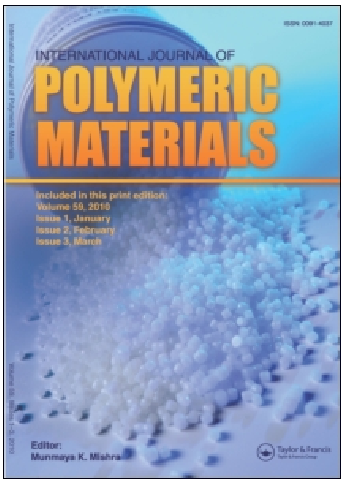

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High Pressure Synthesis and Characterization of Acrylonitrile Based Copolymers in Aqueous Free Radical Polymerization Using NMR Spectroscopy[†]

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The influence of reaction pressure on rate of polymerization and intrinsic viscosity in acrylonitrile (AN), methyl acrylate (MA) and itaconic acid (IA) ternary suspension polymerization system has been studied using free radical forming potassium persulphate and sodium metabisulphite water soluble redox initiator pair. The resulting polymers synthesized at various reaction pressures were characterized for tacticity and composition by NMR and other spectroscopic (FT-IR, ESCA) techniques. These polymers were also subjected to differential scanning calorimetric (DSC) analysis and significant change in heat of cyclization were observed with the change in reaction pressure.

Keywords: Polyacrylonitrile; high pressure synthesized terpolymers; microstructure; NMR.

INTRODUCTION

Generally, NMR studies of polymers and copolymers give valuable information about the structure, composition, tacticity, sequence and number-average sequence length of monomer units in the polymer chain [1–7]. These structural parameters can be correlated to physical and chemical

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[†] IPCL Communication No: 302

properties of polymers [1, 2]. Pichot *et al.* [8] have employed ^{13}C NMR to elucidate the sequence distribution of AN–MA copolymers. However, a great deal of controversy exists in the literature as regards to the crystal structure and molecular chain confirmation of PAN[9, 10]. Imai *et al.* [11] have shown that PAN can be atactic, syndiotactic or isotactic depending on its method of preparation. According to these authors, radically initiated polymer has nearly an atactic confirmation while radiation induced polymerization of AN in urea canal has predominantly isotactic configuration. Using ^{13}C NMR, it has been established [12, 13] that PAN prepared in water medium using persulphate/bisulphite redox initiator has a greater percentage of isotactic units (33.4%) than PAN prepared in water–acetone (2:1 v/v) medium (28.3%).

The physico-mechanical and chemical properties of these polymers are critically dependent on monomeric composition and steric configuration of PAN which inturn depends on polymerization conditions [14]. It has also been suggested by various authors [15, 16] that tacticity in PAN determines the degree of intramolecular cyclization and it is easier to cyclize isotactic sequences than syndiotactic configurations.

The use of AN polymers and copolymers as precursors for carbon fibers (CF) has promoted indepth studies on thermal behaviour of PAN [17, 18] and it has been established that the exothermicity during the heat treatment of PAN is caused by the nitrile group oligomerization. The exothermic nitrile oligomerization and the mechanism of the reaction were found to be affected by the introduction of various comonomers [19, 20] into the molecular chain of PAN. Although AN homopolymers have widespread applications, its copolymers with acrylic ester (methyl acrylate, ethyl acrylate etc.,) and terpolymers with vinyl monomers (itaconic acid, acrylic acid etc.,) are used in manufacturing of CF precursors [21, 22]. An extensive study of these polymers synthesized by radical polymerization technique using NMR spectroscopy has revealed that introduction of second and third monomer is not significantly changing the steric configuration of the PAN segment [20]. As PAN with stereo regular configuration possesses very specific properties, it is desirable to develop a process to synthesize stereoregular acrylonitrile based copolymers which can be commercially exploited for carbon fiber production.

With this objective, synthesis of terpolymers (AN-MA-IA) has been carried out using suspension free radical polymerization technique to understand the kinetics and mechanism of this ternary system under high pressure reaction conditions. These polymer samples were characterized by NMR, FT-IR and ESCA techniques for obtaining composition and tacticity data. Thermal behaviour of these polymers was studied by DSC to support the microstructural changes observed in the spectroscopic studies.

