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### POLYACRYLONITRILE PRECURSORS FOR CARBON FIBER WITH IMIDOCARBOXYLIC ACID UNITS: COPOLYMERIZATION OF ACRYLONITRILE WITH MALEIMIDOBENZOIC ACID

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## POLYACRYLONITRILE PRECURSORS FOR CARBON FIBER WITH IMIDOCARBOXYLIC ACID UNITS: COPOLYMERIZATION OF ACRYLONITRILE WITH MALEIMIDOBENZOIC ACID

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### ABSTRACT

4-Maleimidobenzoic acid (MBA) was explored as a comonomer in polyacrylonitrile (PAN) precursors for carbon fiber. The copolymerization of acrylonitrile (AN) with MBA was carried out in DMF. The reactivity of MBA was considerably less than that of AN, which was manifested as a negative reactivity ratio for the former. The  $r_{\text{MBA}}$  values from  $-0.24$  to  $-0.33$  and  $r_{\text{AN}}$  values of  $1.07$  were obtained by Kelen-Tudos and extended Kelen-Tudos methods. The penultimate reactivity ratios were determined by both linear and non-linear methods. The values were  $r_1 = 0.0093$ ,  $r_1' = 0.0132$ ,  $r_2 = 1.063$  and  $r_2' = 1.625$ . The relative MBA concentration in the copolymer decreased drastically on enhancing its content in the monomer mixture. The penultimate model could satisfactorily explain the feed-copolymer composition profile for the whole composition range. MBA caused a decrease in the apparent copolymerization rate and molecular weight in agreement with the observed trends in the reactivity ratios. A statistical prediction of monomer sequences based on reactivity ratios implied that MBA existed as a lone monomer unit between the long sequences of AN units. This sequence distribution is

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suiting for the efficiency of MBA in cyclisation reaction, which stabilizes PAN during its pyrolysis. Optimum thermal stabilization effect and char yield were observed for copolymers with around 3 mol% MBA in the chain.

*Key Words:* Polyacrylonitrile; Reactivity ratio; Penultimate-unit effect; Maleimidobenzoic acid

## INTRODUCTION

Carbon fibers find an important place in high-tech areas like aerospace industry and defense applications due to their excellent properties such as the ability to withstand high temperature and resistance to chemical and environmental effects, etc.<sup>[1-4]</sup> Among the precursors available, polyacrylonitrile (PAN) based fibers remain one of the best materials for making carbon fibers.<sup>[2-11]</sup> The quality of the ultimate carbon fiber depends largely on the quality of the precursor material. PAN homopolymer as precursor results in poor quality of the carbon fibers.<sup>[2-4]</sup> PAN precursor is modified to improve its properties by incorporation of suitable acidic comonomers during polymerization, which increases its hydrophilicity and catalyzes the cyclization of nitrile groups during the heat treatment of PAN precursors, producing thermally stabilized acrylic fibers.<sup>[3-11]</sup>

Although several acidic vinyl comonomers have been experimented as comonomers in PAN precursors for carbon fiber, 4-Maleimidobenzoic acid (MBA) has not yet been explored. With a view to develop PAN precursors with imidocarboxylic acid units, MBA has been used in the present study for copolymerization with AN. Such copolymers containing 5-membered planar rings in the chain can hinder the chain rotation, resulting in greater structural stiffness and possibly improved thermal stability.<sup>[12,13]</sup> The quality of PAN precursor could depend on the proportion and distribution of MBA in the polymer precursor chain, which in turn is decided by the monomer reactivity ratios. In this paper, we report the reactivity ratio of MBA with AN in DMF solvent, and the detailed kinetic studies relating to the copolymerization. The molecular weights and thermal properties of the copolymers are discussed.

## EXPERIMENTAL

### Materials

Acrylonitrile (AN) (Ottokemi, Mumbai) was purified by alkali washing followed by distillation. p-amino benzoic acid (Aldrich), maleic anhydride

(CDH, Mumbai) and acetic anhydride (Qualigens, Mumbai) were used as received. Tetrahydrofuran (THF), (Qualigens, Mumbai) was dried over calcium hydride and distilled. Dimethylformamide (DMF) (Ranbaxy, New Delhi) was dried over phosphorous pentoxide and distilled under vacuum.  $\alpha$ ,  $\alpha'$ -azobisisobutyronitrile (AIBN) (Spectrochem, Mumbai) was recrystallized from methanol. 4-Maleimidobenzoic acid was prepared as reported earlier.<sup>[14]</sup>

### Instruments

The water bath used was a Julabo-make digital water-bath with a temperature precision of  $\pm 0.1^\circ\text{C}$ .

Gel Permeation Chromatography (GPC) analyses were performed on a 'Waters' Alliance GPC with 410 RI and 2487 UV detectors. DMF was used as eluent at 1 mL/min on Waters HR3 and HR4 columns and Millennium 32 data acquisition software was used for data handling. Polystyrene was used for molecular weight calibration.

