



## Synthesis and Characterization of Functional Acrylic Copolymers of Acrylonitrile and N-Phenyl Methacrylamide

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### ABSTRACT

Functional monomer, N-phenyl methacrylamide (PMA) was synthesized by reacting methacryloyl chloride with aniline and its copolymers with acrylonitrile (AN) in various feed ratios were synthesized using free radical initiator (benzoyl peroxide) in N,N-dimethylformamide at 70°C. Copolymer structure was elucidated by infrared and proton nuclear magnetic resonance spectroscopy. The copolymer composition was determined from the corresponding <sup>1</sup>H NMR spectra of the copolymers. The relative reactivity of PMA and AN were determined by Finemann–Ross and Kelen–Tudos methods. Intrinsic viscosity was calculated for all the copolymers in dimethylformamide. Thermal characterization of the copolymers was carried using thermo gravimetric analysis. Activation energy for degradation of the copolymers was determined by Briado and Horowitz's methods.

**Key words:** N-phenyl methacrylamide, Acrylonitrile, Free radical solution Copolymerization, Reactivity ratios.

### 1. INTRODUCTION

Copolymerization is the most general and powerful method of effecting systematic changes in polymer properties and is widely used in the production of commercial polymers and fundamental investigation of the structure – property relations. Copolymers can be tailored depending on the desired properties by changing the monomers, monomer compositions, and techniques of copolymerization. Hence, copolymers found extensive uses in various fields of applications in different ways. The detailed study of microstructure and compositional heterogeneity of copolymers is of great importance in considering the copolymer properties, which is particularly important in designing sophisticated polymer materials for special purposes.

Knowledge of the copolymer composition is an important step in the evaluation of its utility. The copolymer composition and its distribution depend on the reactivity ratios. Reactivity ratios for copolymerizing monomers have become essential in the prediction of types of monomers that will combine to make polymers and in determining the regularity of such polymeric materials. Reactivity ratios are the most important parameters for composition evaluation of copolymers, which can offer information such as relative reactivity of monomer pairs and estimate the copolymer composition. The design of copolymer

with special characteristics has always been a research field of both industrial and academic interest.

Copolymerization of acrylonitrile (AN) with vinyl acetate and sodium methallylsulfonate was investigated by Qui et al. [1] copolymerization of 2-(3-mesityl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate with AN was reported by Kadir et al. [2] poly(acrylonitrile-co-p-trimehtylsilylstyrene) synthesis and its properties were evaluated by Khotimsky et al. [3] Sanghvi et al. [4] discussed the sequence distribution of monomers in styrene-AN copolymers synthesized in microemulsion medium. Radiation initiated copolymerization of AN with allyl glycidyl ether [5] and allyl alcohol [6] was reported. Simionescu et al. [7] studied the synthesis of the copolymers based on AN with methyl styrene/vinyl acetate. Kim et al. [8] copolymerized AN with a diethyl carboxy vinyl phosphate using benzoyl peroxide (BPO) as an initiator in dimethylformamide. Copolymer systems of n-acryloxy phthalimide with methyl acrylate/methyl methacrylate/AN were synthesized and characterized by Shabban et al. [9] Alfrey et al. [10] studied the rate of copolymerization of AN and ethylene-sulfonic acid in aqueous zinc chloride solution. Copolymerization of methacrylic acid with methacrylonitrile was studied by Cameron et al. [11] Witnauer et al. [12] synthesized the copolymer of AN and ethylene sulfonic acid system and

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determined the reactivity ratios using the copolymer composition determined by elemental analysis. Copolymers of phenyl methacrylamide with methyl methacrylate, acrylamide, glycidylmethacrylate, and ethylmethacrylate were reported by Jayasimha Reddy et al. [13-16].

Basing on the above literature, functional acrylic copolymers containing N-phenyl methacrylamide (PMA) and acrylonitrile monomers were synthesized by free radical solution copolymerization and their characterization was presented in this paper. Structure of the copolymers was elucidated using infrared and nuclear magnetic resonance techniques. For the purpose of the determination of relative reactivity of the monomers, reactivity ratios were determined by linear methods such as Fineman–Ross (F-R) and Kelen–Tudos (K-T) methods. Thermal properties such as thermal stability, glass transition temperature, and activation energy for the degradation of the copolymers of the copolymers were determined by differential scanning calorimetry and thermo gravimetric analysis (TGA).

