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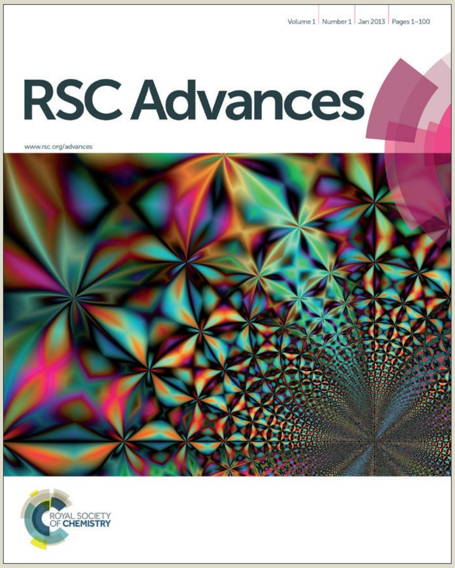

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# Synthesis, Characterization, and Thermo-mechanical properties of Poly (acrylonitrile-co-2,3-dimethyl-1,3-butadiene-co-itaconic acid) as carbon fibre polymer precursors

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Novel carbon fibre polymer precursor(CFP),viz.,Poly(acrylonitrile-co-2,3-dimethyl-1,3-butadiene-co-itaconic acid) was synthesized using solution polymerization process. Structural identification, bonding network were established using infrared,and nuclear magnetic resonance spectroscopic techniques. Molecular characteristics, such as different kinds of average molecular weights were estimated applying solution viscometry and size exclusion chromatography. The char yield of the polymers were found to be 45 % wt. through thermal gravimetry. The thermomechanical behaviour of novel carbon fibre polymers were investigated employing several thermal techniques. Thermomechanical data confirm that newly synthesized copolymers exhibit higher coefficient of linear thermal expansion in the range 74−1716 °C$^{-1}$, softning temperature at 51 °C in constrat to the conventionally used (37−810 °C$^{-1}$). Differential scanning calorimetry results show a distinct bimodal curves with a wider thermal exotherm starting from220 °C with two peaks at a teperature difference of 25 °C and an slower energy release rate 2.5 −5.0 Jg$^{-1}$s$^{-1}$, thereby releasing the heat over a extended period of time than a sudden release of heat (14.75 Jg$^{-1}$s$^{-1}$) as sharp peak as observed in the conventional precursors. The above facts indicate that new polymers can be used as polymer precursor for high tensile carbon fibres.

## 1. Introduction

Polyacrylonitrile based copolymers (PAN) have emerged as the most successful precursors for making high specific strength carbon fibres. PAN-based acrylic fibres are produced in large quantities, and have become one of the most important industrial synthetic polymers.[1-3] Structurally PAN copolymers are synthesized as three different stereo-structures viz., isotactic, atactic, and syndiotactic. Both isotactic and atactic conformations of acrylonitrile copolymer are known for their improved crystallinity over syndiotactic structure.[4,5] The high-order structure of special acrylic fibre (SAF) originates from the crystalline/non-crystalline phases that exist in the atactic/isotactic PAN polymer. PAN polymer has bulky and high polar nitrile groups as side chains that induce very high intermolecular repulsive forces, thereby hindering the molecular orientation of the fibre during

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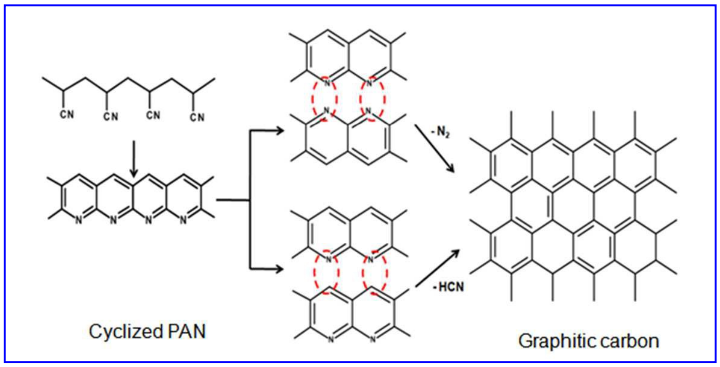
primary and secondary drawing processes .[6,7]

Generally, industrial manufacture of carbon fibre involve several stages including wet jet wet spinning, coagulation, glycerine or hot water bath drawing, and secondary saturated steam assisted stretch process, thermo-mechanical shrinkage or extension during oxidative stabilization(200-280 ℃) and carbonization (300-2800 ℃) processes. In the recent past, researchers have been focussing on the synthesis of facile PAN copolymers to be used as precursor in the fabrication of SAF for high tensile carbon fibres with tensile strength over 6.5 GPa.[8,9]

Current research efforts aim at addressing the problems related to processes and improving the fibre and polymer characteristics. Some approaches in this direction involve increase of intrinsic viscosity (dL/g); decreasing the fibre linear density (dtex); optimisation of the density of stabilised acrylic fibre (gcm$^{-3}$); minimizing the gelling tendency of the polymer spin dope, and enhancement of overall stretch ratio of the spun fibre in order to improve the crystalline orientation of the SAF. The improvements of molecular properties often result in adverse effects in the production processes such as low productivity, high cost and process instability. Previous investigators revealed the influence of stretching method, molecular weight, stereo-regularity, and polymer solute concentration of the spin dope used for spinning operation on the drawing behaviour of high-order polyacrylonitrile.[10-12] To be a successful carbon fibre precursor, PAN polymers require certain physicochemical properties including a set of tensile characteristics. Major reasons for the notable dominance of PAN over other two predominant precursors namely viscose rayon and pitch are its structure, as in Scheme I that permit faster rate of pyrolysis without much disturbance to its basic structure and preferred orientation of the molecular chains along the fibre axis.