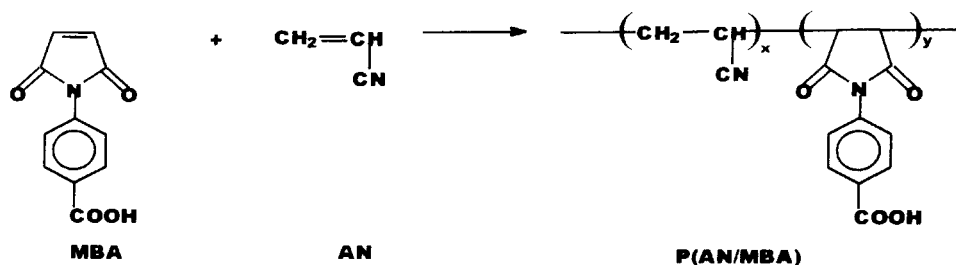
Differential thermal analyses were performed on a TA Instruments Thermal analyzer, Model SDT-1960 under nitrogen atmosphere.

### Polymerization

In a typical experiment, freshly distilled AN (99 mol%, 8.06 g), MBA (1 mol%, 0.333 g), AIBN (100 mg) and 20 mL DMF were charged into a flask fitted with a vacuum adaptor. The contents of the flask were thoroughly deaerated for 30 min at  $-25^\circ\text{C}$ , sealed in vacuum and then polymerized at  $60^\circ\text{C}$ . After the reaction, the polymer was isolated by precipitation into excess of methanol and was purified by reprecipitation from DMF into methanol. The polymer was further purified by Soxhlet extraction using methanol for 8 hr. It was dried in vacuum at  $50^\circ\text{C}$ . The copolymer composition was determined from the acid value analysis of the copolymer, by dissolving it in dimethyl sulphoxide and titrating against standard alcoholic KOH (approx 0.1 N) using thymol blue as indicator. Copolymers with different compositions were prepared similarly, keeping the overall monomer concentration identical.

## RESULTS AND DISCUSSION

MBA was copolymerized with AN according to the following scheme.



*Scheme 1.* Copolymerization of Acrylonitrile and Maleimidobenzoic acid.

The solvent used for the polymerization was DMF. Several copolymers from different feed compositions were prepared and analyzed for their compositions with the aim to determine the reactivity ratios of the pair MBA ( $M_1$ ) – AN ( $M_2$ ) and to study the general copolymerization behavior. The feed and copolymer composition are compiled in Table 1.

It is found that the relative concentration of MBA in the polymer decreases on enhancing its concentration in the feed.

### Determination of Reactivity Ratios

The terminal model reactivity ratios were determined using Kelen-Tudos<sup>[15]</sup> and extended Kelen-Tudos methods.<sup>[16]</sup>

The versatile equation relating the feed and copolymer composition is given as:

$$f_1 = \frac{r_1 F_1^2 + F_1 F_2}{r_1 F_1^2 + 2F_1 F_2 + r_2 F_2^2} \quad (1)$$

*Table 1.* Feed and Copolymer Composition and Molecular Weights

$F_1$ (MBA)	Conversion %	Acid Value (mg of KOH/g)	$f_1$ (MBA)	Molar Mass GPC	
				$M_n \times 10^{-5}$	$M_w \times 10^{-5}$
0.01	7.07	9.54	0.009	13.89	20.37
0.03	4.41	26.55	0.027	11.72	16.89
0.05	6.13	41.26	0.044	8.97	13.03
0.07	9.54	54.10	0.060	8.08	11.79
0.09	18.55	65.43	0.076	6.70	9.66
0.11	15.09	75.50	0.091	5.89	9.39
0.13	11.83	84.51	0.106	5.55	8.82

where  $f$  and  $F$  stand for the mole fractions of the monomer in the polymer and in the feed respectively,  $r_1$  and  $r_2$  being the respective reactivity ratios.

The Kelen-Tudos (KT) method for determining the reactivity ratios uses a modified form of the Mayo-Lewis equation given by:<sup>[15]</sup>

$$\eta = \left( r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (2)$$

where  $\eta$ ,  $\xi$  and  $\alpha$  were determined as described in the original article:<sup>[15]</sup>

A plot of  $\eta$  vs.  $\xi$  gives a straight line with:

$$\text{slope} = r_1 + \frac{r_2}{\alpha}$$

$$\text{intercept} = \frac{-r_2}{\alpha}$$

The K-T plot is shown in Fig. 1 and the reactivity ratios are included in Table 2.

