Molecular and thermal studies of carbon fiber precursor polymers with low thermal-oxidative stabilization characteristics

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ABSTRACT: In this investigation, terpolymers, copolymers, and homopolymer of acrylonitrile with dimethylaminopropyl acrylamide (DMAPA), itaconic acid (IA) viz., poly(acrylonitrile-ran-3-dimethylaminopropyl acrylamide-ran-itaconic acid) [P(AN-DMAPP-IA)], poly(acrylonitrile-co-3, dimethylaminopropyl acrylamide) [P(AN-DMAPP)] were synthesized with varying amounts of comonomers using solution polymerization process. The chemical structure, composition, bonding network were determined employing infrared, 1H and, 13-carbon nuclear magnetic resonance spectroscopic techniques. Molecular characteristics of as-synthesized polymers such as different kinds of average molecular weights, molecular weight distribution were estimated applying solution viscometry and size exclusion chromatography. The influence of comonomers (DMPAA, IA) on the thermal stabilization characteristics of acrylonitrile terpolymers in comparison with copolymers and homopolymers of acrylonitrile were studied using differential scanning calorimetry (DSC), hyphenated thermal techniques (thermal gravimetry coupled with differential thermal analyzer).The DSC curves of P(AN-DMAPP-IA) exhibit a distinct broader bimodal peaks with thermal exotherm initiating at as low as 165 °C, and followed by two peaks with temperature difference of 42 °C, releasing the evolved heat at a release rate of 0.7–0.11 J g^{-1} s^{-1}over 10 min as compared to 1.2, 7.5 J g^{-1} s^{-1} in 4.5, 2 min as observed in P(AN-DMAPP), polyacrylonitrile, respectively. The thermal stability of P(AN-DMAPP-IA) and P(AN-DMAPP), as evidenced by TGA-DTA was found to be higher than PAN homopolymers. Specific heat capacity measurements confirmed the DSC results. Bulk densities of P(AN-DMAPP-IA) were in the range 0.31–0.35 g/cc. These results confirm the low-temperature stabilization characteristics and suitability of P(AN-DMAPP-IA) as low cost carbon fiber precursor polymers. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2018, 135, 46381.

INTRODUCTION

Polyacrylonitrile-based copolymers (PAN) are considered as one of the most widely used and industrially manufactured substituted poly-olefins. PAN-based copolymers account for more than 90% share of the precursors used in the industrial manufacture of carbon fibers.[1,2] PAN-based carbon fibers (CF) are known for their high mechanical properties including high specific strength, modulus, and other functional properties.[3–5] Among many precursors available for CF manufacture, PAN have become the most successful for high-tensile carbon fibers owing to their specific morphology, processability, and tensile elasticity.[6–8] Based on the market segments, CFs are produced in two kinds; firstly, small tow CF comprising of 3000–12,000 filaments (usually, called as 3 K, 6 K, and 12 K), which caters to the requirements of traditional domains of aeronautics, space, and, defense applications. On the other hand, the large to very large tow CF consisting of filaments in the range 40,000–250,000 (40–250 K) are manufactured targeting massive industrials demands such as windmill blades, off-shore oil platforms, and automobile sectors.[2,9] As the tow size increases, the energy requirements (cost) for CF manufacture rises exponentially. Although there exists sufficient literature on the selection of monomer and composition of the precursor polymer, yet the design of PAN copolymer synthesis, composition, and other molecular parameters required in polymer precursors targeting a set of tensile characteristics in CF remains a formidable challenge. In other words, optimum molecular, physical characteristics of the polymer/fiber precursors such as copolymer composition, molecular weight, molecular weight distribution, linear density (dtex), and tensile properties are a prerequisite. Extensive research in the field of PAN-based carbon fibers (CFs) focused on developing new precursors and modifying the process of stabilization and carbonization in order to control and to maximize their mechanical performance.

