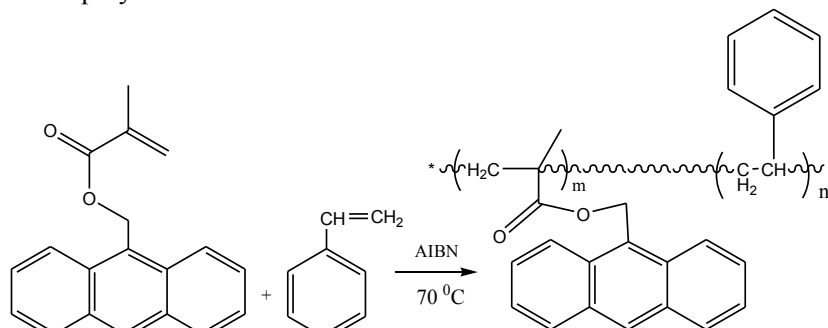
Methacryloyl chloride (0.01 mol, 1.1 g) and 9-anthracene methanol (0.007 mol, 1.5 g) was added to round-bottom flask containing THF as solvent (10 mL). The mixture was stirred in ice-bath for 1 hour. Then pyridine (1 mL) and  $\text{Et}_3\text{N}$  (1.5 mL) were added and stirring was continued for 1hrs in room temperature. The progress of the reaction was monitored by TLC. After completion, the mixture was extracted with  $\text{Et}_2\text{O}$  (30 mL) and washed with  $\text{NaHCO}_3$  and  $\text{HCl}$ . The product was evaporated to dryness. The pure monomer was obtained as yellowish crystal by recrystallization from methanol.



**Scheme 1.** Synthesis of 9-anthryl methyl metacrylate monomer

## Preparation of 9-anthryl methyl metacrylate -styrene copolymer:

To a stirred solution of styrene (0.002 mol, 0.3 mL) and 9-anthryl methyl metacrylate monomer (0.34 g, 0.001 mol) in DMF (10 mL) was added AIBN (0.0001 mol, 0.03 g) under  $\text{N}_2$  (as inert atmosphere) and the mixture was heated to  $70^\circ\text{C}$  for 48hrs. After completion of the reaction, as indicated by TLC, the mixture was dropwise poured into cold methanol (20 mL). The synthesized copolymer was filtered and washed with methanol and then dried in vacuum.

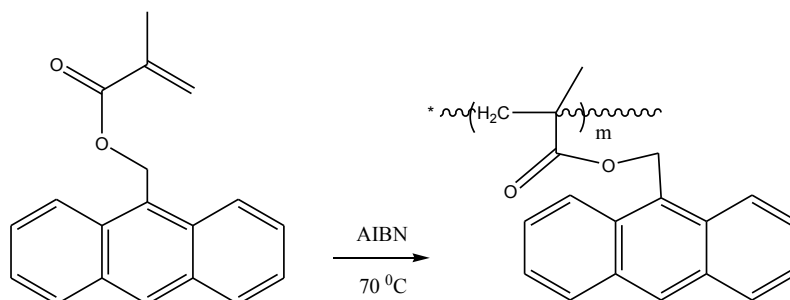


**Scheme 2.** Synthesis of copolymer (Npma-co-MMA)

## Homopolymerization of 9-anthryl methyl metacrylate:

Homopolymer was prepared by the reaction of poly anthryl methyl methacrylate (0.0009 mol, 0.26 g) with AIBN (0.0001 mol, 0.03 g) as initiator catalyst in DMF (10 mL) for 48 hrs at  $70^\circ\text{C}$  in  $\text{N}_2$  atmosphere. After completion of reaction (controlled by TLC), the mixture slowly pour into cold methanol. Homopolymer synthesized were filtered, washed several times and the dried.