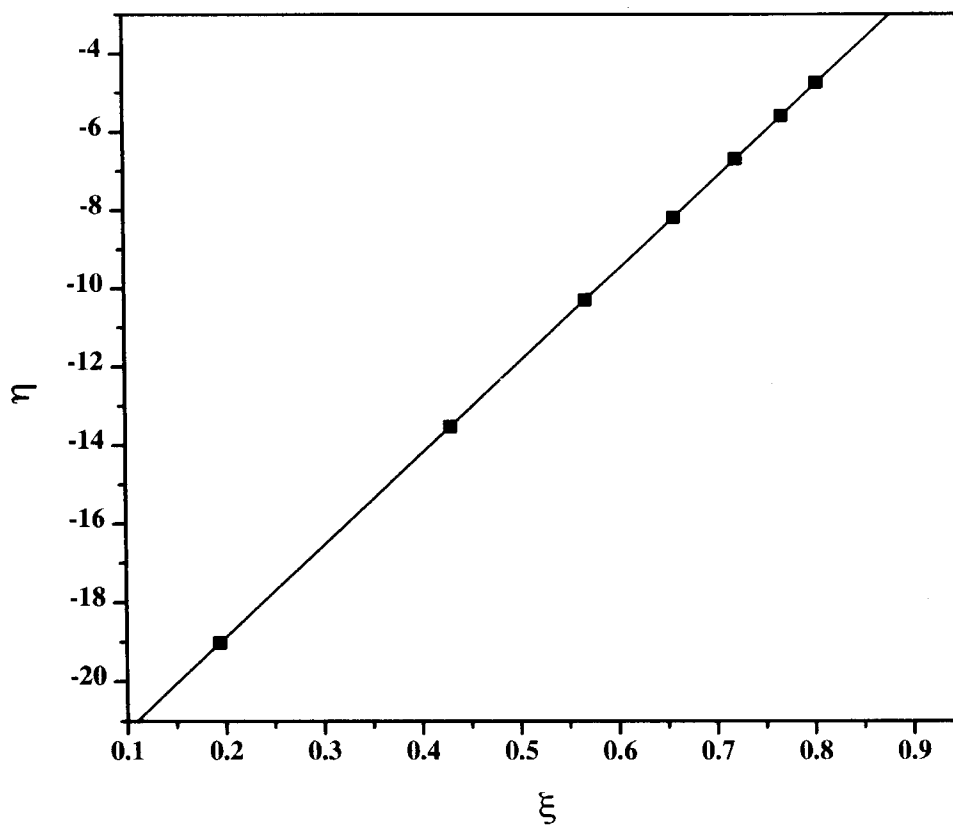


Figure 1. Kelen-Tudos plot for determination of reactivity ratios.

**Table 2.** Terminal Model Reactivity Ratios

Kelen-Tudos		Extended Kelen-Tudos	
$r_1$	$r_2$	$r_1$	$r_2$
-0.24	1.07	-0.33	1.07
$\pm 0.02$	$\pm 0.003$	$\pm 0.01$	$\pm 0.001$

The terminal model reactivity ratios were also calculated by the Ex K-T method,<sup>[16]</sup> which takes into account the possible drift in the composition of the copolymer as a result of considerable monomer conversion. In this method,  $H$  and  $G$  are redefined using a conversion dependent constant  $Z$  expressed as in the original article:<sup>[16]</sup>

$$Z = \frac{\log(1 - \zeta_1)}{\log(1 - \zeta_2)} \quad (3)$$

$\zeta_1$  and  $\zeta_2$  are respectively the partial molar conversions in monomers  $M_1$  and  $M_2$  and are given as:

$$\zeta_1 = \frac{\zeta_2 x}{X} \quad (4)$$

and:

$$\zeta_2 = \frac{w(\mu + X)}{\mu + x} \quad (5)$$

$$X = \frac{F_1}{F_2} \quad (6)$$

and:

$$x = \frac{f_1}{f_2} \quad (7)$$

and:

$$\mu = \frac{\mu_2}{\mu_1} \quad (8)$$

where  $\mu_1$  and  $\mu_2$  are the molecular weights of monomers 1 and 2 and  $w$  the total fractional conversion.

Typical Ex-KT plot is shown in Fig. 2 and reactivity ratios included in Table 2.

Both methods give excellent linear fit for the experimental data.