**Scheme 1** PAN polymer structure with pendant nitrile groups leading to graphitic structure

The characteristic drawing behaviour of PAN polymers during the spinning process make it possible to achieve a high degree of orientation of the molecular chains and, thereby induce high tensile properties in the fibre precursor stage. PAN-based carbon fibre precursor polymers are usually synthesized as copolymer with some selective functional monomers to improve certain physical properties of the resulting polymers in order to meet the down-stream process requirements[13-16]. Neutral comonomers such as methyl acrylate, methyl methacrylate, or vinyl acetate are used to modify the acrylic fiber morphology and act as drawing promoter, while acid comonomers viz., itaconic acid, methacrylic acid, and acrylic acid are incorporated in the acrylonitrile polymer to improve their solubility in organic solvents used in the polymer dope preparation and improve the stabilization process. Comonomers also improve the spinnability and facilitate thermal oxidative stabilization, cyclization, and aromatization processes.[17] Many acrylonitrile based pseudo-terpolymers such as P (AN-MA-IA), P (AN-MMA-IA), P(AN-MA-AA) have been investigated mainly from the stabilization and spinnability points of view.[18] Chunlei Cao et al have studied the thermal behavior of pseudo terpolymer system consisting of acrylonitrile (AN), methyl methacrylate (MMA) and itaconic acid (IA) and found that IA facilitates low temperature thermal cyclization reaction during carbon fibre manufacture. P.Catta et al copolymerized neutral comonomers like methyl acrylate, methyl methacrylate with acrylonitrile to improve the spinnability of PAN precursors.[19, 20]

As PAN-based special acrylic fibres are mostly used for high tensile type carbon fibres, their physical and mechanical properties significantly influence the tensile characteristics of the resultant carbonized fibres. Mostly, acrylic fibre precursors undergo a highly exothermic reaction in the temperature range 250-320 ℃ with sudden release of heat. This reaction can induce thermal run away during pyrolysis, and is likely to result in the fusion of the precursor fibres and loss of orientation. It is imperative to control the exothermic energy released in the early part of thermal processing, and vital to the development of superior mechanical properties in the carbon fibre filaments. Since majority of the acrylonitrile-based precursors exhibit sharp exotherm, the thermal oxidative stage during the carbon fibre manufacture is conducted in prohibitively slow heating rates and line speeds. This leads to low production rate and high cost of carbon fibre, specifically in the case of high tensile carbon fibres. Generally, the onset of exotherm starts temperature in excess of 230 ℃. There are no major chemical transformations taking place before this process.

In addition, fibres are subjected to a sudden temperature rise, which is far higher than its glass transition temperature, in all probability leading to annealing and fusion of filaments, which in turn retards the orientation of molecular chains in the ladder type polyacrylonitrile structure. So, it is proposed to modify this exotherm by spreading over a wide range of temperature, thereby eliminating the previously mentioned issues. Many investigations on carbon fibre pre on carbon fibre precursors are related to their synthesis, solution characteristics, rheology, thermal degradation behaviour, and carbonization etc.[21-28] Therefore, there exists a need to synthesize a polyacrylonitrile copolymer that can be used as potential polymer precursor with improved drawing characteristics, and is expected to undergo thermal reactions over a wide temperature range and investigate the relationship between structure and thermo-mechanical properties. In general, butadiene based monomers are known to impart better elastic properties to polymerized structures, therefore an attempt has been made to synthesize a novel PAN copolymer, viz., Poly(acrylonitrile-co-2,3-dimethyl-1,3-butadiene-co-Itaconic acid) (VCP01/02 (VCP01/02) with different number average molecular weights. The molecular and structural characteristics of as-synthesized copolymer were established with spectral techniques. The thermo-mechanical behaviour has been investigated using several thermal analytical techniques.

## 2. Experimental

### 2.1 Materials and methods

Acrylonitrile (AN, 99%, Aldrich, Germany) was dried over $CaH_2$, distilled under reduced pressure and stored in a freezer under nitrogen prior to use. 2,3 dimethyl-1,3-butadiene,(99%, Alfa Aesar), Itaconic acid (IA, 99%, Aldrich) and 2,2-azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich) were used as received. N, N-dimethylformamide (DMF, 99.8%, Aldrich) were distilled and stored in the presence of molecular sieves. All other solvents were used without further purification.

### 2.2 Synthesis of acrylonitrile based homo and copolymers

Polymerization was carried-out in a 500 ml three-necked round bottom flask, equipped with a reflux condenser, mechanical stirrer, and inert gas ($N_2$) supply system. The reaction flask was purged with $N_2$ gas for about 30 min. at a minimum flow rate to ensure an oxygen-free atmosphere. Dimethylformamide (DMF) was added as reaction medium, and the reaction flask was kept in a heater block and maintained at 55 ℃. Acrylonitrile (1.815 mol), 2, 3 dimethyl-1, 3-butadiene (28 mmol), and Itaconic acid (9.2 mmol) based on their respective reactivity ratios were mixed together and fed into the reaction flask. A degassed solution of initiator [2, 2-azobis (2-methylpropionitrile)] was added to the reactant mixture. The amount of initiator was varied between 1.5-2.5 % wt. based on total monomer weight to get the polyacrylonitrile copolymers of different molecular masses. The progress of free-radical solution polymerisation was monitored by measuring specific viscosity ($\eta_{sp}$) of the reaction mixture at different time intervals. The specific viscosity is a ratio of the viscosity of the reaction mixture $(\eta - \eta_s)$ to that of the reaction medium ($\eta_s$), which gives the change in viscosity of the reaction mixture because of polymerization. The polymerization reaction was stopped after 5 h at 55 ℃ by quenching the reaction mixture in chilled methanol. The copolymer was recovered by the precipitation of reaction mixture in methanol-water mixture (1:1 ratio). The resulting polymer precipitate was filtered and washed several times with methanol, and then dried at 60 ℃ under vacuum to a constant mass.