EXPERIMENTAL

Materials

Acrylonitrile (AN) and methyl acrylate (MA) were washed with 5% NaOH and then by diluted sulphuric acid, followed by distilled water to remove the inhibitor. The washed monomers were dried over anhydrous sodium sulphate and then distilled under N_2 atmosphere. Potassium persulphate (KPS), sodium metabisulphite (MBS), sodium lauryl sulphate (NaLS) and itaconic acid (IA) were used without further purification.

Polymerization

Polymerization was carried out at 50 °C constant temperature using a 21 capacity Buchi jacketed stainless steel reactor provided with an excellent variable agitator facility. This reactor also has an arrangement of conduction polymerization at higher reaction pressure. The reaction temperature has been maintained by circulating hot water through the jacket from a Haake Model NB 22 water circulator. Initially, calculated amount of demineralized water was purged with N_2 for complete deoxygenation with constant stirring. Monomer mixture (AN and MA) along with IA was added in the presence of N_2 followed by the addition of required amount of emulsifier to the polymerization system. The initiator solution (KPS/MBS) freshly prepared in DM water under N_2 atmosphere was added quickly to the reaction vessel. The sudden appearance of a haze or turbidity indicated the end of induction period and the onset of polymerization. The pH of the polymerization medium was always >2.5. The nitrogen purging was maintained through out the reaction. Finally, after 3 hours of reaction the polymerization was stopped by terminator and the reaction mixture was allowed to cool. The precipitated polymer was collected by filtration with suction, washed several times with hot DM water and dried at 50°C in vacuum to a constant weight. Several experiments were conducted at various reactor pressure (i.e., 0.5 to 6 bar) under identical experimental conditions and they were designated as TP1–TP6 respectively. These polymers were characterized by spectroscopic and thermal analysis techniques.

Intrinsic Viscosity

Intrinisic viscosity of polymers was determined in N–N′ DMF at 30 °C using 0.2% polymer solution containing 0.1% LiBr in a Ubbel-hode suspension level viscometer. The M_w of the polymer was estimated from the intrinsic viscosity data using the Mark-Houwink equation [23] i.e.,

$[\bar{\eta}] = K(M_v)^{\alpha}$ where $K = 2.525 \times 10^{-4}$ and $\alpha = 0.75$;

IR and Thermal Measurements

The FT-IR spectra of the polymers were recorded on Brucker IFS-113V model spectrometer using KBr disk and solvent cast film method.
DSC studies of the polymers were carried out on Mettler model DSC-25 thermal analyser.

NMR Measurements

NMR spectra were recorded for samples TP1-TP6 using 15–20% solution in dimethyl sulphoxide (DMSO)-d_6 at 80 °C on a JEOL JNM FX-100 FT-NMR spectrometer (^1H frequency of 100 MHz and ^{13}C frequency of 25 MHz). Hexamethyl disiloxane (HMDS) was used as an internal reference. ^1H NMR measurements were carried out under the following experimental conditions. Spectral width of 2000 Hz, pulse width (PW) 13 μs; No. of pulses accumulated = 20; Pulse interval of 1 s and pulse repetition (PR) time of 5.0 s; No. of data points = 8 K. ^{13}C NMR measurements were carried out using complete decoupling mode under the following conditions: PW1 = 13 μs, PR = 5 s; No. of pulses accumulated 2000.

XPS Measurements

A VG ESCALAB MK II spectrometer with twin anode (Mg K_α and AlK_α) X-ray source was used for X-ray photoelectron spectroscopic (XPS) measurements. The anode was operated at 10 KV and 10 mA and the vacuum in the analysis chamber was maintained better than 5×10^{-8} mbar. Polymer powders were dusted onto double side adhesive tape and mounted on a sample holder. The spectrometer was calibrated using Cu ($2p_{3/2}$) photoelectron line [24] at 932.7 ± 0.1 eV. The N(1S) photoelectron line at

399.6 eV was used as internal reference [25] for charge correction of C (1S) and O (1S) photoelectron lines in polymers.