## 2. EXPERIMENTAL METHODS

### 2.1. Materials

Methacrylic acid (Merck), benzoyl chloride (S.D. Fine Chem.), and Aniline (Merck) triethylamine (S.D. Fine Chem.) were purified according to standard procedures [17]. Methacryloyl chloride was prepared by Gudio et al. [18] using the methacrylic acid and benzoyl chloride. AN (Merck) was recrystallized to remove the inhibitor and impurities. BPO (Merck) has been recrystallized from chloroform:methanol (1:1) mixture used as initiator. The solvents were purified by distillation.

### 2.2. Synthesis of PMA

Aniline (0.1 mol), triethylamine (0.12 mol) and ethyl methyl ketone (100 ml) were taken in a 250 ml round bottom flask equipped with a magnetic stirrer, dropping funnel, and thermometer. The reaction mixture was cooled to 0-4°C using ice and salt mixture. Then, 0.12 mol of methacryloyl chloride in ethyl methyl ketone (50 ml) was added drop-wise to the reaction mixture over a period of 1 h while maintaining the temperature of the reaction mixture at 0-5°C. After the addition, the reaction mixture was stirred for 1 h at the same temperature, and then at room temperature for 4 h. After removing the formed solid quaternary ammonium salt, the solution was transferred to a separating funnel, washed thoroughly with 5% sodium hydroxide solution, dilute hydrochloric acid and water, respectively, and then dried over anhydrous sodium sulfate. On evaporation of the solvent, solid phenyl methacrylamide was obtained. It was washed with petroleum ether and recrystallized in ethanol-water mixture. The formation of PMA was confirmed by IR and <sup>1</sup>H NMR spectroscopic techniques. Yield: 68%.

### 2.3. Copolymerization of PMA and AN

Polymerizations were carried out in pyrex glass tubes containing an inlet and outlet for the passage of nitrogen. The copolymers were synthesized using PMA and AN. The copolymerization has been carried out in N,N-dimethylformamide at 70°C using BPO as initiator by varying the feed ratio of the monomers. Predetermined quantities of monomers, initiator and solvent, were mixed in a reaction tube and nitrogen gas was passed for 20 min and sealed the tubes in order to ensure the inert atmosphere in the polymerization tubes. The sealed tubes were kept in the water bath maintained at 70 ± 0.1°C. In order to maintain the copolymer composition in the same ratio throughout the polymerization, the molar conversion of monomer to polymer was restricted to less than 10% by precipitating the polymerization mixture in water at an appropriate time. Pouring the reaction mixture into the nonsolvent stops the polymerization and precipitated polymer was filtered. All the copolymers were purified by dissolving in N,N-dimethylformamide and reprecipitated in water. The same was repeated for three times and finally dried under vacuum at room temperature for 3 days.

### 2.4. Characterization Methods

IR spectra of the monomer and polymers as KBr pellet or in chloroform solution were recorded on a Perkin Elmer 983 G infrared double beam spectrophotometer. High resolution <sup>1</sup>H NMR spectra were obtained with a Bruker 500 MHz FT-NMR spectrometer at room temperature in CDCl<sub>3</sub>/DMSO(d) solution for all the copolymers and PMA. The intrinsic viscosities of the copolymers were determined using Ubbelohde viscometer. TGA of the copolymers has been carried out using a Shimadzu DT 50 thermal analyzer. Thermograms were recorded in the nitrogen atmosphere at a heating rate of 10°C/min. The glass transition temperature of the copolymers and homopolymer were measured using Shimadzu DT 50 differential scanning calorimeter at a heating rate of 10°C/min in the nitrogen atmosphere.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Characterization of Poly (phenyl methacrylamide)

The IR spectrum of poly (PMA) exhibits bands around 3392 (broad), 987 and 750 cm<sup>-1</sup> which are due to N-H stretching, N-H wagging and out of plane N-H bendings, respectively. The absorptions at 1660 cm<sup>-1</sup> are assignable to amide carbonyl (C=O) stretchings. The peak at 1324 cm<sup>-1</sup> may be due to the amide C-N stretching (Scheme 1).