### 2.3 Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectra were recorded using IR spectrophotometer with attenuated total reflection technique (ATR) FTIR/ATR spectrophotometer, Model: Nicolet 6700 (Make: The Scientific). Typical conditions were as follows: wave number: 400−4000 $cm^{-1}$; resolution: 2 $cm^{-1}$; scanning: 32 counts and purging gas, $N_2$ (flow rate, 100ml. $min^{-1}$).

### 2.4 $^{13}$C-Nuclear Magnetic resonance measurements (NMR)

$^{13}$C NMR (Bruker AMX-400, at Indian Institute of Science, Bangalore, India) spectra of the copolymers were recorded in DMSO using tetramethylsilane (TMS) as an internal standard.[29] Samples were concentrated in dimethyl sulphoxide about 5% (w/w) for $^{13}$C NMR by using a 5 mm NMR tube at room temperature. $^{13}$C NMR spectra were acquired using 24996 data points, spectral width 22 kHz, broadening 3 Hz, pulse delay 2s, pulse width 90$^o$, and 1024 scans.

### 2.5 Size exclusion chromatography (SEC)

The chromatography parameters (average molecular weights, molecular weight distribution ($M_w/M_n$)) were determined by SEC-TDA max instrument of Malvern Viscotek TDA 305 (Triple Detector Array) equipped with I-MBHMW-3078 column, a differential refractometer, a precision low angle light scattering detector, and a viscometer. The molecular weight parameters were computed using SEC data processing system (Omni SEC software).[30] The instrument was operated at 50 ℃ with DMSO as solvent. A flow rate of 1 ml min$^{-1}$ and injection volume of 100 µL was maintained. A concentration of ~ 2.0 mg/ml was maintained in all samples. Low angle laser light scattering (LALLS) instrument was used as a detector at a fixed wavelength of 633 nm. A set of polymethyl methacrylate (PMMA) standards of narrow molecular weight distribution (PolyCALTM, Viscotek, US) of molecular weight $2.0 \times 10^4 - 4.51 \times 10^5$ Dalton was used to calibrate the SEC-LALLS instrument. The carrier solvent was DMF containing 0.05m Lithium bromide (LiBr) with a flow rate of 1 ml min$^{-1}$.

### 2.6 Thermogravimertic Analysis (TGA)

The thermal stability of polyacrylonitrile polymers was evaluated on a Q 500 Thermogravimertic analyser (T.A. Instruments-UK model) at a heating rate of 10 ℃ min$^{-1}$ under a constant nitrogen flow (100 mlmin$^{-1}$). The samples were run from 40 to 600 ℃.

### 2.7 Differential scanning calorimetry (DSC)

Polyacrylonitrile copolymers were studied by employing a Differential Scanning Calorimeter (Make: Mettler Toledo, Model: DSC 821e) at a heating rate of 10 ℃ min$^{-1}$ under nitrogen atmosphere at a flow rate of 60 ml min$^{-1}$, using Aluminium pan). The operational conditions are: sample weight 10 mg, heating rate 10 ℃ min$^{-1}$, and nitrogen flow (100 ml min$^{-1)}$.

### 2.8 Thermomechanical Analysis

Thermomechanical analysis (TMA) was performed using TA Instruments (UK, Model: TMA Q400). TMA experiments were conducted in nitrogen atmosphere at a flow rate of 60 ml min$^{-1}$, at a heating rate of 5 min$^{-1}$. Polymer sample was dissolved in

DMF at 70 °C and cast in to thick films of 5 mm X 5 mm size. Both top and bottom surfaces of the film were polished before analysis.

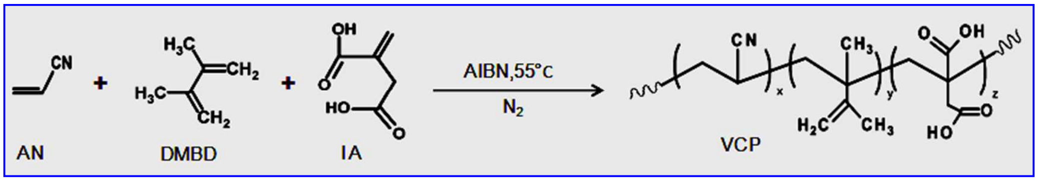
### 2.9 Dynamic Mechanical analysis

The dynamic mechanical analysis (DMA) was carried out with a Q 800 DMA apparatus (TA, USA) at a measurement frequency of 1 Hz and at a heating rate of 10 ℃ $min^{-1}$from room temperature to 280 ℃.

## 3. Results and Discussion

### 3.1 Synthesis of Poly (acrylonitrile-co-2,3-dimethyl-1,3-butadiene-co-itaconic acid)

The methodology used for the synthesis of VCP01/02 copolymers can be described as a one-pot semi-batch solution polymerization process. Initially, polymerization was started with the addition of monomer mixture consisting of three monomers in precalculated quantities, followed by the addition of initiator, and sequential addition of monomers over 135 min to reaction medium. The rate of monomer addition during polymerization reaction was estimated using the relationship between monomers and copolymer in an isothermal free radical copolymerization as expressed by copolymerization equation.[31] The over-all conversion of the polymerization was found to be in the range 74-78 % wt by analytical gravimetric measurements. The intrinsic viscosities of as-synthesized VHP, VCP01 and 02 polymers were 1.74, 1.75, and 1.62 $dLg^{-1}$, respectively. The free-radical reaction used in the synthesis of PAN copolymers is shown in scheme II.