RESULTS AND DISCUSSION

The present work deals with a study of acrylonitrile terpolymerization containing MA and IA as comonomers in aqueous medium using KPS/MBS redox initiator system. When the influence of reaction pressure on conversion and intrinsic viscosity was examined, it is found that the conversion decreases whereas intrinsic viscosity increases with an increase in reaction pressure from normal to 6 bar as shown in Table I. This decrease in polymerization rate may result in the increase of polymer molecular weight (M_v) as the degree of polymerization (DP) [26] is inversely proportional to reaction rate (R_p) in a fixed monomer concentration i.e.,

$$DP = K_p{}^2[M]/K_t{}^2R_p.$$

It also appears from the M_v data shown in Table I that the reaction pressure during polymerization will influence the mode of termination of polymerization reaction. It is believed [20] that the initiation reaction would influence the composition and configuration of monomer in copolymer whereas the propogation reaction will primarily influence the composition with a minor effect on the configuration unless very wide temperature range

TABLE I Effect of reaction pressure on conversion and intrinsic viscosity of polymers

Sample Code	*Reaction* Pressure in Bar	*Percent* Conversion (%C)	*Intrinsic* V iscosity [η] dl/g	$\bar{M}_v \times 10^{-5}$
TP	0.0	82.25	1.72	1.29
TP1	1.0	62.50	2.15	1.74
TP2	2.0	58.12	2.50	2.12
TP3	3.0	55.20	2.75	2.41
TP5	5.0	53.28	3.20	2.95
TP6	6.0	51.18	3.82	3.74

Recipe :
[AN:MA:IA] = 93:6:1 (wt%)
concentrations with respect to aqueous phase :
[KPS] = 1.9×10^{-3} mol/1,
[MBS] = 4.8×10^{-3} mol/1,
[NaLS] = 1.7×10^{-3} mol/1,
Temperature = 50 °C; Time = 3 hrs; stirring speed = 250.

is considered. The termination reaction on the other hand will control the molecular weight distribution (MWD) and rate of polymerization (R_p). However, the molecular weight data shown in Table I, indicates that the rate of chain initiation and termination steps are lower as compared to propagation step due to the influence of reaction pressure on chain termination and initiator efficiency. In addition, the comonomer used during polymerization has a better chance to combine with the reaction initiating species $SO_4^{\cdot -}$ and $SO_3^{\cdot -}$ generated from KPS/MBS redox initiator system which may initiate the reaction. Pichot *et al.* [8] in emulsion polymerization of AN and methacrylic acid (MAA) reported that the higher rate of polymerization in the presence of MAA was due to the preferential initiation involving the MAA molecule whereas the polymerization conducted at high pressure may not favour initiation involving IA molecule which eventually may lead to decrease in rate of polymerization and consequently to increase in the molecular weight of polymer (Tab. I).

The acrylonitrile based terpolymers synthesized from aqueous suspension free radical polymerization within pressure range (normal pressure to 6 bar) were characterized by the combined use of ^1H and ^{13}C NMR respectively under optimised experimental conditions reported elsewhere [20]. The proton decoupled ^{13}C NMR spectra of the terpolymers synthesized under normal and 6 bar pressure are shown in Figure 1 along with the expansion of nitrile and methine carbon lines which shows three well resolved peaks appearing at 119 and 27 ppm respectively. The methine and nitrile signals are stereo specific and showed stereo chemical splitting [7, 12] which is quite clear in the expanded spectra. Turska *et al.* [27] have reported pentad resonances for the nitrile band using high resolution ^{13}C NMR, but under our experimental conditions only triads were observed even with the longer pulse delays. The triad abundance values were measured from the resolved spectra of nitrile band shown in Figure 1. In the nitrile carbon signal the peaks due to iso-, hetero-, and syndiotactic triads appear from higher to lower field respectively whereas in the methine carbon signal, these peaks appear from lower to higher magnetic field. Similar observations have also been made by Minagawa *et al.* [28]. Figure 2 shows the ^1H NMR spectra of these samples in d_6-DMSO which consists of the strong absorption peak originated from methine proton at lower field around 3.05 ppm and a broad envelope assigned to the resonance of methylene protons at higher field around 2.05 ppm of PAN segment. Methyl protons in methylacrylate are observed at 3.65 ppm. Since all the polymers have predominant composition of AN ($\approx$92%), the spectra possess features resembling to the ^1H NMR spectrum of PAN. A well resolved and distinct signal corresponding