	Let-off creel	Multi-zone oven	1° Carbonizer	2° Carbonizer	Surf. Treat. Bath	Winder
Time, min		90 - 180	2 - 3	~2	~2	~
Temperature, °C		180-270	320 - 650	650 - 1650	~	~
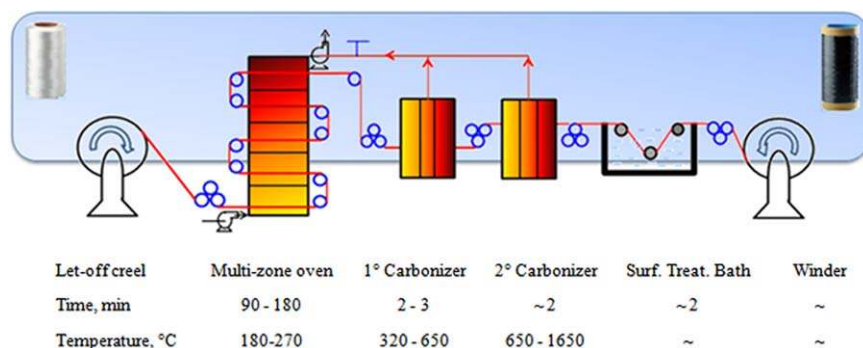
Scheme I. Heat treatment processes in the carbon fiber manufacture. [Color figure can be viewed at wileyonlinelibrary.com]

Generally, industrial manufacture of carbon fiber involves several stages of energy-intensive processes such as hot-water bath drawing, secondary saturated steam-assisted drawing process, thermo-mechanical shrinkage or extension during oxidative stabilization (200–280° C) and carbonization (300–2800° C), leading to a high cost barrier and complex intermediate equipment technologies.[10] Among them, thermal oxidative stabilization (TOS) is very critical and highly energy-intensive process.

Several heat treatment processes involved in the manufacture of carbon fiber is illustrated in Scheme I. The cost structure of the carbon fiber is dominated by PAN precursor and energy for heat treatment process including TOS close to 70%.[11,12]

Since majority of the acrylonitrile-based precursor's exhibit sharp exotherms, accompanied by the sudden uncontrolled release of heat in the order of 4500 calories/g in an oxidizing atmosphere, the thermal oxidative stage during the carbon fiber manufacture is conducted in prohibitively slow heating rates and line speeds, typically <10 m min.[13–17] In this account of the high exothermic nature of the TOS, particular attention is being given to the various possible ways in which the magnitude and general characteristics of the exotherm may be influenced. Uncontrolled oxidative-stabilization reaction of precursor tows may lead to the fusion of filaments, coalescence, and fragmentation of chain segments resulting in the reduction of tensile properties of the obtained carbon fibers.

TOS process imparts the necessary heat resistance to acrylic fiber precursor to endure the high temperature carbonization and graphitization processes of CF manufacture. In general, thermal stabilization process is a slow, time consuming, and energy intensive process. Conventional TOS takes approximately 100–200 min for attaining desired level of heat resistance, in terms of oxidized fiber density as well as limiting oxygen index. Therefore, the recent attention in the CF research is focused on the development of an over-all cost-effective processes; low-energy intensive heat treatment furnaces/ovens for flame resisting process, and polymer/fiber precursors to facilitate low-cost manufacturing processes.

It is known that the desirable properties such as heat resistance and electrical conductivity of thermally treated polyacrylonitrile polymer are caused by their structures formed upon dehydrogenation and ring closure. However, the ring closure of most commonly used carbon fiber precursor is occurring at thermal stabilization reaction temperature in the range 280–310 °C.[18,19] These reactions obviously interfere with adequate completion/formation of the cyclized structures. Kenneth et al. performed TOS process in presence of various catalysts, such as primary and secondary amines while it was possible to somewhat lower the heat treatment temperature for the ring closure reaction,[20–22] however such reactions were accompanied by other undesirable effects such as brittleness and insufficient crystallinity and strength reduction. A typical copolymer having improved physical properties, facile cyclized structure formation, and crystal formation after heat treatment are very much desired. Some copolymers quickly form the cyclized structure under relatively mild heating conditions.

Many industrial researchers attempted to optimize the tensile and molecular characteristics of both fiber and polymer precursors using several chemical and mechanical processes. They include the polymerization of additional comonomers in to polymer structures, control of right range of molecular weight distribution, and thermally assisted mechanical drawing.[23] Among them, copolymerization and terpolymerization of acrylonitrile with certain functional comonomers have stimulated significant interest due to their beneficial influences in spinning and stabilization processes of precursors fibers, which have been reported by previous studies.[15,16,24]