**Scheme 2** PAN copolymerization reaction used in this study

### 3.2 Structural Characterizations

The average chemical composition of PAN-based copolymers as estimated from the ratio of the integrations of nitrile carbon, methyl carbon, methylene carbon and carbonyl carbon as observed in $^{13}C$ NMR spectra is given in Table 1. The IR spectra of the (a) PAN homopolymer (VHP01) and (b) copolymers (VCP01/02) are shown in Fig.1

**Table 1** Average chemical composition and molecular characteristics of VHP &VCP polymers

| Polymer Code | Polymer Composition mol % | | | Conversn. % wt. | $M_w$ x$10^{-5}$ Da | $M_n$ x$10^{-4}$ Da | $\eta_{iv}$ dLg$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | AN | DMBD | IA | | | | |
| VHP/01 | 100 | 0.0 | 0.0 | 78 | 2.35 | 6.18 | 1.74 |
| VCP/02 | 98.0 | 1.5 | 0.5 | 74 | 2.38 | 6.23 | 1.75 |
| VCP/03 | 98.0 | 1.5 | 0.5 | 74 | 1.95 | 5.74 | 1.62 |

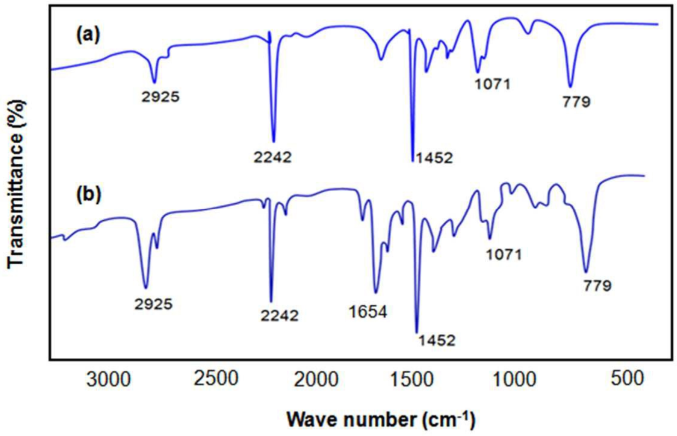


**Fig. 1** FTIR spectra of (a) VHP01 & (b) VCP02/03 polymers

**Table 2** Principal IR bands in solid VHP and VCP01/02

| Polymer Code | Functional Group | Wave Number cm$^{-1}$ |
|---|---|---|
| VHP/01 | **$CH_2$,CH,CN,-C=C-,-C-H** | 2925,1380,2242,1071,1620±10,779 |
| VCP/01 & 02 | **$CH_2$, CH, CN, -C=C-, -C-H, -C=O,-C=C-H** | 2925, 1380, 2242, 1071,1654,1390, 1740, 779 |

The principal infrared absorption band frequencies corresponding to the different functional groups of VHP01 and VCP01/02 polymers are presented in Table 2. The assignment of the characteristic absorption bands observed in both polymers (VHP01 and VCP01/02) is as follows: 2925 cm$^{-1}$ ( stretching vibrations $\nu_{C\text{-}H}$ in $CH_2$ or $CH_3$ ), 2242 cm$^{-1}$ ($\nu_{CN}$ ), 1452 cm$^{-1}$ ($\delta_{C\text{-}H}$ in $CH_2$ );

they are found to exist in the group frequency regions of both spectra confirming the basic structure of polyacrylonitrile. However, the characteristic strong, wide absorption peaks observed at 1654 $cm^{-1}$($\nu_{C=O}$ in -COOH), 1651 $cm^{-1}$ ($\nu_{C=C}$ in $CH_2$= $CH_2$), 1071 $cm^{-1}$ ($\nu_{C-OH}$ in -COOH, $\nu_{C-N}$ ) 779 $cm^{-1}$ ($\nu_{C-H}$ in – $CH_3$ or $CH_2$ ) are found in the finger print region of IR spectra of VCP01/02 polymers only, corresponding to the comonomers in VCP01/02 copolymers, thereby confirming the formation of copolymers.