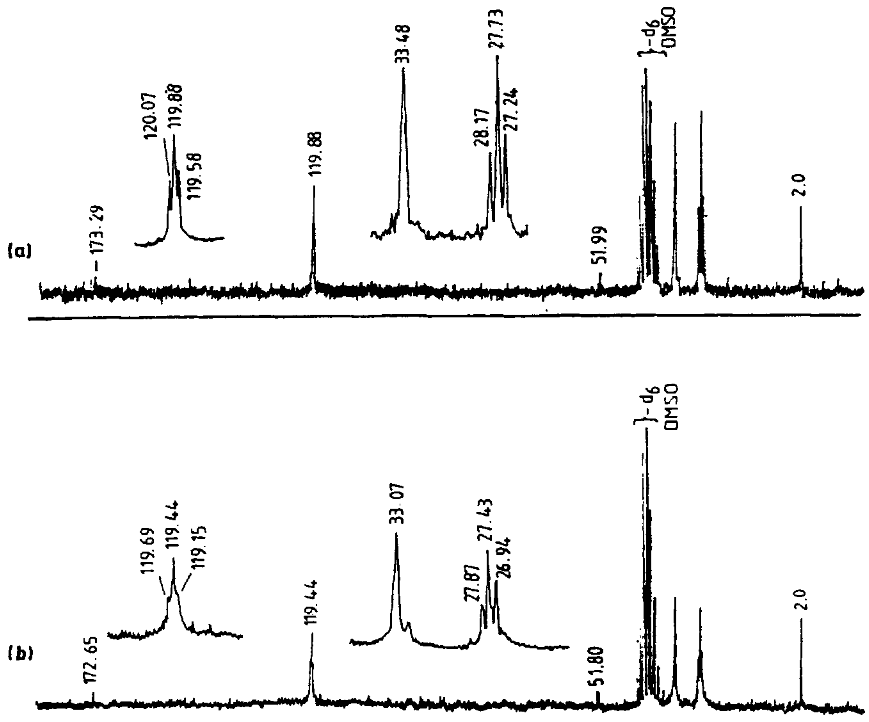


FIGURE 1 ^{13}C NMR spectra of (a) AN-MA-IA terpolymer obtained under normal pressure (b) AN-MA-IA terpolymer obtained under 6 bar pressure.

to the carboxylic proton of the third monomer itaconic acid was observed at 9.00 ppm.

The composition of these high pressure synthesised polymers are determined by FT-IR and NMR spectroscopy. A good correlation is observed in the compositional data of AN and MA segments estimated by ^1H NMR, ^{13}C NMR and FT-IR spectroscopy as shown in Table II. Typical IR spectrum of polymer synthesised at normal pressure is shown in Figure 3. In fact, the ratio of the intensity of C=O stretching band around 1740 cm^{-1} to the C≡N stretching band at 2240 cm^{-1} (I_{CO}/I_{CN}) was used for estimation of MA in AN-MA copolymers. However for obtaining composition from NMR data, a weighted regression equation was developed [29] by using standard polymers of M/S DuPont and M/s. Polyscience, USA. In case of ^1H NMR spectra, peak intensities correspond to methylene protons

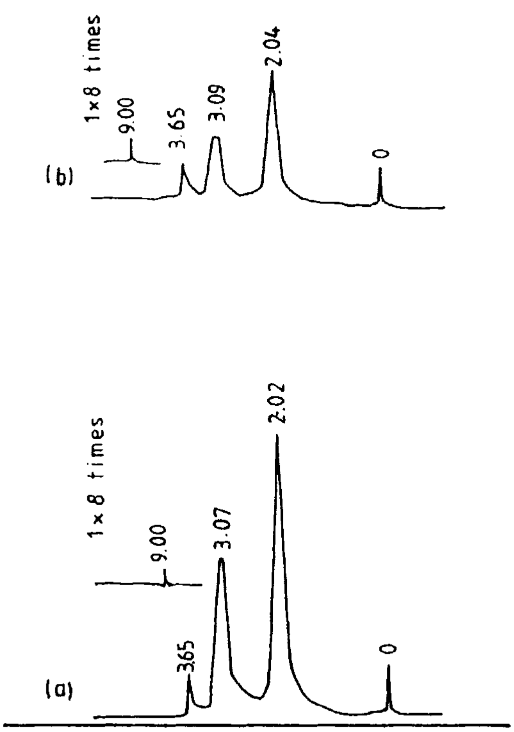


FIGURE 2 ^{1}H NMR spectra of (a) AN-MA-IA terpolymers obtained under normal pressure (b) AN-MA-IA Terpolymer obtained under 6 Bar pressure.

TABLE II Compositional data of (AN-MA-IA) terpolymers synthesized at various reaction pressures.