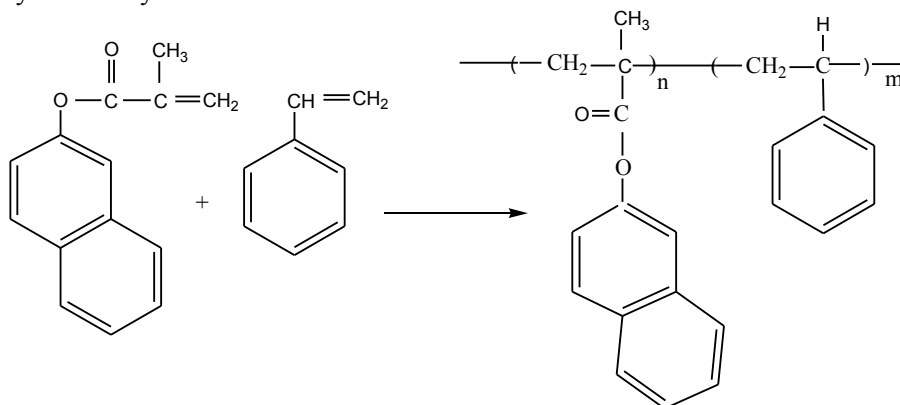
## Synthesis, Homopolymerization and Copolymerization of 9-anryl methyl metacrylate and $\beta$ -naphthyl metacrylate



**Scheme 3.** Preparation of Homopolymerization of 9-anryl methyl metacrylate

### Preparation of $\beta$ -naphthyl methacrylate-styrene copolymer:

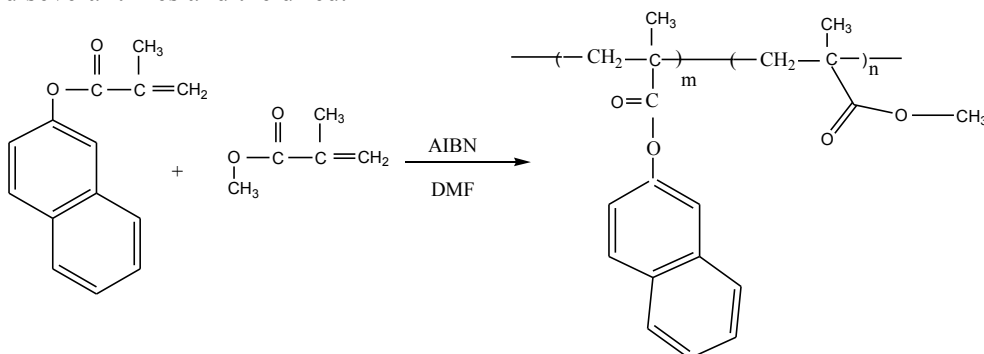
To a stirred solution of  $\beta$ -naphthyl methacrylate monomer (0.003 mol, 0.66 g) and styrene (0.006 mol, 0.8 mL) in DMF, AIBN (0.0004 mol, 0.08 g) was added under inert atmosphere and then mixture was heated to 70°C for 42 hrs. Target copolymer was prepared in a similar way from methyl methacrylate.



**Scheme 4.** Synthesis of copolymer (Npma-co-ST)

### Preparation of $\beta$ -naphthyl methacrylate-methyl metacrylate copolymer:

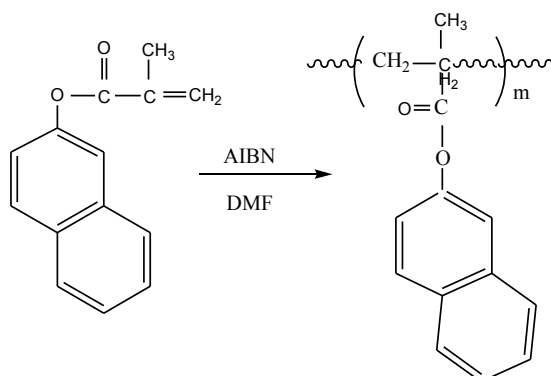
$\beta$ -naphthyl methacrylate monomer (0.002 mol, 0.44 g), methyl methacrylate (0.004 mol, 0.5 mL) and AIBN (0.0003 mol, 0.05 g) were added simultaneously to a round-bottom flask containing DMF under  $N_2$  atmosphere (10 mL). The mixture was under reflux for the 48 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture slowly pours into cold methanol. White powder copolymer synthesized were filtered, washed several times and the dried.