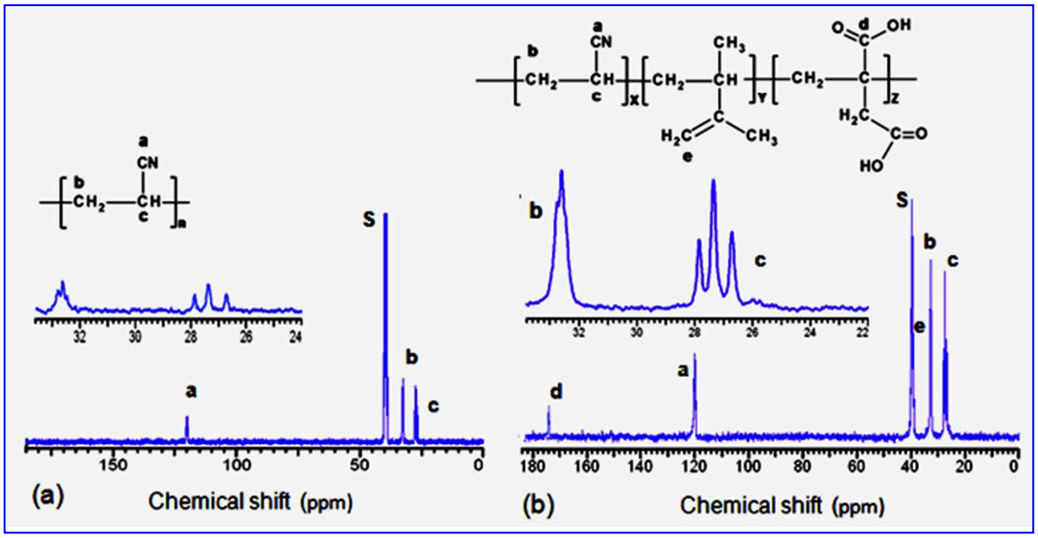


**Fig. 2** $^{13}$C NMR Spectra of (a) VHP and (b) VCP polymers in DMSO; Methine and methylene carbon region expanded.

Fig. 2. Presents $^{13}$C NMR spectra of (a) VHP01 polymer and (b) VCP01/02 copolymers. In total, there are five types of distinct carbons observed in VCP01/02 copolymers and VHP polymer corresponding to methine (CH), methylene ($CH_2$), methyl ($CH_3$), carboxyl (-COOH) and cyano-carbon (CN), respectively. In case of VCP01/02, the spectrum is a complex multiplet owing to the coexistence and overlapping of similar monomeric and configurational sequences in detectable amounts. The signals due to methine carbon, methylene carbon, nitrile carbon and carboxyl group appear around chemical shift values ($\delta$) 26.3-26.7, 32-33.2, 119.5-120, and 171-172.5 ppm, respectively. The presence of characteristic signals corresponding to chemical shift values of the respective functional carbons confirms the formation of copolymer and its structure.

### 3.3 Molecular characterizations

The molecular characteristics of VCP01/02 copolymers and VHP polymer, viz. number, weight average molecular weights as estimated from size exclusion chromatography are summarized in Table 1. The average molecular weights ( $M_w$, $M_n$ ) and the molecular weight distribution ($M_w$,/ $M_n$ ) of polymers synthesized in this study were estimated using size exclusion chromatography with low angle laser light scattering detector(LALLS).Fig. 3 represents the traces of SEC-LALLS elution curves, indicating the increase of elution time from @ 42 to 44 min.  as the average molecular weight decreases. Average molecular weights of the copolymers were varied to study their differential thermal behaviour. The weight and number average molecular weight of the VHP01 and VCP01/02 are in the range 2.35 x $10^5$ Da, 6.18 x $10^4$Da and 2.38 −1.95 x$10^5$ Da, 6.23 − 5.74 x $10^4$ Da, respectively. The molecular weight distribution was found to be in the range 3.80 – 3.39.

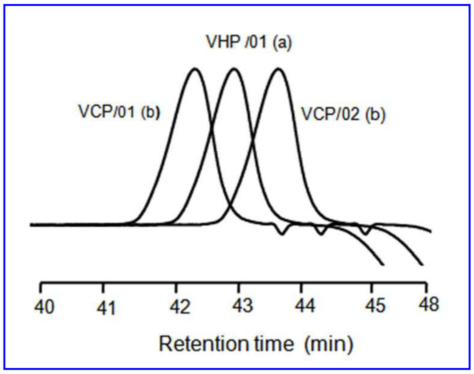


**Fig. 3** Traces of SEC-LALLS elution curves (a) VHP and (b) VCP polymers in dimethylformamide

### 3.4 Thermo-mechanical characterizations

Glass transitions are characterized by certain experimental observations that occur as the imposed environment of the material changes. Experiments aimed at the determination of glass transitions are performed for either isobaric cooling or isothermal compression of the material. Glass transitions in polymers are accompanied by the change in the specific heat, specific volume, and isothermal compressibility. Recently, improvements in tensile characteristics such as tensile strength and modulus of carbon fibres were achieved using fine denier special acrylic fibre precursors.[32] The fabrication of such fine sized SAF involve multi-step drawing process during fibre spinning as shown in Fig. 4. Though several heating mediums such as Ethylene glycol, oil, hot water baths, and hot plates are suggested for performing steam drawing operation, the use of saturated steam in a drawing apparatus with some specialized interior design for steam leak-free operation has become the state of the art. The thermo-chemical and mechanical properties of the PAN precursors influence their drawing behaviour significantly. PAN precursors with broad range of softening ($T_\alpha$), drawing ($T_D$), and annealing($T_A$) temperatures facilitate steam drawing operation to fabricate fibre tows with low denier and high tensile characteristics. PAN polymer precursors with poor drawing characteristics often result in the low tensile strength, crystallinty, and degree of crystalline orientation of SAF. The softening points and glass transition temperature influence the stretch behaviour of the polymer substantially. Therefore, the glass transition points as a function of temperature, pressure are crucial for the drawing characteristics and certain service applications of PAN polymers.