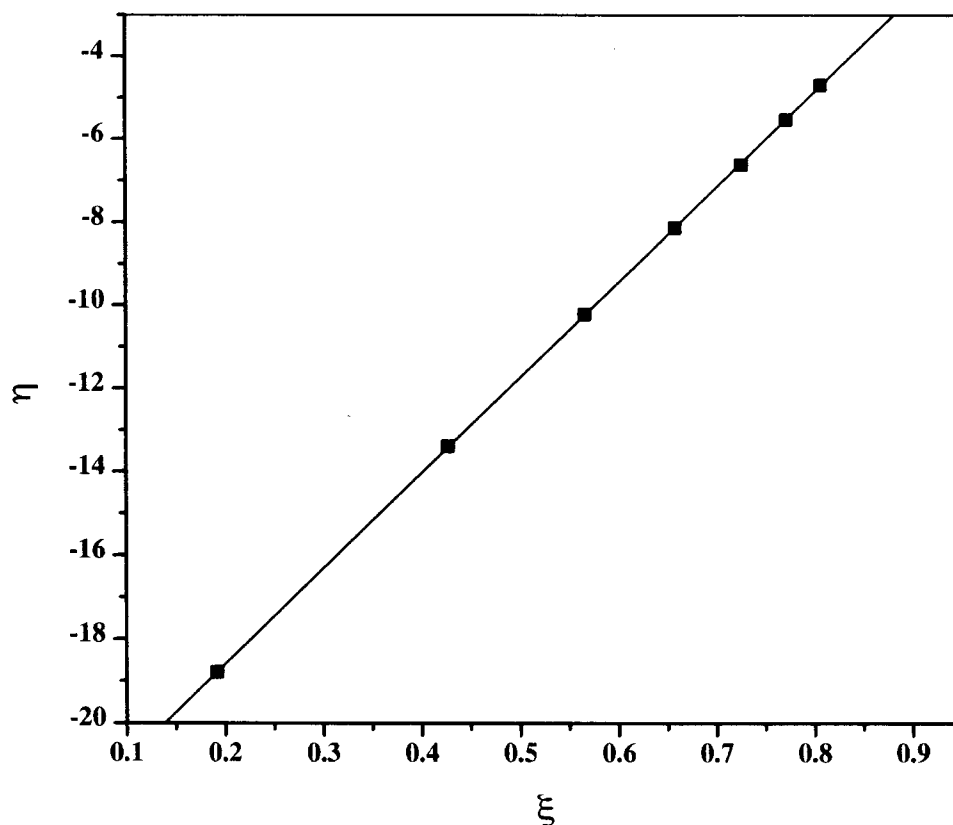


Figure 2. Extended Kelen-Tudos plot for determination of reactivity ratios.

### Terminal Model Reactivity Ratios

The calculated reactivity ratios reveal an apparent negative value for  $r_1$  in all the cases. It is absurd since the minimum value theoretically possible for the reactivity ratio is zero. Both the methods gave negative values despite excellent fits for experimental points. The good fit in all three cases rules out any experimental artifacts in the estimation of reactivity ratios. The  $r_1$  values vary marginally with the method, and the extended K-T values are more authentic.<sup>[16]</sup> The  $r_1$  value of less than unity implies that MBA has very little tendency to add on to its own monomer. The reluctance of MBA to homopolymerise may be attributed to its bulky and strongly electron-withdrawing nature, which can sterically and electronically hinder the approach of another MBA molecule.<sup>[14]</sup> The  $r_2$  value close to unity implies that AN-terminated radicals do not have preference for either of the monomers. The negative value of  $r_1$ , obtained from the terminal model proved the inadequacy of the model to describe the copolymerization behavior. Since a negative reactivity ratio could possibly be associated with a penultimate unit



effect, this model was used to analyze the experimental data. Negative reactivity ratio also failed to predict a rational composition profile for the copolymer (discussed later).

### Penultimate Model

The terminal model reactivity ratios could not account for the general copolymerization behavior. It also fails to predict precisely the composition profile of the polymer for the whole range. The inadequacies of the terminal model led us to use the penultimate model. MBA has manifested penultimate unit effect with certain monomers.<sup>[14]</sup> The mathematical treatment of the penultimate effect involves eight propagating species and four reactivity ratios defined as:

$$r_1 = \frac{k_{111}}{k_{112}}, \quad r'_1 = \frac{k_{211}}{k_{212}}, \quad r_2 = \frac{k_{222}}{k_{221}}, \quad r'_2 = \frac{k_{122}}{k_{121}} \quad (9)$$

Therefore, each monomer is characterized by two monomer reactivity ratios, one representing the propagating species in which the penultimate and the terminal monomer units are the same ( $r_1, r_2$ ), and the other representing the propagating species in which the penultimate and terminal units differ ( $r'_1, r'_2$ ). The equation relating the copolymer compositions to the feed composition when a kinetic penultimate effect is operative is given as:<sup>[14]</sup>

$$x = \frac{f_1}{f_2} = \frac{1 + \frac{r'_1 X(r_1 X + 1)}{(r'_1 X + 1)}}{1 + \frac{r'_2 (r_2 + X)}{X(r'_2 + X)}} \quad (10)$$

### Penultimate Reactivity Ratio by Barson-Fenn Method

The values of  $r_2$  and  $r'_2$  for the two systems could be determined by a graphical method based on the original method of Barson and Fenn<sup>[17]</sup> that was modified.<sup>[14]</sup> The  $r_1$  values were taken from the terminal reactivity ratios for each case. In this method, it is assumed that the penultimate group effect is felt only with respect to the radicals terminated in AN. This is true since the reactivity of MBA is not influenced by the preceding unit because of its relatively bulky size and steric factors. Moreover in a system deficient in MBA, the probability for formation of radicals of the type  $\text{MBA-MBA}^*$  will be negligible particularly when  $r_{\text{MBA}}$  tends to zero. Hence the Barson-Fenn approach is valid for this pair.