The <sup>1</sup>H NMR spectrum of poly (PMA) shows peak at 9.0 ppm corresponds to the N-H proton. The aromatic protons are observed as a multiplet at 7.0-7.6 ppm. A singlet at 2.6 ppm may be due to backbone methylene (CH<sub>2</sub>) protons. Peaks at 0.8-1.2 ppm due

to  $\alpha$ -CH<sub>3</sub> protons indicate the presence tacticity in the polymer chain.

The number- and weight-average molecular weights and molecular weight distribution of PMA, determined by gel permeation chromatography, were 34, 340, 69, 700, and 2.030, respectively.

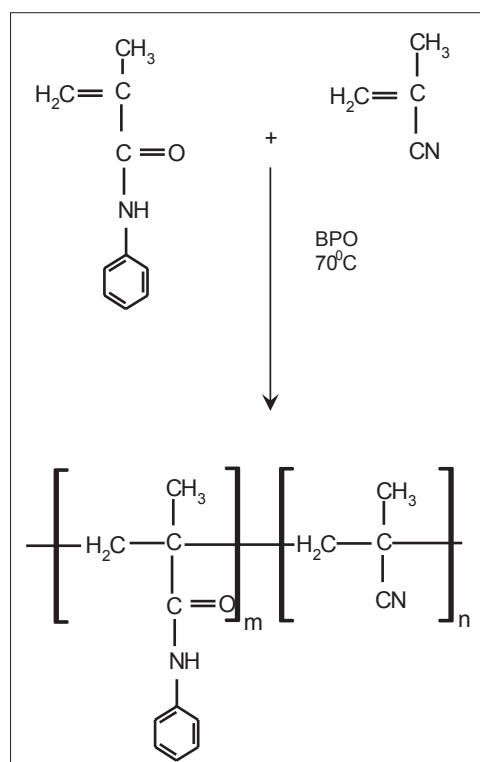
### 3.2. Copolymer Characterization

#### 3.2.1. Solubility

The copolymers containing different amount of PMA and AN are soluble in chloroform, dimethylsulfoxide, dimethylformamide, tetrahydrofuran, ethyl methyl ketone, and insoluble in hexane, heptane, petroleum ether, and water.

#### 3.2.2. Infrared spectra of PMA-AN copolymers

IR spectrum of the PMA-AN copolymer (Figure 1) exhibits bands at 3317, 927 and 751 cm<sup>-1</sup> which are due to N-H stretching, N-H wagging and out of plane N-H bending, respectively. A strong absorption peak at 2226 cm<sup>-1</sup> is attributed to the nitrile group. The absorption at 2898 cm<sup>-1</sup> indicates C-H stretching of CH<sub>3</sub> group. The absorption at 1597 cm<sup>-1</sup> is assigned to carbonyl stretching of amide moiety. The absorptions at 1497 and 1436 cm<sup>-1</sup> are due to the C-H scissoring and terminal CH<sub>2</sub> scissoring, respectively. The peak at 1386 cm<sup>-1</sup> is due to the C-N stretching of amide.



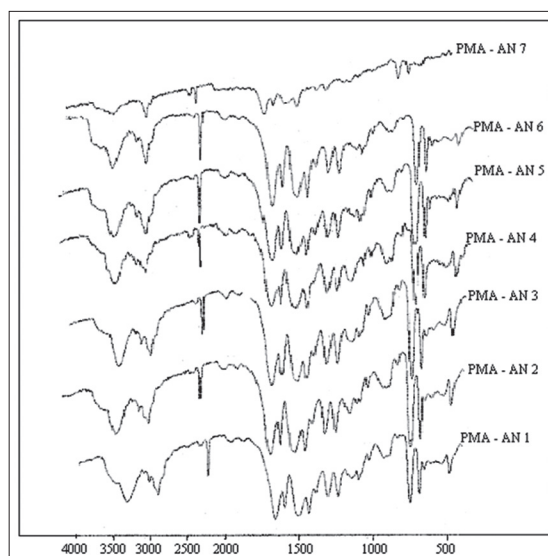
**Scheme 1:** Copolymerization of N-phenyl methacrylamide and acrylonitrile.