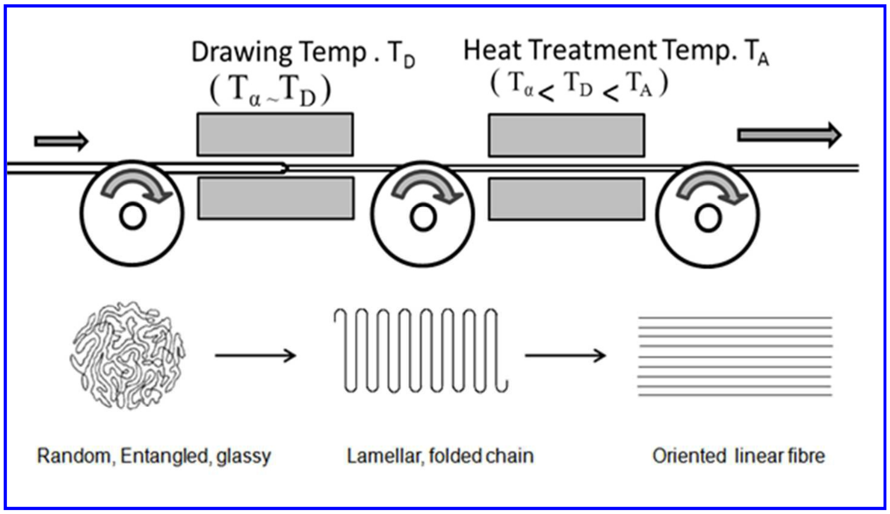


**Fig. 4** Schematic diagram of multi-stage steam drawing unit for fabrication of fine sized SAF ($T_\alpha$, $T_D$ & $T_A$ refers to temperature of softening, drawing and annealing, respectively)

The drawing process pulls the molecules of the spun fiber so that they solid past one another until the molecular chains are aligned parallel to one another. The mechanical and thermal properties of substances in the glassy state are known to be functions of the glass transition temperature, and the history of how the material enters the glassy state. This can be observed in the plots of Tan δ versus temperature of the VCP copolymers and VHP polymer as shown in Fig. 5. There exist four main possible regions in case of PAN polymers; they are a) The area between 90 ℃ and 120 ℃ where the first possibility ($\alpha_I$) for drawing or stretching exits, b) Dynamic elastic region between >130 ℃ and < 160 ℃ where any kind of chemical reactions pertaining to thermal oxidative stabilization are yet to start ($\alpha_{II}$), c) the region of temperature <180℃ and >220 ℃, where certain thermal cyclization reactions progressed to a negligible extent($\alpha_{III}$), d) the thermal region in the dynamic elastic spectra ranging 225−235 ℃, where the oxidative thermal reactions such as dehydrogenation, cyclization has progressed to an extent of around 10 %.

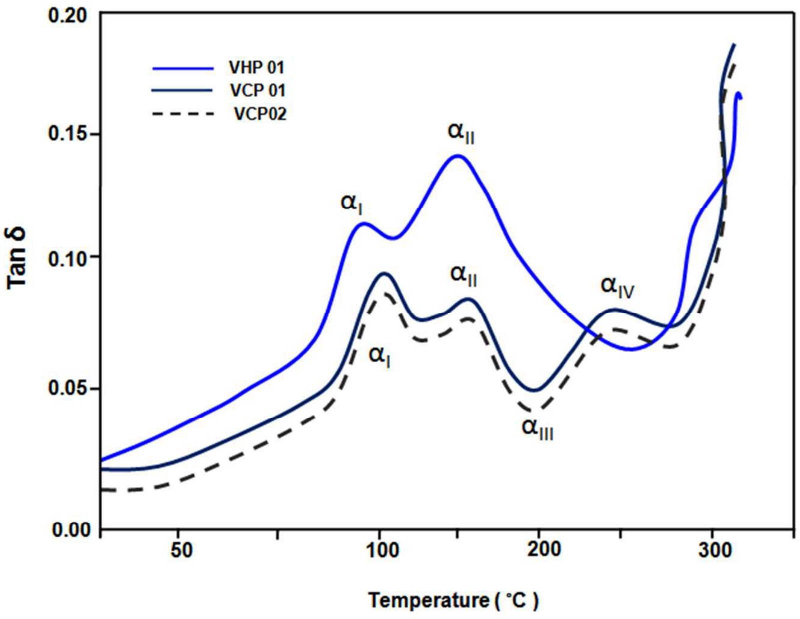


**Fig.5** Plots of Tan δ versus temperature of the VCP 01/02 and VHP/01 polymers

The determination of glass transition temperature ($T_g$) using differential scanning calorimetry has been difficult due to the strong exothermic reaction; minor transitions like $T_g$ cannot be observed. A typical thermomechanical analyzer (TMA) measures volumetric changes in the dimensions of the sample as a function of time, temperature or force.TMA is a highly sensitive method for the measurement of expansion and contraction of polymeric materials. The coefficient of linear thermal expansion (CLTE, α, or, $\alpha_l$) is a material property that is a measure of the extent to which a material expands on heating. The thermal expansion of uniform linear objects is proportional to temperature change. The plots as in Fig. 6 a, b and c show the dimensional changes as function of temperature of two kinds of VCP01/02 copolymers and VHP polymer. The values of CLTE in different temperature ranges and thermal transitions as observed from thermo mechanical curves are presented in Table.3. It can be observed that there are two inflection points in each figure, corresponding to thermal relaxation/mobility and transitions of side functional groups in the PAN polymers. There is a notable decrease of temperature related the transition points, i.e. $T_1$ from 57.27℃ to 51.28 ℃ and $T_2$ from 94℃ to 87 ℃ in case of VCP01/02.