Numerous copolymer compositions have been investigated with targets to find out ultimate processing conditions viz. high stream drawing ratio, coagulation, thermal oxidation at faster rates. Although it is evident that different compositions will require different processing conditions for optimal properties, copolymerization of acrylonitrile (AN) with some comonomers, such as acrylic acid (AA), methacrylic acid (MAA), and itaconic acid (IA), has been found to be effective in reducing the exothermic effect and promoting cyclization and dehydrogenation during stabilization.[25] However, the extent of cyclization is limited to a certain level because some nitrile groups start to decompose before cyclization.[26] Several types of pretreatments to the PAN-based fibers have been employed to promote the cyclization.[23,27] For example, pretreatments with plasma, Gamma ray, electron beam, and UV irradiation and chemical treatment with boron, bromide agents have been reported to promote the intermolecular cyclization as well as the crosslinking of the nitrilegroups.[28,29] However, excessive irradiation could induce surface defects, which had negative impacts on the

mechanical properties of the resulted fibers. Many investigators attempted to produce acrylonitrile copolymers as CF precursors with enhanced thermal properties, but these candidate precursors suffer from the poor drawing characteristics during the heat treatment process due to high brittleness and causes a high frequency of fluff/loose filaments per meter of precursor.[30,31] Considering the foregoing drawbacks observed in the currently used polymer precursors, the development of anew polymer precursor with enhanced ability to undergo thermal-oxidative stabilization at a lower temperature range as compared to the conventionally used temperature of 230–300 °C, decreasing the intensity of the exotherm by broadening it over a wider temperature range without inhibiting the total reaction, would be a huge step towards the low-cost manufacture of CF for high volume applications. In this context, an attempt has been made to synthesize a new PAN terpolymer composition consisting of functional comonomers viz., N-[3-(dimethylamino)propyl acrylamide] (DMPAA), Itaconic acid, which promotes simultaneous TOS reaction at relatively low temperature and faster flame resisting process due to remarkably low heat release rate. It is proposed that DMPAA with acrylamide and amine functional groups play a catalytic role to facilitate low-temperature stabilization process in addition to itaconic acid. This article presents the results of the synthesis, molecular structure, morphology, and thermal characteristics of a new acrylonitrile pseudo-random terpolymers system viz., poly(acrylonitrile-ran-Itaconic acid-ran-dimethyl amino propyl acrylamide) with low thermal stabilization characteristics and discusses their low thermal stabilization characteristics.

EXPERIMENTAL

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. N-[3-(Dimethylamino) propyl acrylamide] (>98%, Tokyo Chemical Industries), Itaconic acid (IA, 99%, Aldrich) were used as received. 2,2-azobis(2-methyl-propionitrile) (AIBN, 98%, Aldrich) was used as initiator after recrystallization from methanol 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.

Synthesis of Acrylonitrile Based Homo and Copolymers

Acrylonitrile based homopolymer, copolymers and terpolymers with DMPAA, and IA were prepared by solution polymerization process. 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 °C. Acrylonitrile (1.815 mol), (28 mmol), N-[3-(Dimethylamino) propyl acrylamide], and Itaconic acid (9.2 mol.) 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 PAN polymers of different molecular masses. The progress of free-radical solution polymerization was monitored by measuring specific viscosity of the reaction mixture at different time intervals. The specific viscosity is a ratio of the viscosity of the reaction mixture to that of the reaction medium, which gives the change in viscosity of the reaction mixture because of polymerization. The polymerization reaction was stopped after 5 h at 55 °C by quenching the reaction mixture in chilled methanol. The polymers were 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 °C under vacuum to a constant mass.

Fourier Transform Infrared Spectroscopy and Nitrile Group Survival Ratio. Fourier transform infrared spectroscopy (FTIR) spectra of acrylonitrile-based polymers 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, 100 mL min^{-1}). The temperature at which, nitrile group content of the acrylonitrile copolymer fiber/film becomes @ 35% wt when it is heated in air at 100 min, known as critical thermos-oxidative-temperature was determined using FTIR. Residual nitrile group content, usually expressed in terms percentage is used to control the optimum level of thermal stabilization treatment that should be given to acrylic white fibers tows. This parameter is often used in industry to know the degree of completeness of thermal-oxidative stabilization reaction in addition to the conventional density measurement of the oxidized acrylic fiber tows.