The original Barson-Fenn equation is given as:

$$r_2 = \frac{Xk}{x} + \frac{X^2k}{xr'_2} - X \quad (11)$$

where  $k = 1 + r_1X - x$ . This equation was linearized by appropriate restructuring assuming the value of  $r_1$ .<sup>[14]</sup> In the present case, both  $r_1$  and  $r_1'$  are assumed to be 0. (The nearest rational  $r_1$  value):

$$X[k/x - 1] = \frac{-X^2k}{xr_2'} + r_2 \quad (11a)$$

A plot of the left-hand side of Eq. (11a) vs.  $X^2k/x$  gives the intercept as  $r_2$  and the slope as  $-1/r_2'$ . The linear plots are shown in Fig. 3. The reactivity ratios are compiled in Table 3. The B-F method can be used a priori for examining the existence of the penultimate unit effect for AN monomer when one of the reactivity ratios can be assigned without great error.

This good colinearity of the experimental points giving precise and distinct  $r_2$  and  $r_2'$  values confirms the existence of penultimate unit effect for AN radical.

#### Penultimate Reactivity Ratio by Multiple Regression Analysis

The four reactivity ratios could be calculated by a non-linear multiple regression method using a computer program. The values obtained from B-F

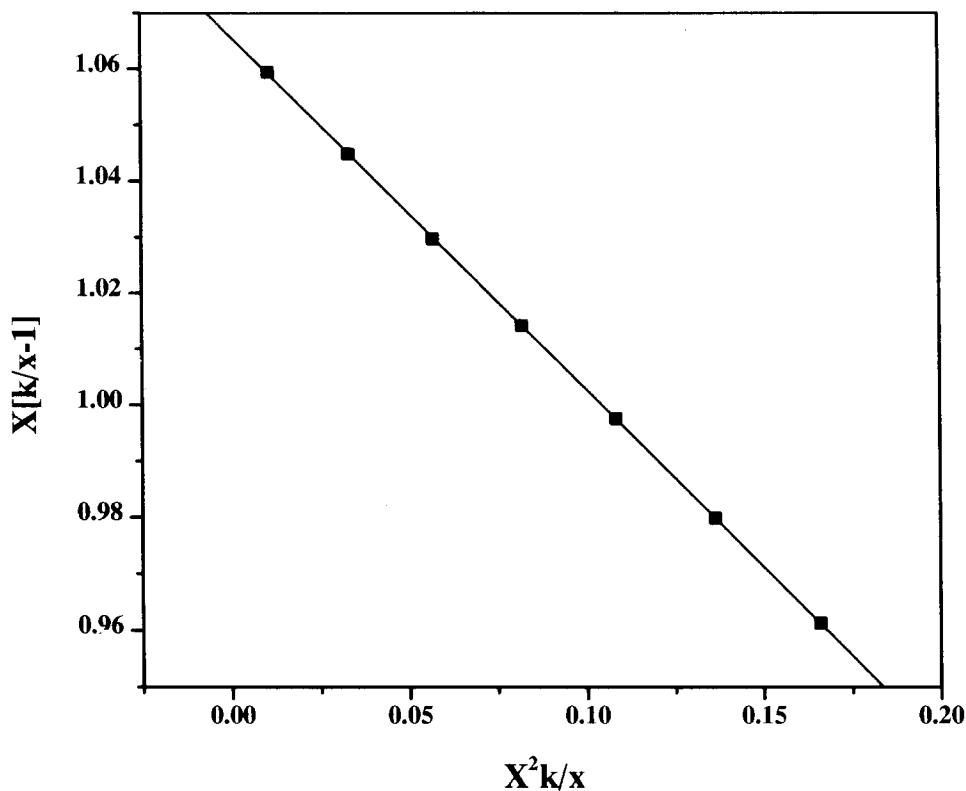


Figure 3. Barson-Fenn plot for determination of penultimate reactivity ratios.

**Table 3.** Penultimate Model Reactivity Ratios

Barson-Fenn Method				Regression Method			
$r_1$	$r_1'$	$r_2$	$r_2'$	$r_1$	$r_1'$	$r_2$	$r_2'$
0	0	1.065	1.584	0.0093	0.0132	1.063	1.625
		$\pm 0.001$	$\pm 0.003$	$\pm 0.0007$	$\pm 0.001$	$\pm 0.003$	$\pm 0.005$

method were useful for serving the ranges of the reactivity ratios, required as initial input for computer calculation. The values of  $r_2$  and  $r_2'$  are same in both the methods. The assumed as well as calculated values of  $r_1$  and  $r_1'$  are given in Table 3. The calculated  $r_1'$  values are in the proximity of zero, confirming the validity of the above hypothesis, used in the Barson-Fenn equation.

The penultimate unit effect on the AN radical is evident from the difference in the  $r_2$  and  $r_2'$ . The tendency of AN\* radicals to add to another AN unit is increased by about 50% when MBA unit precedes AN\* radical. MBA has very little tendency to add to its own monomer due to the steric repulsion and also due to the electron deficient nature of the monomer. Thus the steric repulsion of the penultimate MBA group reduces the reactivity of the AN radical to an incoming MBA unit. This effect principally accounts for the reduced reactivity of MBA at higher concentrations of it in the feed and the apparent negative  $r_1$  value in the terminal model. Similar observations have been made in previous studies on the copolymerization of phenylmaleimide derivatives.<sup>[14,18]</sup>

### Copolymer Composition Curves

The theoretical and experimental feed copolymer composition profiles are shown in Fig. 4.