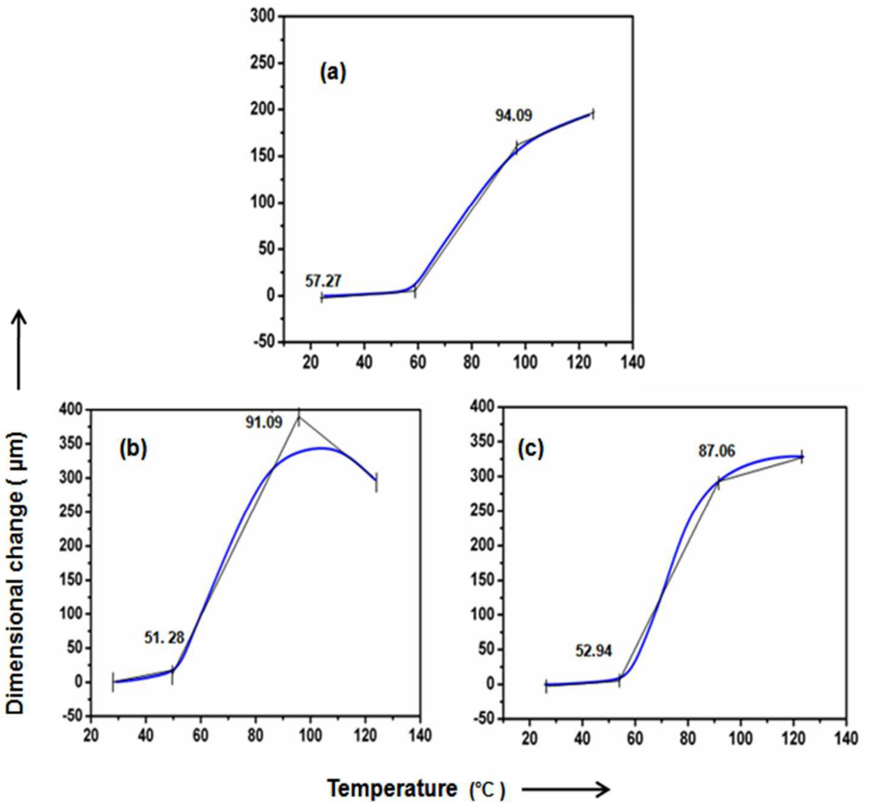


**Fig.6** TMA curves of (a) VHP/01, (b) & (c) VCP 01/02polymers

**Table 3** Softening and glass transition temperatures and Coefficient of linear thermal expansion (CLTE) of (a) VHP and (b &C) VCP01/02 polymers

| Polymer Code | $\eta_{iv}$ dL/g | Temperature ranges °C | | | Inflection Points* | |
|---|---|---|---|---|---|---|
| | | CLTE | | | $T_1$ | $T_2$ |
| | | 30 – 50 °C | 50-80°C | >90°C | - | - |
| VHP/01 | 1.74 | 37 | 810 | 896 | 57 | 94 |
| VCP/02 | 1.75 | 74 | 1138 | 1601 | 51 | 91 |
| VCP/03 | 1.62 | 122 | 1716 | 1742 | 53 | 87 |

*Inflection points from figure 6 (a-c) $T_1$ and $T_2$ indicate softening and glass transition temperature, respectively

### 3.5 Thermo-chemical characterizations

The thermal mass loss behaviour of VCP01/02 copolymers and VHP polymer is shown in Fig. 7. VHP01 polymer is stable up to 301 ℃ and begins to lose the mass abruptly after this temperature, however, the mass loss, in case of VCP01/02 starts at 267 ℃ and gradually degrades. The over-all mass loss of new copolymers was found to be around 35 % wt. at 450 ℃ and that of VHP01 is 53 wt.% . This differential degradation pattern may be ascribed to the presence of itaconic acid monomer in VCP01/02, indicating its suitability as precursor polymer for high tensile carbon fibres.

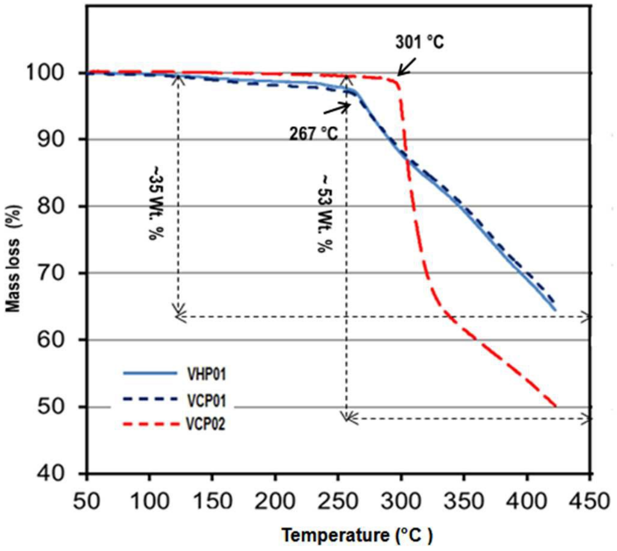


**Fig. 7** Thermogravimertic mass loss curves of VCP01/02 and VHP polymers.

Fig. 8 (a-c) show the DSC exotherm of VHP polymer and copolymers under nitrogen, The stabilization of acrylic fibres of acrylonitrile homo and copolymers in an oxygen-containing atmosphere involves essentially two major thermal reactions: firstly, an oxidative cross-linking reaction of adjacent functional molecules, and secondly, a cyclization reaction of pendant nitrile groups to a condensed dihydropyridiene structure. The thermal cyclization reactions of pendant nitrile groups in the PAN copolymers are highly exothermic in nature irrespective of oxygen or nitrogen-containing atmosphere. In the absence of heat removal arrangements during thermo-oxidative stabilization process, PAN precursor fibre surface approaches this critical temperature very quickly, though sometime it may exceed. If uncontrolled, the thermal runaway reactions may result in the destruction of fibre skeleton or configuration of the starting raw materials. More often, the fibre precursor will rupture, disintegrate, and/or coalesce when certain critical temperature is reached In general, this critical exotherm occurs around 300

℃ in many of the polymer precursors. The reduction in the residual heat of reaction before and after the stabilization step during carbon fibre manufacture reflects the flame resistance gained by the fibre precursor