Determination of Residual Nitrile Group Content. Dried acrylonitrile based polymer powdery samples were dissolved in dimethyl formamide to make a 6.0% wt solution. The resulting solution was casted on a glass plate in uniform thickness. Further the glass plate was dried in hot air circulation oven at 110 °C. After the evaporation of the solvent, a film of 20–40 μ thickness is obtained. The obtained film was subjected to TOS treatment for 100 min by heating in the temperature range of 180–250 °C at a heating rate of 5 °C/min. The heat treated/stabilized film was powdered. An FTIR spectrum of the powdery samples at 2242 ± 10 was obtained after mixing with KBr salt. The intensity of the Carbon–Nitrogen triple bond of Nitrile group (—C≡N) before and after heat treatment was estimated. The residual nitrile group content was determined using the following relationship.

$$X = D_a / D_b \times 100 \qquad (1)$$

D_a and D_b denotes the intensity of the nitrile group (—C≡N), before and after heat treatment.

^{1}H, ^{13}C-nuclear magnetic resonance measurements (NMR) The liquid ^{1}H-NMR spectra were obtained on a Bruker Avance 400 MHz, Switzerland. Samples were concentrated in deuterated dimethyl sulfoxide (DMSO-d$_6$) about 20% (w/v) for ^{1}H-NMR

spectra. ^{1}H-NMR spectra were acquired using 21,738 data points, spectral width 6 kHz, broadening 0.3 Hz, pulse delay 1 s, pulse width 90°, and 32 scans. ^{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.[27] Samples were concentrated in dimethyl sulfoxide about 5% (w/w) for ^{13}C-NMR using a 5 mm NMR tube at room temperature. ^{13}C-NMR spectra were acquired using 24,996 data points, spectral width 22 kHz, broadening 3 Hz, pulse delay 2 s, pulse width 90°, and 1024 scans.

Solution Viscometry. Specific viscosity (η_{sp}) was measured at 30 °C in DMF with an Ubbelohde capillary tube viscometer maintained in a constant temperature bath. Intrinsic viscosity (η) was obtained as η_{sp}/C extrapolated to $C = 0$ according to the eq. (2).

$$[n] = \left[\left(1.44 \times \eta_{sp} + 1 \right) \right]^{1/2} - 1/0.36 \tag{2}$$

where C is polymer concentration, η_{sp} is the specific viscosity. The viscosity average molecular weight of PAC was calculated by eq. (3).

$$[n] = 3.35 \times 10^{-4} [M_V]^{0.72} \tag{3}$$

Size Exclusion Chromatography

The molecular parameters [average molecular weights, molecular weight distribution (M_w/M_n)] were determined by size exclusion chromatography (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),[29] the instrument was operated at 50 °C 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 poly(methyl methacrylate) standards of narrow molecular weight distribution (PolyCAL™, Viscotek, Malvern Instruments, Malvern, United Kingdom) of molecular weight (2.0×10^4–4.51×10^5) Dalton was used to calibrate the SEC-LALLS instrument. The carrier solvent was DMF containing 0.05 m Lithium bromide (LiBr) with a flow rate of 1 mL min^{−1}.

Differential Scanning Calorimetry

The nature of exothermic reactions that occur as part of the thermal-oxidative stabilization process of newly designed terpolymers, copolymers, and homopolymer of acrylonitrile were investigated by employing a differential scanning calorimeter (Make: Mettler Toledo, Model: DSC 821e) at a heating rate of 10 °C min^{−1} under nitrogen/air atmospheres at a flow rate of 60 mL min^{−1}, using aluminum pan. The operational conditions are: sample weight 10 mg, heating rate 10 °C min^{−1}, and nitrogen flow (100 mL min^{−1}) in the temperature range up to 500 °C. The differential scanning calorimetry (DSC) parameters observed in the exotherms viz., cyclization initiation (on-set) temperature (T_i), peak temperature (T_{pk}), end-set temperature (T_{cl}), and total heat evolved (ΔH), were estimated using the instrument software. Specific heat (C_p) measurements of polymers under investigation were performed with DSC using sapphire method. Three tests, one each for blank, sapphire and the sample were carried out. DSC base curve was obtained by blank measurements. With known value of specific heat, the rate of change of heat flow as a function of time t, of the sample and sapphire were calibrated with base curve. Specific heat values of the polymers were estimated by comparison with that of sapphire.

Thermogravimetric Analysis–Differential Thermal Analysis (TG-DTA).