The theoretical curve based on the penultimate model and terminal models were constructed using Eqs. (10) and (12), respectively.

$$f_1 = \frac{F_1^2(r_1 - 1) + F_1}{F_1^2(r_1 + r_2 - 2) + 2F_1(1 - r_2) + r_2} \quad (12)$$

where  $F_1$  is the mole fraction of MBA in the feed, and  $f_1$  the instantaneous mole fraction of MBA in the copolymer,  $r_1$  and  $r_2$ , the respective reactivity ratios of MBA and AN from the terminal method.

The experimental points are found to conform to the theoretical curves based on both the terminal and penultimate reactivity ratios in the limited

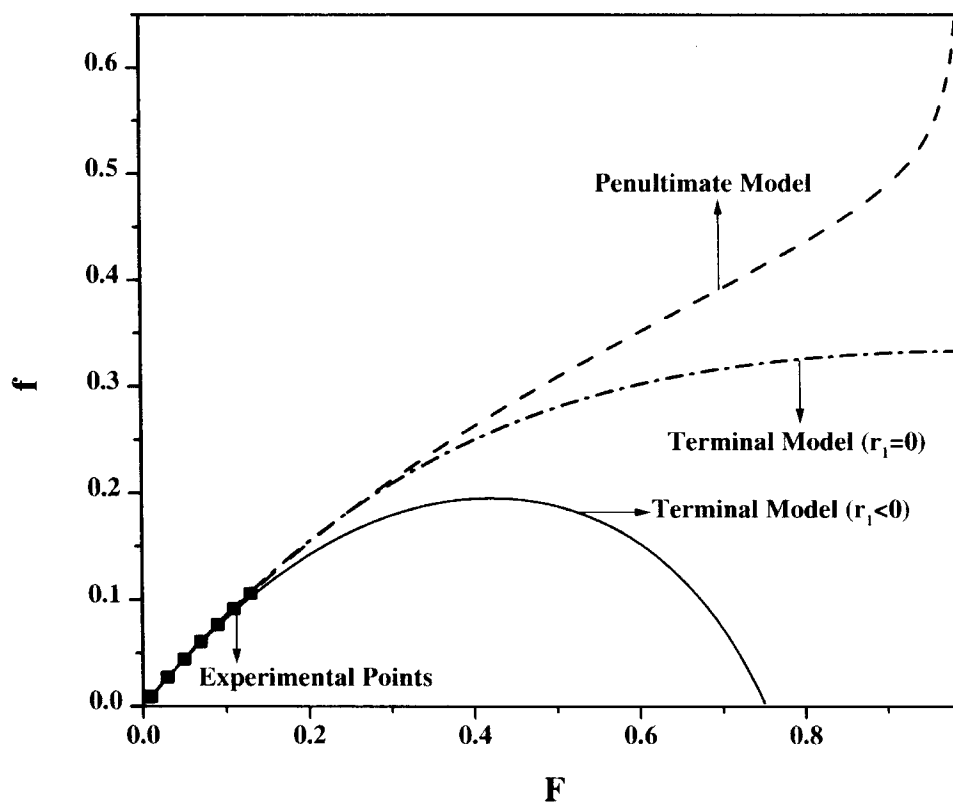


Figure 4. Copolymer composition curves.

concentration range studied. Two theoretical curves based on the terminal reactivity ratios are shown, one using the nearest rational value for  $r_1 = 0$  and the other with the experimental value of  $r_1$ . In the terminal model, theoretical curve behaves abnormally at higher MBA concentrations and does not represent a real picture, particularly when  $r_1$  assumes a negative value. The penultimate model gives a more realistic picture of the copolymer composition curve for the entire range. It predicts that the concentration of MBA in the polymer cannot exceed 50%. Copolymers with very high concentrations of MBA could not be prepared due to the tremendous retardation in polymerization.

#### Statistical Prediction of Microstructure

The copolymerization behavior of AN/MBA predicts that the copolymer cannot accommodate more than 50% of IA in the chain and that MBA-MBA sequences will be negligible. At lower concentrations of MBA, one can expect long sequences of AN bridged by MBA units. Since MBA is the carrier of  $-\text{COOH}$  functions, the  $-\text{COOH}$  groups will be distributed at

intervals in the chain. This is an ideal situation where the MBA can effectively bring about the cyclization of the long sequence of AN units. The probabilities of finding the sequences of the type  $MBA(AN)_nMBA$  are given as:

$$N_{(AN)_n} = P_{MBA.AN.AN} \cdot P_{AN.AN.AN}^{n-2} \cdot (1 - P_{MBA.AN.AN}) \quad (13)$$

The various Ps represent the probabilities of the concerned triads calculated from the penultimate reactivity ratios.<sup>[19]</sup>  $N_{(AN)_n}$  is the number of fraction of n sequences of AN. The weighted probabilities of such sequences are:

$$\frac{N_{(AN)_n} n}{\sum N_{(AN)_n} n} = \frac{N_{(AN)_n} n}{W_{AN}} \quad (14)$$