Sample code	^{1}*H NMR*		^{13}*C NMR*		*FT-IR*	
	AN	*MA*	*AN*	*MA*	*AN*	*MA*
TP	93.3	5.9	93.4	5.8	93.4	5.9
TP1	93.2	5.9	93.2	5.9	93.3	5.9
TP2	92.8	6.1	92.8	6.1	92.9	6.1
TP3	93.5	6.1	93.5	6.2	93.5	6.2
TP6	93.7	6.2	93.6	6.3	93.7	6.3

of PAN segment (at 2.05 ppm) and methyl protons (at 3.05 ppm) of PMA were considered, whereas in ^{13}C NMR spectra, signals correspond to OCH_3 carbons of PMA (at 52.00 ppm) and methine carbon (—CH) of PAN (27.6 ppm) were considered for analysis.

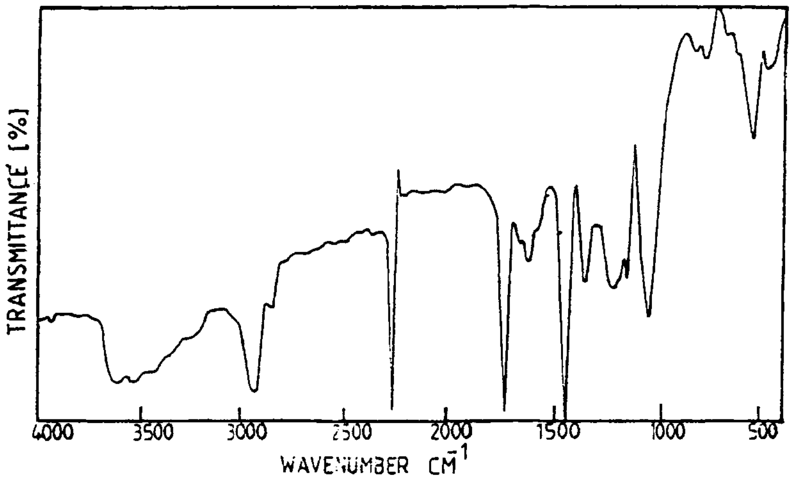


FIGURE 3 FT-IR spectrum of (AN-MA-IA) Terpolymer synthesised at normal pressure.

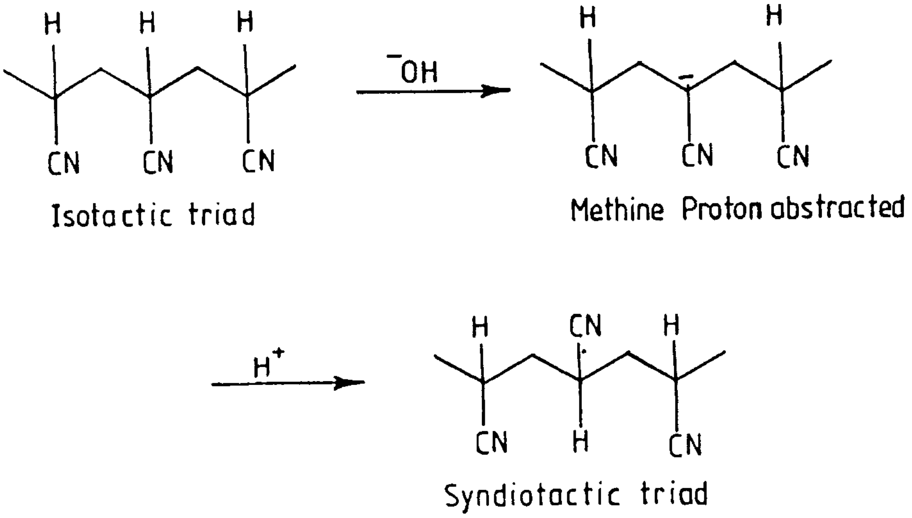
The tacticity of AN sequence in terpolymer was analysed on the basis of stereo sensitive CN signal in ^{13}C NMR spectrum shown in Figure 1. A systematic change in the triad tacticity of cyano group were observed with increase in reaction pressure. The visible splittings of three signals were assigned as isotactic (I), heterotactic (H) and syndiotactic (S) triads respectively from lower to upper field. The distribution of meso and racemic triads, corresponding Bernoullian probabilities and average chain length [14] of these triads are shown in Table III.