#### 3.2.3. <sup>1</sup>H NMR spectra of PMA-AN copolymers

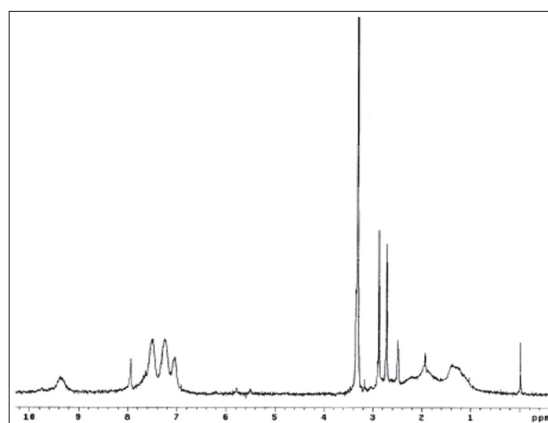
The proton nuclear magnetic resonance spectra of PMA-AN copolymer with composition is presented in Figure 2. The aromatic protons of PMA are observed as multiplet in the range of 7.0-7.8 ppm. Singlets at 3.2 ppm infer the presence of CH<sub>3</sub> group protons of PMA. The signals in between 2.3 and 2.9 are due to the backbone protons of both the monomeric units. The signals in between 0.8 and 1.2 ppm show the presence of  $\alpha$ -CH<sub>3</sub> protons of both the monomeric units.

#### 3.3. Copolymer Composition of PMA-AN Copolymers

The average composition of the copolymers of PMA and AN at different feed ratios is determined using <sup>1</sup>H NMR spectroscopy. The assignment of resonance peaks allows accurate determination of the content of the each kind of the monomeric unit incorporated into the copolymer chain. Thus, the mole fraction of the PMA in the copolymer chain is determined from



**Figure 1:** IR spectra of N-phenyl methacrylamide-acrylonitrile copolymers.



**Figure 2:** <sup>1</sup>H NMR spectrum of copolymer N-phenyl methacrylamide-acrylonitrile.

the integrated intensities of aromatic protons of PMA and intensity of aliphatic protons present in both the monomeric constituents in the copolymer.

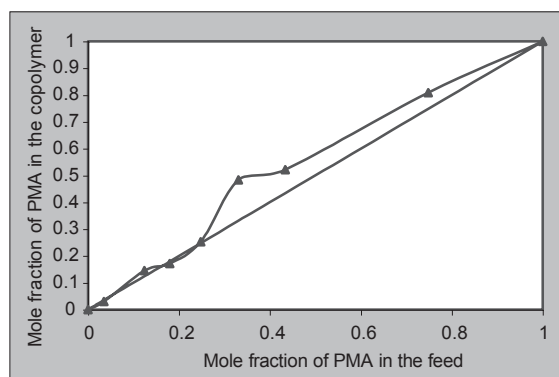
Let “ $m_1$ ” be the mole fraction of PMA and “ $(1-m_1)$ ” that of AN. There are five aromatic protons, five aliphatic protons in PMA, and three aliphatic protons in AN. Therefore,

$$\frac{5m_1}{5m_1 + 3(1 - m_1)} = \frac{\text{Intensity of aromatic protons}}{\text{Intensity of aliphatic protons}} = C \quad (1)$$

On the simplification gives,

$$m_1 = \frac{3C}{5 - 2C} \quad (2)$$

The intensities of the aliphatic (0.7-4.1 ppm) and aromatic (7.1-7.9 ppm) protons present in the copolymer are determined from the corresponding  $^1\text{H}$  NMR spectrum and the mole fractions of PMA and AN monomeric constituents in the copolymer are calculated using the equation (2) are presented in Table 1. To ascertain the normal copolymer kinetic behavior, a plot was drawn (Figure 3) between the mole fraction of the PMA in