The thermal stability of acrylonitrile based terpolymers/copolymers was evaluated on a Q500 Thermogravimetric analyzer (T.A. Instruments-UK model) at a heating rate of 10 °C min^{−1} under a constant nitrogen flow (100 mL min^{−1}). The samples were run from 40 to 600 °C.

RESULTS AND DISCUSSION

Synthesis of Poly(acrylonitrile-ran-3-dimethylaminopropyl acrylamide-ran-itaconic acid) and Poly(acrylonitrile-co-3,-dimethylamino propyl acrylamide)

Though PAN is insoluble in its own monomer, that is, acrylonitrile, it dissolves substantially in dimethyl formamide: water mixture and precipitates out beyond certain critical concentration levels. Free radical ter/copolymerization of acrylonitrile with 3-dimethylaminopropyl acrylamide, and itaconic acid was carried-out under inert atmosphere using AIBN as initiator at 55 °C. The free-radical reaction used in the synthesis of PAN terpolymers is shown in Scheme II. Initially, a solvent mixture (DMF: H$_2$O) as reaction medium
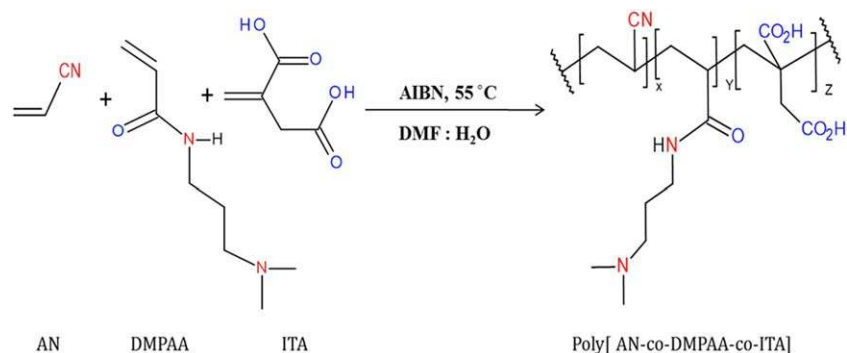
Scheme II. PAN terpolymerization reaction used in this study. [Color figure can be viewed at wileyonlinelibrary.com]

Table I. Average Chemical Composition and Molecular Characteristics of PAC Polymers

Polymer code	Polymer composition (mol %)			Convsn. (wt %)	η_{iv} (dL g^{-1})	$M_v \times 10^{-5}$ (Da)	$M_w \times 10^{-5}$ (Da)	$M_n \times 10^{-4}$ Da	M_w/M_n	Bulk density (g cm^{-3})
	AN	DMAPA	IA							
PAC-H01	100	0.0	0.0	78	1.74	1.44	1.19	3.8	3.71	0.41
PAC-C01	97.0	3.0	0.0	74	2.02	1.79	1.53	4.32	3.65	0.35
PAC-T01	95.0	3.0	2.0	72	2.32	2.16	1.85	5.74	3.23	0.31
PAC-T02	94.0	4.0	2.0	70	2.38	2.23	1.88	4.89	3.85	0.31

was heated to the reaction temperature; polymerization was started with the addition of monomer mixture consisting of three monomers in predetermined quantities, followed by the addition of initiator, and sequential addition of monomers over 165 min. The rate of monomer addition during polymerization reaction was estimated using the relationship between monomers and copolymer/terpolymer in an isothermal free radical ter/copolymerization as expressed by copolymerization equation.[32–34] In contrast to the regular acrylonitrile polymerization reaction, polymerization of acrylonitrile with 3-dimethylaminopropyl acrylamide was very slow and yellow pasty turbidity appeared after a delay of 30 min. This may be attributed to the bulkiness of the comonomer as compared to other conventionally used vinyl monomers. The average chemical composition as estimated from 1NMR spectra of the polymers, conversion of the polymerization, average molecular weights, and bulk density are presented in Table I.

The over-all conversion of the polymerization was found to be in the range 70%–78% wt by analytical gravimetric measurements, which is an average of five measurements in each case. The intrinsic viscosities of as-synthesized PAC H01, C01, T01/T02 polymers were 1.74, 2.02, 2.38, and 2.38 d Lg^{-1}, respectively. The conversion of P(AN-DMAPP-IA) terpolymer and P(AN-DMAPP) copolymers are almost in same range with that of PAN, but decreases with increase of DMAPP content. This is probably due to low reactivity of the DMAPP toward acrylonitrile by steric hindrance.