**Table 4** DSC data of VHP and VCP 01/02 polymers

| Polymer Code | $\eta_{iv}$ dL/g | | $T_i$ °C | $T_f$ °C | ΔT °C | $T_{peak}$ °C | ΔH J/g | ΔH/Δt $Jg^{-1}s^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| VHP/01 | 1.74 | | 290.28 | 296.52 | 6.24 | 290.52 | 546 | 14.75 |
| VCP/02 | 1.75 | $P_1$ | 223.87 | 235.49 | 11.62 | 228.72 | 173 | 2.48 |
| | | $P_2$ | 251.33 | 269.39 | 18.06 | 262.01 | 535 | 4.95 |
| VCP/03 | 1.62 | $P_1$ | 226.8 | 240.39 | 13.59 | 233.04 | 184 | 2.25 |
| | | $P_2$ | 252.94 | 270.18 | 17.24 | 262.11 | 439 | 4.24 |

$P_1$, $P_2$ refer to peaks observed in the respective bimodal DSC isotherms

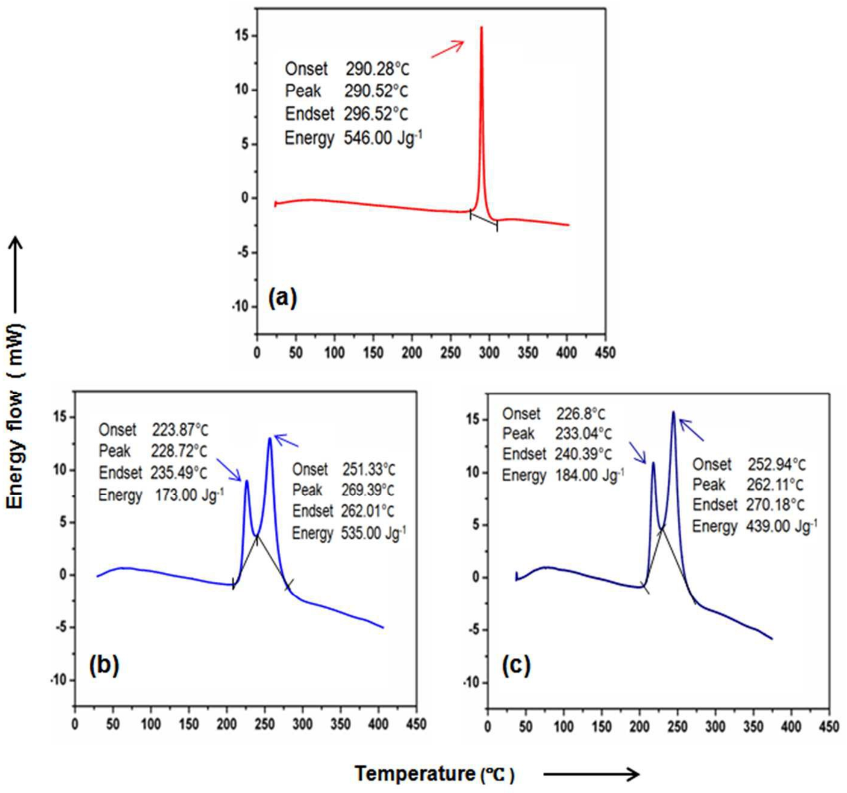


**Fig. 8** DSC exotherm of (a) VHP01 and (b & C) VCP 01/02 polymers in nitrogen

The bimodal curve with two peaks differing in peak temperature ($T_p$) of @ 35 ℃ can be related to two independent competing parallel reactions, viz., an oxidative cross-linking reaction of adjacent functional molecules, secondly, a cyclization reaction of pendant nitrile groups. The average energy released and heat release rate in the first two reactions are 178, 487 $Jg^{-1}$, 2.35, and 4.6 $Jg^{-1}s^{-1}$, respectively. This distinctive thermal exotherm with much lower rate of heat release clearly demonstrates the enhanced thermal characteristics of VCP01/02, which is more desirable as carbon fibre precursor polymer over conventionally used.

## 4. Conclusions

Novel PAN-based carbon fibre precursor polymer with improved thermal characteristics viz., Poly (acrylonitrile-co-2,3-dimethyl-1,3-butadiene-co-itaconic acid) was synthesized using solution polymerization process. Structural identification and bonding networks were established using FTIR-ATR and $^{13}$C-NMR techniques, respectively. Number and weight average molecular weights were estimated with size exclusion chromatography, and found to be in the range of 5.23−6.74 X $10^4$ Da and 1.95−2.38 X $10^5$ Da, respectively. Glass transition temperatures and coefficient of linear thermal expansion of as-synthesized polymer were determined using thermo-mechanical analyzer and compared to that of conventional VHP polymers. VCP01/02 copolymers show a softening/glass transition at a lower temperature @ 52 ℃. The CLTE of VCP01/02 copolymers range from 121 to 1716 ℃$^{-1}$, confirming their improved drawing characteristics over the conventional polymers. VCP01/02 copolymers exhibited distinctive bimodal DSC exotherm consisting of two peaks at a temperature difference of @ 25 ℃ with a delayed heat 1716 ℃$^{-1}$, confirming their improved drawing characteristics over conventional polymer. VCP01/02 copolymers exhibited distinctive bimodal DSC exotherm consisting of two peaks at a temperature difference of @ 25 ℃ with a delayed heat release at a rate of 2.45 – 5.0 $Jg^{-1}$ $s^{-1}$, which is lower than VHP polymers (15 $Jg^{-1}$ $s^{-1}$), thereby proving their enhanced thermal characteristics as desirable polymer precursor for high tensile carbon fibres.

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