**Figure 3:** The variation of N-phenyl methacrylamide mole fraction in the feed with copolymer.

**Table 1:** The feed and copolymer composition of PMA and AN copolymers.

Sample	$M_1$	$M_2$	$m_1$	$m_2$
PMA-AN <sub>1</sub>	0.748	0.252	0.808	0.191
PMA-AN <sub>2</sub>	0.434	0.566	0.522	0.478
PMA-AN <sub>3</sub>	0.331	0.669	0.483	0.517
PMA-AN <sub>4</sub>	0.248	0.752	0.253	0.747
PMA-AN <sub>5</sub>	0.180	0.820	0.172	0.828
PMA-AN <sub>6</sub>	0.124	0.876	0.146	0.854
PMA-AN <sub>7</sub>	0.035	0.965	0.090	0.910

$M_1$  and  $m_1$  are the mole fractions of PMA and AN in the feed and copolymer, respectively.  $M_2$  and  $m_2$  are the mole fractions of PMA and AN in the feed and copolymer, respectively. PMA=N-phenyl methacrylamide; AN=Acrylonitrile; F-R=Finemann-Ross; K-T=Kelen-Tudos

the feed and copolymer. These polymers are slightly following the ideal copolymerization. All the copolymer samples are having the same amount of AN and PMA units to that of the corresponding initial mixtures.

### 3.4. Determination of Reactivity Ratios

From the monomer feed ratio and the resultant copolymer compositions, the reactivity ratios of monomers PMA and AN are estimated by the methods of F-R [19] and K-T [20].

According to the F-R, the reactivity ratios of the PMA and AN can be determined using the equation  $X(X-1)/Y = r_1(X^2/Y) - r_2$

A graphically evaluable linear equation proposed by K-T to determine the reactivity ratio is given as,  $\eta = r_1\xi - r_2(1-\xi)/\alpha$

Here,  $r_1$  and  $r_2$  are the reactivity ratios relating to monomer 1 (PMA) and 2 (AN) respectively.

The values of F-R plot and K-T plot are presented in Table 2. The reactivity ratios of the monomers from F-R and K-T methods have been presented in Table 3.

The reactivity ratios of PMA and that of AN, indicate that the PMA is more reactive than AN. Thus, the copolymer formed is richer with PMA content. The product of reactivity ratios of the PMA and AN (1.258) infers that the copolymer should have a random

**Table 2:** F-R and K-T parameters for PMA-AN copolymers.

Sample	F-R parameters		K-T parameters	
	$G=X(Y-1)/Y$	$H=X^2/Y$	$\eta=G/(\alpha+H)$	$\xi=H/(\alpha+H)$
PMA-AN <sub>1</sub>	2.267	2.083	1.008	0.926
PMA-AN <sub>2</sub>	0.065	0.538	0.092	0.764
PMA-AN <sub>3</sub>	-0.348	0.262	-0.081	0.611
PMA-AN <sub>4</sub>	-0.642	0.321	-1.318	0.656
PMA-AN <sub>5</sub>	-0.837	0.232	-2.099	0.582
PMA-AN <sub>6</sub>	-0.688	0.117	-2.422	0.413
PMA-AN <sub>7</sub>	-0.332	0.013	-2.842	0.074

$\alpha = \sqrt{H_{\min} H_{\max}} = 1.8584$ ;  $X = M_1/M_2$ ;  $Y = m_1/m_2$ ;  
PMA=N-phenyl methacrylamide; AN=Acrylonitrile;  
F-R=Finemann-Ross; K-T=Kelen-Tudos

**Table 3:** Reactivity ratios of PMA and AN.

Method	$r_1$	$r_2$	$1/r_1$	$1/r_2$	$r_1 r_2$
F-R method	1.431	0.758	0.699	1.319	1.085
K-T method	1.476	0.972	0.678	1.029	1.435
Average	1.454	0.865	0.688	1.156	1.258

PMA=N-phenyl methacrylamide; AN=Acrylonitrile;  
F-R=Finemann-Ross; K-T=Kelen-Tudos

distribution of monomeric units [21] in the copolymer chain. The reactivity of the growing radicals of both the monomeric ends prefer to add to the PMA monomer, thus, leading to the formation of a copolymer richer in PMA content with that of corresponding feed ratio. Because, the rate of homo-propagation in the case of PMA is higher than that of AN, and rate of cross-propagation reaction is less in the case of PMA.