The triad values reported in Table III indicated a drop (34%) in syndiotactic triads with a corresponding increase (28%) in isotactic triads with

TABLE III Tacticity and First order Markovian Probabilities for Nitrile Carbon of (AN–MA) copolymers synthesized under different pressure conditions

Sample	*Triad tacticity*			*No. avg. seq. length*		*Markovian probabilities*			
	mm	*mr*	*rr*	n_m	n_r	$P_{m/r}$	$P_{r/m}$	$P_{r/r}$	$P_{m/m}$
TP	0.243	0.435	0.321	2.120	2.480	0.472	0.403	0.597	0.528
TP_2	0.283	0.457	0.260	2.239	2.140	0.447	0.467	0.533	0.553
TP_4	0.299	0.458	0.244	2.031	2.067	0.434	0.484	0.516	0.566
TP_5	0.294	0.472	0.235	2.246	1.994	0.445	0.501	0.499	0.555
TP_6	0.311	0.479	0.210	2.300	1.877	0.435	0.533	0.467	0.565

the increase in reaction pressure. Thus inversion of configuration is taking place, whereby a certain portion of syndiotactic sequences is converted to isotactic sequences. Similar configurational inversion was reported [30] for PAN polymers in the presence of strong bases wherein the methine proton was abstracted and the resulting anion was resonance stabilized by the delocalization of negative charge onto the nitrile group. After the abstraction of the proton from isotactic triad, the nitrile group can rearrange to a syndiotactic configuration on the return of the proton, thus giving an inversion of configuration at the methine carbon. The mechanism is shown below–



Preferential chain cleavage in syndiotactic sequences under high pressure polymerization condition is another possibility of configuration inversion. The inversion of methine carbon during acid hydrolysis of PAN has also been reported in the literature [31]. The number average sequence lengths, n_m, and n_r and the first order Markovian probabilities, $P_{m/r}$, $P_{r/m}$, $P_{r/r}$ and $P_{m/m}$ were calculated [30] from the observed triad abundances of these polymers are shown in Table III. Markovian probabilities of these polymers indicate a slight deviation from the Bernoullian model.

It is worth mentioning that the observed differences in rate of polymerization, molecular weight (M_v), and tacticity of these polymers may be attributed to the influence of comonomer units on certain interaction such as those of the monomer reaction medium, radical reaction medium and the monomer radical (monomer-radical of the growing chain), which affect the transition state in the propagation step. These multiple interactions are reported to alter the stereoregularity [32] as well as the rate of the polymerization reaction [33]. NMR characterization of these polymers show a decrease in syndiotacticity along with an increase in isotacticity. These results are supplemented by the thermal behaviour of these polymers characterized by DSC as shown in Figure 4 and Table IV. The results reveal that the heat of cyclization as well as peak temperature has an increasing trend with increase in reaction pressure. Initiation of cyclization at a lower temperature is found to be achieved by copolymerizing AN with acidic comonomers acrylic, methacrylic and itaconic acids [34, 35]. As is seen from Figure 4, the exothermic transition of polymer synthesised at normal pressure starts at 220 °C with a peak maximum of 283 °C but the exotherm transition of polymer synthesized at higher pressure begins at higher temperature with peak maximum at 304 °C.