**Scheme 5.** Synthesis of copolymer (Npma-co-ST)

### Homopolymerization of $\beta$ -naphthyl methacrylate

Homopolymer was prepared by the reaction of  $\beta$ -naphthyl methacrylate monomer (0.003 mol, 0.66 g) with AIBN (0.0004 mol, 0.08 g) as initiator catalyst in DMF (10 mL) for 48 hrs at 70°C in N<sub>2</sub> atmosphere. After completion of reaction (controlled by TLC), the mixture slowly pour into cold methanol. White powder homopolymer synthesized were filtered, washed several times and the dried.



**Scheme 6.** Synthesis of homopolymer  $\beta$ -naphthyl methacrylate

Figure 1, represents the IR spectrum monomer and copolymers. The IR spectrum of monomer showed absorption bands due to the C=C of the alkene at 1631 cm<sup>-1</sup> and the C=O ester group at 1743 cm<sup>-1</sup>. Preparation of copolymer confirmed by disappearance of C=C absorption in the IR spectra of copolymer. The corresponding <sup>1</sup>HNMR spectra of copolymer showed a singlet (3H) for CH<sub>3</sub> at  $\delta$  1.02, a broad band (2H) for CH<sub>2</sub> at  $\delta$  2-2.30 and a singlet (3H) for O-CH<sub>3</sub> at 3.6 ppm, respectively.

The <sup>1</sup>HNMR spectrum of copolymer 2 did not show any -C=CH<sub>2</sub> couplag constant due to the information of copolymer cross chain band. Figure 2, represents the <sup>1</sup>HNMR spectrum monomer and copolymers.

## 2.2. Solubility studies

Solubility of the polymers, copolymers and homopolymers were tested in various polar and non-polar solvents 0.05 g of the polymer was added to 1 mL of the solvent test tube and remained for 24 h at room temperature. The homopolymer and copolymers were soluble in acetone, chloroform, DMSO and THF. It is insoluble in n-hexan, methanol and ethanol. The solubility polymers are shown in table 1 and Table 2.

**Table 1.** Solubility test of Poly(AMM-CO-MMA), Poly(AMMA-co-ST) in various solvents.

Compound	POLY(Npma -CO - MMA)	POLY(Npma -CO- ST)
Solvent		
CHCl <sub>3</sub>	++	++
THF	++	++
DMSO	++	++
n-hexene		-
Ethanol		
Methanol		
Accone	++	++

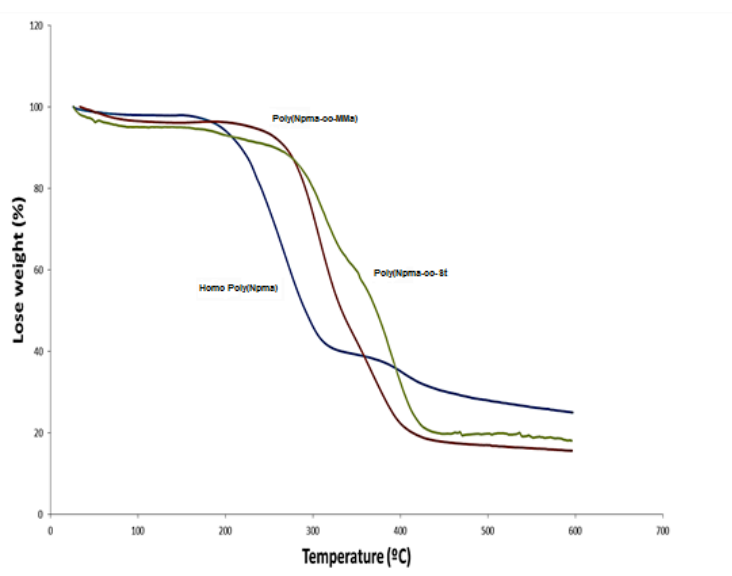
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**Table 2.** Solubility test of  $\beta$ -naphthyl meta crylate copolymers and homopolymers with styrene and methyl metacrylate in various solvents.