3.5. Thermal Studies

The thermal behavior of the copolymers is studied by thermogravimetric analysis from room temperature to the complete degradation. The degradation characteristics based on the TGA data are presented in the Table 4. The TGA curves of copolymers of PMA and AN shown in the Figure 4, clearly indicate that the polymers undergo single stage decomposition. The initial decomposition temperatures of the copolymers are varying from 170-180°C that depends on the PMA composition in the copolymer. As the PMA mole

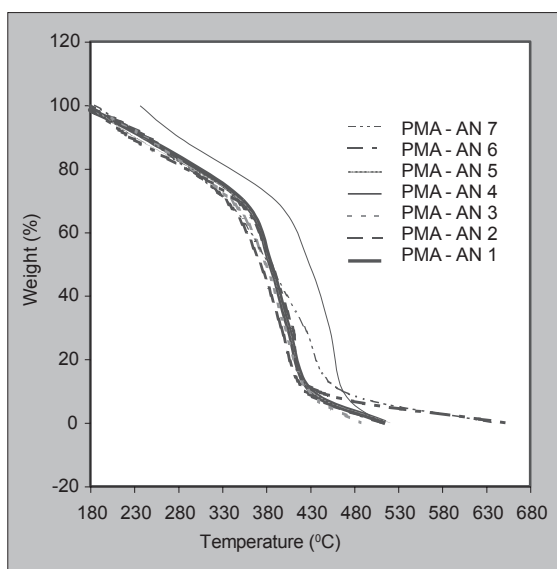


Figure 4: Thermogravimetric analysis plots of the copolymers of N-phenyl methacrylamide and acrylonitrile.

fraction in the copolymer composition increases, the thermal stability of the copolymers increases. The increment in the initial degradation temperature and final degradation temperature with the increase of PMA mole fraction in the copolymer may be attributed to the increase of phenyl groups in the copolymer. The activation energy of the copolymers using the TGA data is calculated by Broidto [22] and Horowitz's [23] methods and are presented in Table 5. Broidto and Horowitz's plots are presented in the Figures 5 and 6.

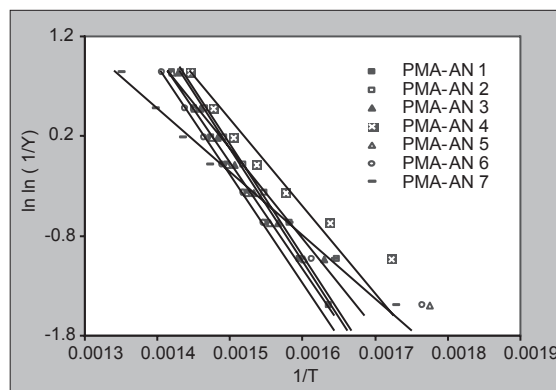


Figure 5: Broidto's plots for the copolymers of N-phenyl methacrylamide and acrylonitrile.

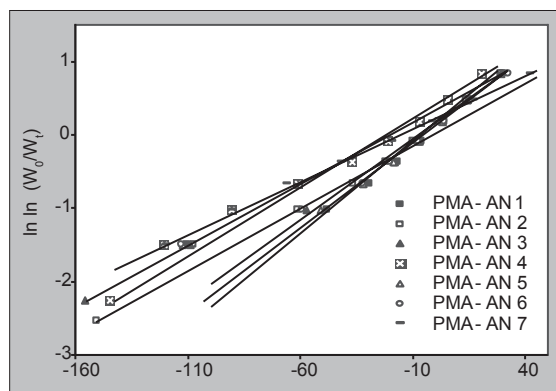


Figure 6: Horowitz's plots for the copolymers of N-phenyl methacrylamide and acrylonitrile.