$W_{AN}$  is the weighted composition of all such A's given as:

$$W_{AN} = 1 + (P_{MBA.AN.AN}/P_{AN.AN.MBA}) \quad (15)$$

The distribution of AN sequences in the copolymers under different polymerization conditions are shown in Fig. 5. It is seen that for a copolymer containing 1 mol% of acid, large sequences of MBA can be found. Enhancing the acid content shows a steady decrease in the length of AN sequences. It is evident that at lower concentrations of MBA there will be long sequences of AN bridged by MBA units. Since MBA is the carrier of -COOH functions, the -COOH groups will be distributed at intervals in the chain. This is an ideal situation, when a -COOH can catalyze the cyclization of long sequences of nitrile groups during stabilization reaction.

### Apparent Copolymerization Rate and Copolymer Molecular Weights

From the polymer yield and time of polymerization, it was possible to get the trend in the apparent rate of polymerization at fixed molar concentration of the monomer and initiator. The apparent copolymerization rate as a function of feed composition is shown in Fig. 6.

With the addition of MBA, there is a rapid fall in the rate. Although the  $r_1$  value implies an enhanced rate for cross-propagation, the overall rate falls because of the low  $k_p/k_t^{1/2}$  value for MBA. The cross-termination also could increase with an increase in the concentration of this comonomer. These factors resulted in the sharp decrease in the polymerization rate on enhancing the MBA content.

A similar trend is also seen in the variation of copolymer molecular weight with MBA as shown in Table 1 and Fig. 6. It is seen that the molecular weight goes on decreasing with an increase in the MBA concentration in the feed. The bulky nature of MBA decreases the probability of

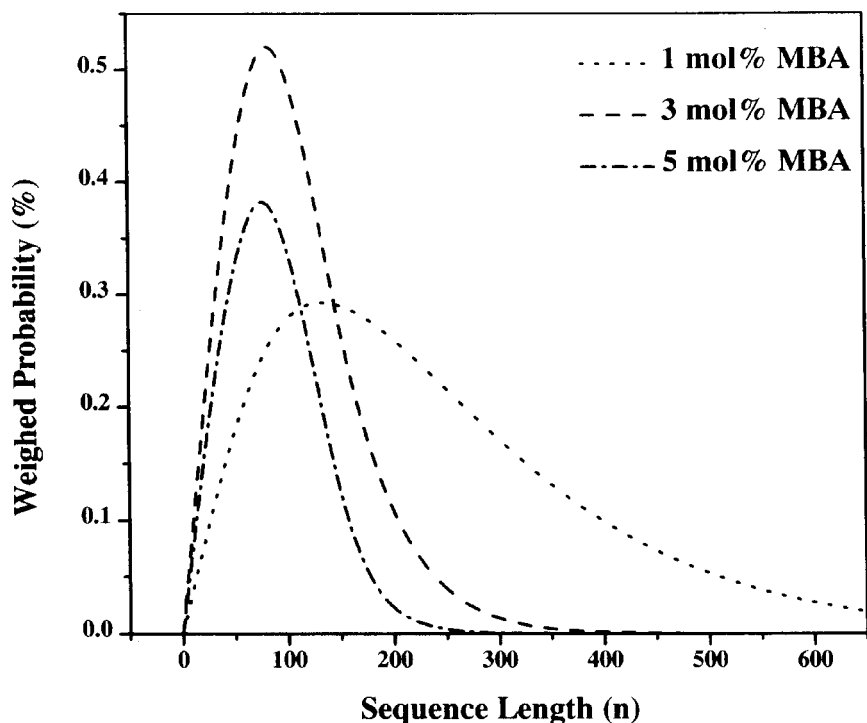


Figure 5. Statistical acrylonitrile sequence distribution.

its self-propagation. As a result, enhancement of the MBA concentration results in a fall in the DP.

### Thermoanalytical Investigations

Thermal behavior of PAN precursors possessing varying amounts of MBA was studied by simultaneous TG/DTA technique in nitrogen atmosphere. Rapid heating of PAN polymers initiates an exothermic reaction followed by loss of weight, attributed to cyclisation reaction of nitrile group.<sup>[3-11]</sup> A sharp exothermic peak between 225–300°C was observed in all cases. The thermograms are shown in Fig. 7, which compares the thermal behavior of PAN polymer synthesized in DMF with different MBA concentrations. PAN homopolymer cyclizes at a higher temperature in comparison to the copolymers. On incorporating small concentration (1%) of MBA, the char residue and thermal stability of the copolymer is better in comparison to the homopolymer (34%). The cyclization peak shifts to a lower temperature compared to the homopolymer. On enhancing the MBA