Structural Characterizations

The FTIR, ^{1}H, ^{13}C-NMR spectral analysis of copolymers were performed to establish and identify the bonding and structure in the P(AN-DMAPP-IA) terpolymers and P(AN-DMAPP) copolymers. As described in the polymerization reaction Scheme III, as synthesized terpolymers are presumed to contain acrylonitrile (94–95 mol %), N-[3-(dimethylamino) propyl acrylamide] (3–4 mol %), and itaconic acid (2 mol %). It is essential to confirm their identification in the polymer structure of the newly formed terpolymers. Figure 1(a–c) shows FTIR spectra of (a) polyacrylonitrile, (b) P(AN-DMAPP-IA) terpolymers, and (c) P(AN-DMAPP) copolymer. The major Infrared absorption band frequencies corresponding to the different functional groups of PAC-H01, PAC-C01, and PAC T01/02 polymers are presented in Table II.

The assignment of the characteristic absorption bands observed in all polymers under investigation is as follows: 2925/

2927 cm^{-1} (stretching vibrations ν_{C-H} in —CH or —CH$_2$), 2242 (ν_{CN}), 1452 cm^{-1} (δ_{C-H} in CH$_2$ bending vibrations); they are found to exist in the group frequency regions of both spectra confirming the basic structure of PAN.

However, the characteristic strong, wide absorption peaks observed at 1446 [ν_{N-C} in —N(CH$_3$)$_2$ stretching], 1536 ($\nu_{C=O}$ in —CONH), 1654 (ν_{C-O} in —COOH), 1651 ($\nu_{C=C}$ in CH$_2$=CH$_2$), 1071 (ν_{C-OH} in —COOH, ν_{C-N}) 779 (ν_{C-H} in —CH$_3$ or CH$_2$) are found in the finger print region of IR spectra of PAC-C01 and PAC-T01/02 only. A strong absorption around 3614 cm^{-1} can be assigned to the presence of —OH symmetric stretch from itaconic acid comonomer in PAC-T01/02. Thus, the presence of characteristic functional groups in the as-synthesized polymers originating from comonomers confirms the formation of ter/copolymers.

The ^{1}H-NMR analysis of the reactant monomers was performed to facilitate their functional identification and establish bonding network in the newly polymerized structures viz., P(AN-DMAPP-IA) and P(AN-DMAPP). Figure 2(a,b) show the ^{1}H-NMR spectra of AN monomer and DMAPP comonomer. In the spectrum of AN monomer, multiple signals corresponding to methine (—CH) proton are observed between chemical shifts (δ) 5.96 and 6.03 ppm. Two doublet signals appear at δ 6.27 and δ 6.51 ppm may be assigned methylene (—CH$_2$).The protons labeled as α, β_1, β_2, and γ corresponding to chemical shift signals (δ) 2.2–2.3, 2.43–2.41, 1.61 ppm, respectively, are directly associated to methyl, methylene groups attached to the tertiary N (3° N) atom of [—CH$_2$ N(CH$_3$)$_2$] in DMAPP. These chemical shift values are likely to further shift towards downfield if nitrogen is protonated. The