Table 4: Thermal properties of the copolymers of PMA-AN.

Sample	IDT (°C)	T <sub>max</sub> (°C)	FDT (°C)	Weight loss (%)				
				10	30	50	70	90
PMA-AN <sub>7</sub>	168.8	401.2	515.5	240.8	353.1	384.8	405.3	431.2
PMA-AN <sub>6</sub>	172.3	395.3	511.4	245.1	334.1	373.2	397.0	424.6
PMA-AN <sub>5</sub>	173.4	397.8	486.7	242.2	340.6	379.6	401.1	427.1
PMA-AN <sub>4</sub>	175.6	398.3	474.8	253.9	307.6	361.3	391.2	418.9
PMA-AN <sub>3</sub>	178.2	402.1	521.3	230.6	351.1	383.6	405.3	431.1
PMA-AN <sub>2</sub>	180.3	405.8	650.6	224.9	346.7	385.6	409.7	438.2
PMA-AN <sub>1</sub>	185.5	424.8	638.5	241.2	334.7	383.0	423.7	466.9

IDT=Initial degradation temperature; FDT=Final degradation temperature; T<sub>max</sub>=The temperature at which the degradation is maximum; PMA=N-phenyl methacrylamide; AN=Acrylonitrile



**Table 5:** PMA and AN copolymers' thermal data.

Sample	Temperature range (°C)	Activation energy (KJ/mole)		Glass transition temperature (°C)	Intrinsic viscosity
		Broido's method	Horowitz's method		
PMA-AN <sub>7</sub>	240-510	45.4	58.2	95	0.042
PMA-AN <sub>6</sub>	245-510	46.2	61.3	-	0.071
PMA-AN <sub>5</sub>	240-490	47.0	59.5	-	0.458
PMA-AN <sub>4</sub>	250-480	51.5	63.7	-	0.036
PMA-AN <sub>3</sub>	230-520	42.6	55.7	105	0.192
PMA-AN <sub>2</sub>	220-650	40.5	54.0	108	0.174
PMA-AN <sub>1</sub>	240-640	43.5	55.9	118	0.260

PMA=N-phenyl methacrylamide; AN=Acrylonitrile

The glass transition temperatures of the copolymers are presented in Table 5. The glass transition temperature of the copolymers lies in between the homopolymers of PMA and AN. The glass transition temperature of the copolymers increases with the increase of mole fraction of the PMA in the copolymer. The nonlinearity shows in the plot drawn between the  $T_g$  and mole fraction of PMA monomer in the copolymer may be due to the strong intermolecular attractions between the two monomeric units in the copolymer.

### 3.6. Viscosity Measurements

Intrinsic viscosities for the copolymers of PMA-AN are determined using the Ubbelohde viscometer. The viscosity measurements are made for the dilute copolymer solutions in N,N-dimethylformamide depending on the solubility at 30°C. Concentration of the copolymer solution is 0.4 g/dl used in the present measurements. The intrinsic viscosities for the different copolymers containing different amount of PMA and AN are presented in Table 5.

## 4. CONCLUSIONS

Poly (PMA) and the copolymers of PMA and AN were synthesized by free radical solution polymerization using BPO initiator. The structure of the copolymers was elucidated by IR and <sup>1</sup>H NMR spectroscopic techniques. The solubility of the copolymers was tested for in different organic solvents. Copolymer compositions were determined by <sup>1</sup>H NMR analysis. F-R and K-T methods, evaluated the reactivity ratios of PMA and AN and the values strongly suggest that the reactivity of the growing radicals of both the monomeric ends prefers to add to the PMA monomer, thus, leading to the formation of a copolymer with a higher content of PMA with that of corresponding feed ratio. Thermogravimetric studies indicated that the initial degradation temperature of the copolymers increases with the increase of PMA content in the copolymer due to increase phenyl groups. The glass transition temperature of the PMA-AN copolymers lies in between the homopolymers of PMA and AN, and the variation of glass transition temperature with mole fraction of PMA in the copolymer is nonlinear due to intermolecular attractions.

## 5. ACKNOWLEDGMENTS

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