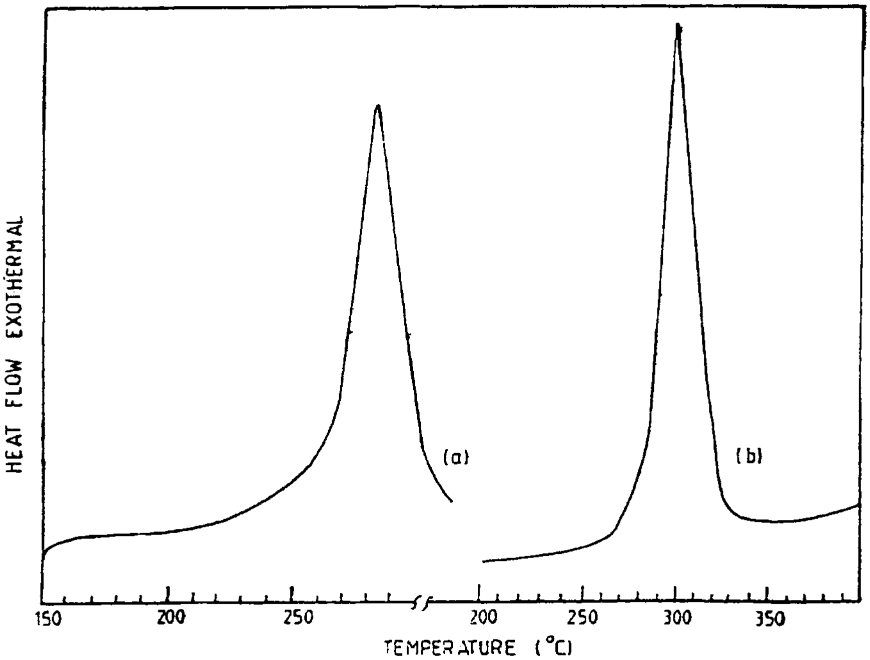


FIGURE 4 DSC Thermograms of AN-MA-IA Terpolymer synthesised at (a) Normal pressure (b) 6 Bar pressure.

TABLE IV Variation of heat of cyclization and peak temperatures of polymers synthesized at different pressures

Sample code	*Reaction pressure in bar*	*Heat of cyclization* ΔH *(J/g)*	*Peak temperature* °*C*
TP	0.0	498.20	282.75
TP1	1.0	516.18	292.80
TP2	2.0	527.50	296.40
TP3	3.0	534.43	298.80
TP6	6.0	547.12	303.90

High peak temperature (T_{pk}) of aqueous redox slurry polymer has been explained interms of the effective inhibition of some kind of branch formation due to strong and rapid chain transfer reaction to the activator. The following reaction scheme are postulated by Minagawa [36] to understand the chain transfer mechanism–

a) Side chain branching:

$$p_n^{\cdot} + p_m \rightarrow p_n p_m^{\cdot} \ldots \text{(i)}$$

b) Main chain branching:

$$p_n^{\cdot} + p_m \rightarrow p_n\mathrm{H} + p_m^{\cdot} \ldots \text{(ii)}$$

c) Hydrogen abstraction:

$$p_n^{\cdot} + \mathrm{HSO_3}^{-} \rightarrow p_n\mathrm{H} + \mathrm{SO_3}^{\cdot -} \ldots \text{(iii)}$$

d) Activator Capture:

$$\mathrm{SO_3}^{\cdot -} + nM \rightarrow \mathrm{SO_3}^{-}\mathrm{p}_n^{\cdot} \ldots \text{(iv)}$$

$$p_n^{\cdot} + \mathrm{SO_3}^{\cdot -} \rightarrow p_n\mathrm{SO_3}(?) \ldots \text{(v)}$$

e) Solvent Capture:

$$p_n^{\cdot} + s \rightarrow p_n s^{\cdot} \ldots \text{(vi)}$$

where $p_n^{\cdot}$, $p_m^{\cdot} = \mathrm{R{-}CH_2{-}C^{\cdot}H}$
M = monomer, s = solvent,

IR and NMR studies have demonstrated that in an aqueous heterogeneous system, other than ordinary propogation reaction, branching reactions, (i) and (ii) occur most often. However, when activator is added, transfer reactions (iii), (iv) and (v) prevails over (i) and (ii). Consequently branching was effectively restrained. An apparent rise in T_{pk} in the presence of activator ($Na_2S_2O_5$) appears to be due to the new forms of the aqueous redox component of low molecular weight giving rise to higher T_{pk}. Hence, the thermal behaviour of these polymers synthesized within the normal to 6 bar pressure range can be interpreted in relation to the above mechanism. Further more, with an increase of reaction pressure, the amount of comonomer incorporated in PAN segment has decreased which may also increase [19,20] the peak temperature of the polymer given in Table IV. High pressure synthesized polymers also show higher heat of cyclization which is influenced by the change in tacticity of polymers (Tab. III).

X-ray photoelectron spectra (XPS) of polymer synthesized at normal pressure is shown in Figure 5 which clearly shows the presence of carbon, nitrogen and oxygen elements in terpolymer powder. As expected the O:N atomic ratio in this powder is slightly higher than 0.080 estimated from AN:MA composition used in the polymerization reaction. The high resolution photoelectron spectra of C (1S), N (1S) and O (1S) for this polymer is shown in Figure 6. The asymmetry and broadening of C (1S) and O (1S) photoelectron lines indicate presence of carbon and oxygen functionalities in various electronic environments. As expected [25] only one type of nitrogen (from PAN) is observed.