Compound	POLY(BNMA-co-MMA)	POLY(BNMA-co-ST)	Homopolymer (BNMA)
Solvent			
CHCl <sub>3</sub>	++	++	++
THF	++	++	++
DMSO	++	++	++
n-hexene			
Ethanol			
Methanol			
Accone	++	++	++

### Glass transition temperature and thermogravimetric analysis

Thermal properties of prepared polymers were carried out by thermo gravimetric analysis. The relevant values and thermograms showed in table 2,3 and figure3. In this investigation, the samples were heated from 25°C to 600°C. For example, Poly(BNMA-CO-MMA) decomposed at 201°C and ended at 290°C. Tg of Homo polymer BNMA exhibit more than compared to Tg of copolymers.



**Figure 3.** TGA data for Poly(Npma-CO-MMA), Poly(Npma-co-ST) and Homo polymer (Npma).

**Table 3.** Tg for Poly(BNMA-CO-MMA), Poly(BNMA-co-ST) and Homo polymer (BNMA).

Compound	T <sub>g</sub>
Poly(BNMA-CO-MMA)	140
Poly(BNMA-CO-ST)	145
Homo polymer BNMA	210

**Table 4.** TGA data for Poly(BNMA-CO-MMA), Poly(BNMA-co-ST) and Homo polymer (BNMA).

Compound	T <sub>5</sub>	T <sub>10</sub>	T <sub>max</sub>
Poly(BNMA-CO-MMA)	201	290	375
Poly(BNMA-co-ST)	203	335	397
Homo Polymer (BNMA)	300	320	365

### 3. CHARACTERIZATION DATA FOR SOME TARGET COMPOUNDS

#### 9-Antryl methyl metacrylate monomer:

Yield 84%, yellow crystal; mp 184-186 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): 1.55-1.77 (CH<sub>3</sub>), 5.88 (OCH<sub>2</sub>), 6.35 (CH<sub>2</sub>), 7.27-7.79 (CH of aromatic) ppm; FT-IR (KBr, cm<sup>-1</sup>) ν<sub>max</sub>: 3055 (C-H, aromatic), 2980 (C-H, aliphatic), 1712 (C=O), 1672 (C=C, aliphatic), 1404, 1624 (C=C, aromatic), 1197 (C-O).

#### 9-Antryl methyl metacrylate -styrene copolymer:

Yield 84%, white powder; mp 184-186 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): 1.0-1.57 (CH<sub>3</sub>, CH<sub>2</sub>), 2.02 (CH), 5.89 (OCH<sub>2</sub>), 7.27-7.75 (CH of aromatic) ppm; FT-IR (KBr, cm<sup>-1</sup>) ν<sub>max</sub>: 3003 (C-H, aromatic), 2927 (C-H, aliphatic), 1716 (C=O), 1456, 1662 (C=C, aromatic), 1095 (C-O).

#### 9-Antryl methyl metacrylate homopolymer:

Yield 84%, white powder; mp 184-186 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): 1.58-1.97 (CH<sub>3</sub>, CH<sub>2</sub>), 5.90 (OCH<sub>2</sub>), 7.27-7.83 (CH of aromatic) ppm; FT-IR (KBr, cm<sup>-1</sup>) ν<sub>max</sub>: 3062 (C-H, aromatic), 2989 (C-H, aliphatic), 1718 (C=O), 1448, 1660 (C=C, aromatic), 1174 (C-O).

#### β-naphthyl methacrylate-styrene copolymer:

Yield 84%, cream powder; mp 184-186 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): 1.70-2.06 (CH<sub>3</sub>, CH<sub>2</sub>), 2.69-2.90 (CH), 7.01-7.71 (CH of aromatic) ppm; FT-IR (KBr, cm<sup>-1</sup>) ν<sub>max</sub>: 3057 (C-H, aromatic), 2922 (C-H, aliphatic), 1751 (C=O), 1452, 1629 (C=C, aromatic), 1132 (C-O).

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