Poly[AN-co-DMPAA-co-ITA]   Naphthyridiene rings
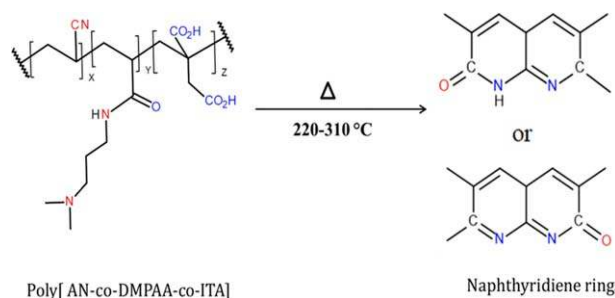
Scheme III. Transformation of DMPAA to cyclic naphthyridine through Intramolecular amidation. [Color figure can be viewed at wileyonlinelibrary.com]
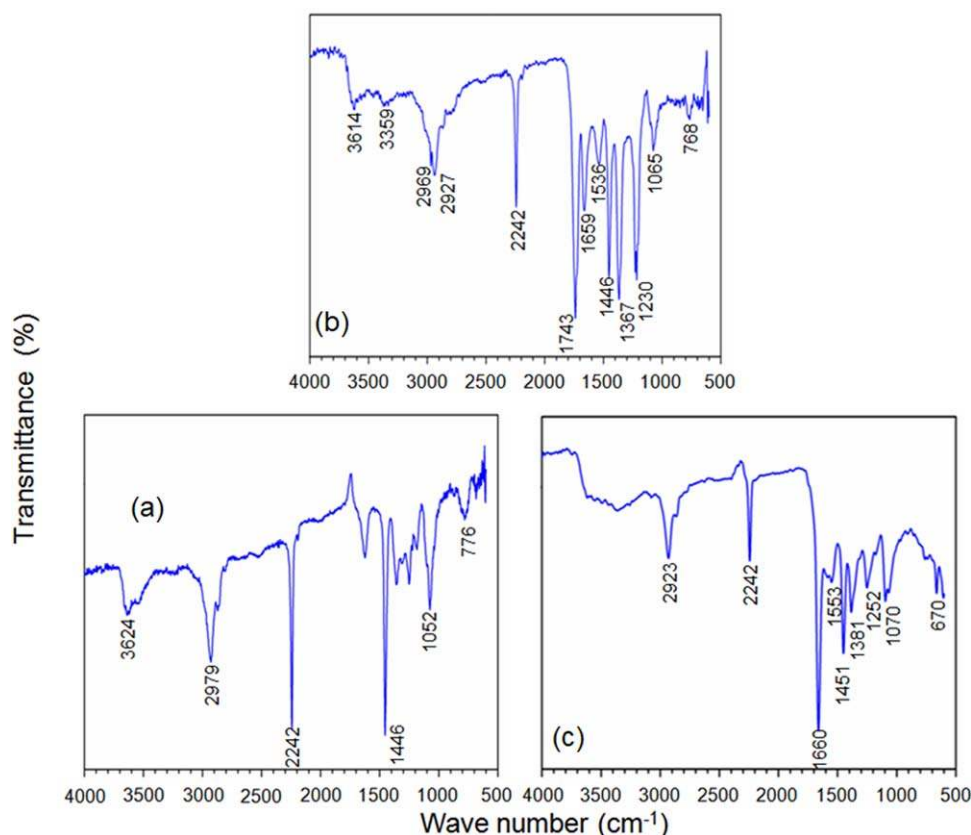
Figure 1. FTIR spectra of (a) PAC-H01, (b) PAC-T01/02, and (c) PAC-C01 polymers. [Color figure can be viewed at wileyonlinelibrary.com]

unsaturated vinyl structure in DMAPP gives an ABX type NMR absorption pattern depending upon the nature of the substituent attached to it, which determines the chemical shift positions of the protons. Protons designated as A, A′, and X are not chemical shift equivalent as the proton A is deshielded compared to proton A′ due to its close proximity to the substituent and absorbsat δ 6. 6.05 ppm whereas the NMR signal at δ 6.0 ppm. Proton X is further strongly deshielded and shows an absorption signal at δ 6.15–6.20, as multiple due splitting by the neighboring protons.

Figure 3 shows the ^{1}H-NMR spectra of P(AN-DMAPP-IA). The protons directly associated to methyl, methylene groups attached to the tertiary N (3° N) atom of [—CH_2 N$(CH_3)_2$] in DMAPP (proton a, b, b_1, b_2, and c) were once again found to move to downfield. As observed in DMAPP, the methyl protons (labeled as a) resonate in two different chemical shift positions. The methylene protons of DMAPP (labeled as b) are assigned to the signals observed at chemical shift values δ 2.5–2.65 ppm. The proton directly attached to the N (3°N) atom was strongly deshielded and shows absorption at δ 7.9 ppm. The absorption