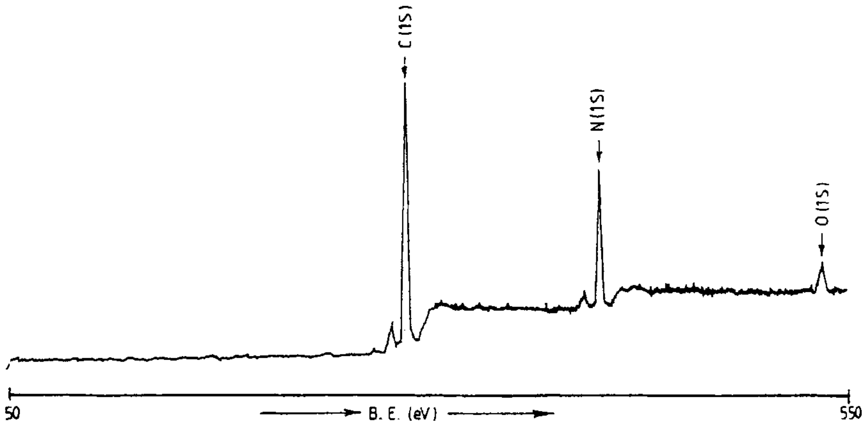


FIGURE 5 XPS survey scan of terpolymer synthesized at normal pressure.

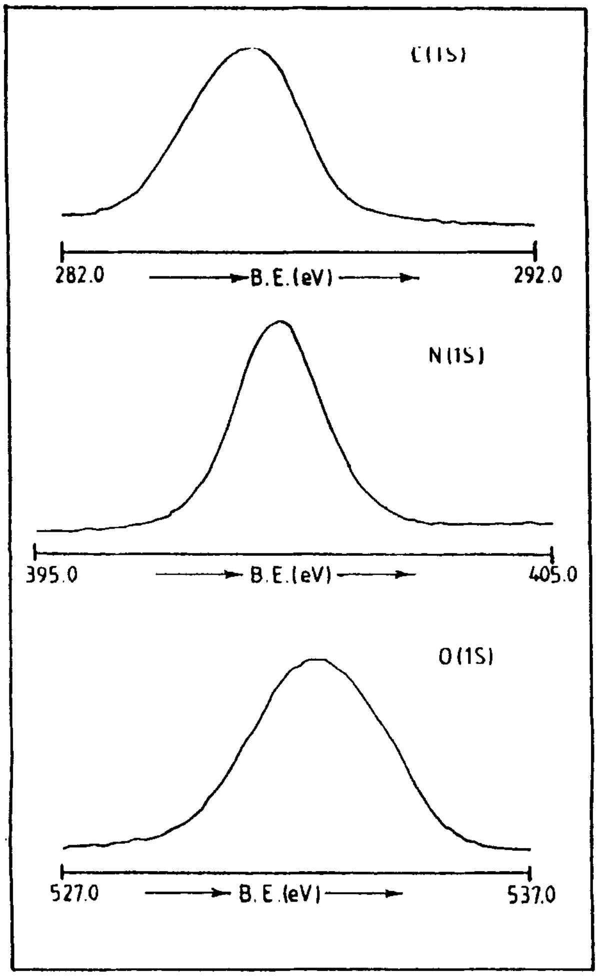


FIGURE 6 C(1S), N(1S) and O(1S) photoelectron lines of terpolymer powder.

CONCLUSIONS

In the present study, an attempt has been made to adequately explain the influence of reaction pressure on the polymerization kinetics as well as polymer characteristics in terms of molecular weight, stereo configuration, composition and thermal behaviour which are important in the development of SAF with desired properties. Based on the present study, the following conclusions can be drawn–

(i) The rate of polymerization decreases while the molecular weight of the polymer increases with an increase in reaction pressure.
(ii) Enrichment of isotactic triads at the expense of syndiotactic triads was observed at higher pressure.
(iii) Increasing trend in heat of cyclization was observed in thermal studies of these polymers.

It is therefore possible to synthesize polymers with enriched isotactic configuration at higher reaction pressure. This should favour intra molecular cyclization resulting in fiber with improved physico-mechanical properties which are suitable for the manufacture of carbon fiber.

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