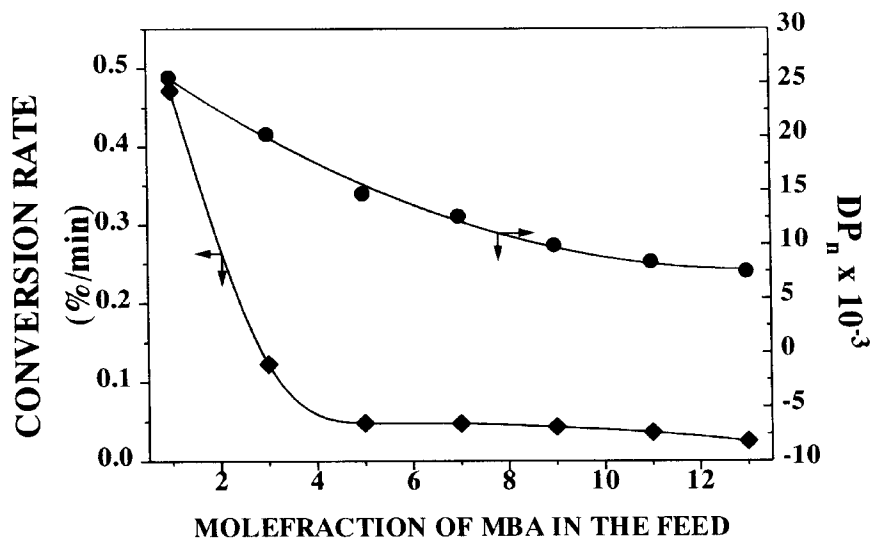


Figure 6. Variation of apparent polymerization rate and polymer molar mass with feed composition.

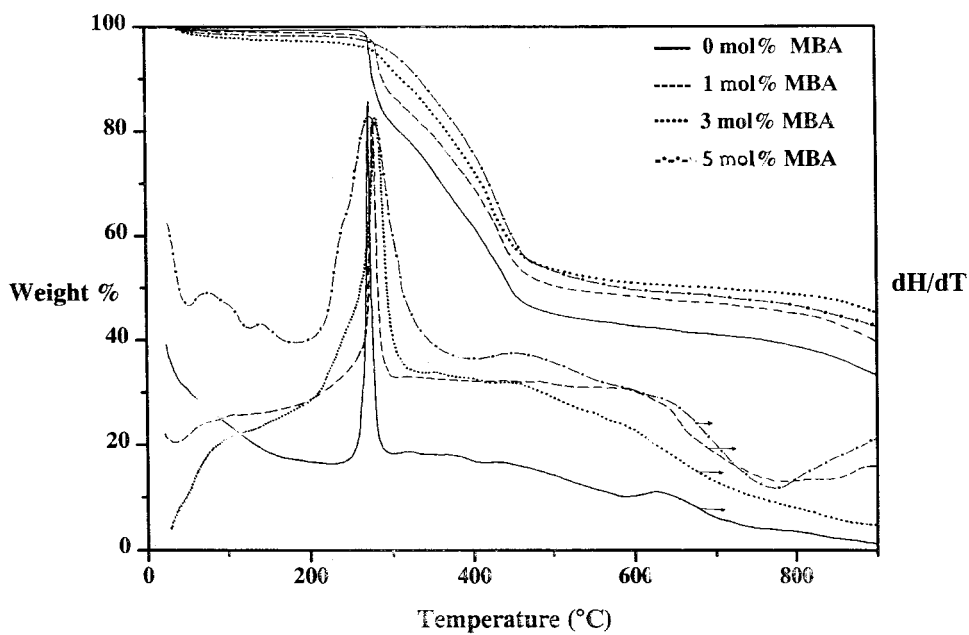


Figure 7. Thermogravimetric analysis of AN/MBA copolymers in nitrogen atmosphere. Heating rate 10°C/min.

concentration to 3%, the thermal stability is further enhanced giving 45% char at 900°C. The temperature of initiation of the cyclization shifts to a lower temperature regime and the peak becomes broader. However, on enhancing the MBA concentration to 5%, its effect is less pronounced in the thermal characteristics. The char yield also stagnates. It can be concluded that a small concentration of MBA  $\sim$ (3%) is conducive for better stability of PAN during pyrolysis reactions. MBA is found to be comparatively less effective than IA in its ability to stabilize PAN. The optimum concentration of IA for maximum thermal stability and char yield is 1–1.5 mol%.<sup>[3,4,8]</sup>

### CONCLUSION

The copolymerization of MBA/AN is associated with a mild penultimate unit effect for radicals terminated in AN. MBA radical has very little reactivity towards its own monomer. AN radical has a greater preference for its own monomer when MBA is the penultimate unit. The terminal model gave a negative value for  $r_{\text{MBA}}$  and failed to predict a rational composition profile for the entire composition range. The penultimate model gave a realistic feed copolymer composition curve. The calculation predicted that it is impossible to incorporate more than 50% MBA in the polymer chain. Enhancement of MBA concentration decreases both the polymerization rate and the molar mass. A statistical prediction of monomer sequences based on reactivity ratios implied that MBA existed as a lone monomer unit between the long sequences of AN units. Incorporation of MBA enhanced the thermal stability. The thermal stability and char yield is maximum for a copolymer incorporating 3 mol% of MBA in the PAN polymer.

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