Table II. Principal IR Bands in Solid PAC-H01, PACC01, and PAC-T01/02

| Polymer code	Functional groups	Wave number (cm^{-1})	Assignments of characteristic groups
PAC-H01	—CH_2, —CH, —CN, —C=C— —C—H	2925, 1380, 2242, 1071, 1620 ± 10,779	2242→ —CN stretching (s)
PAC—C01	—CH_2, CH, CN, —C=C—, —C—H, —C=O, —C=C=H —CONH, —N$(CH_3)_2$, —C≡N, —NH, —N—H	2925, 1380, 2242, 1071, 1654, 1390, 1740, 1536, 779	1536 → =CONH group (s) 1446 → =N$(CH_3)_2$(s) 2242→ =CN stretching(s)
PAC—T01/02	—C—H, —CH_2, —C—N, —C=C, —C=O, —OH, —N—H —CONH, —N$(CH_3)_2$, —C≡N.	768, 1065, 1230/1217, 1367, 1446, 1536, 1659, 1743, 2242, 2927/2969, 3359, 3614	2242→ —CN stretching (s) 1536 → —CONH group(s) 1743 → —C=O stretch 1446 → —N$(CH_3)_2$(s) 3614 → —OH Asymmetric stretch
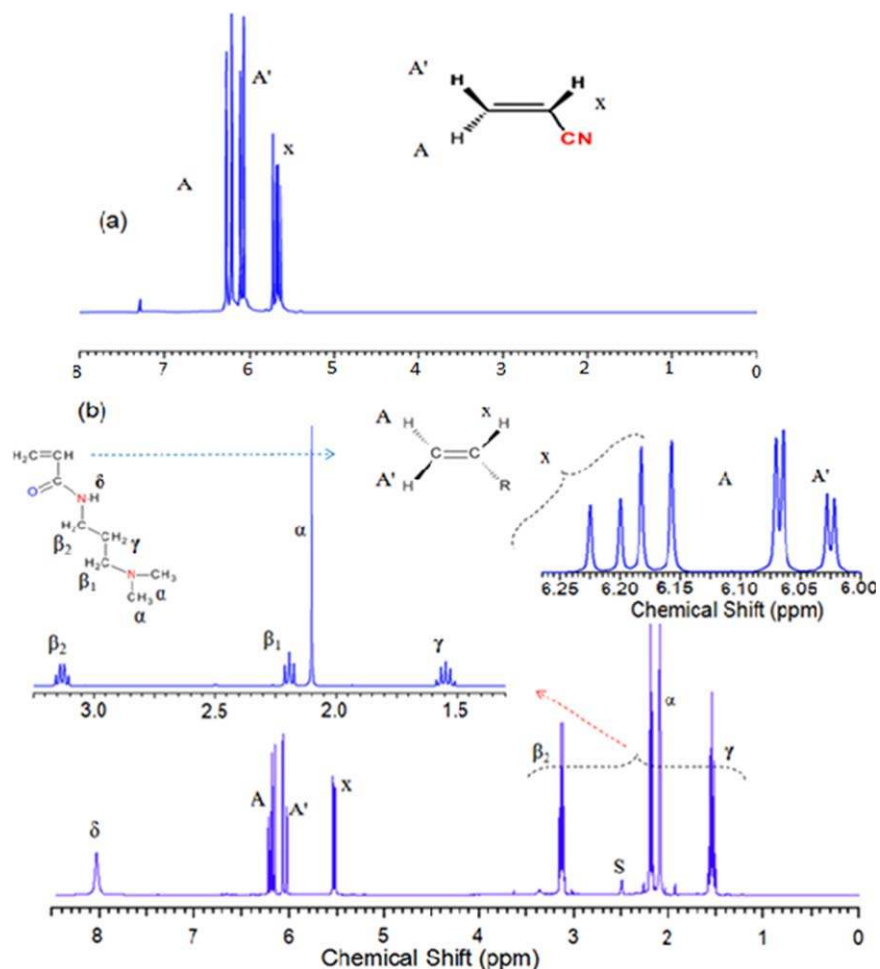
Figure 2. ^{1}H-NMR spectrum of (a) acrylonitrile, (b) DMAPP in deuterated-DMSO. [Color figure can be viewed at wileyonlinelibrary.com]

peaks observed at δ 1.6–2.5 is heavily broadened due to the overlap and mixing of NMR signals due to the methylene protons originating from acrylonitrile as well as itaconic acid, and DMPAA. The protons of ─COOH groups from itaconic acid can be identified with broad absorption signals at δ 3.0–3.5

Figure 3. ^{1}H-NMR spectra of Poly (acrylonitrile-ran-3-dimethylamino-propyl acrylamide-ran-itaconic. [Color figure can be viewed at wileyonlinelibrary.com]

ppm. A weak absorption at δ 1.4 ppm can be assigned to the methine proton from the itaconic acid. Therefore, the presence of the NMR absorptions of all functional groups from different monomers confirms the formation of a terpolymer synthesized in the present study.
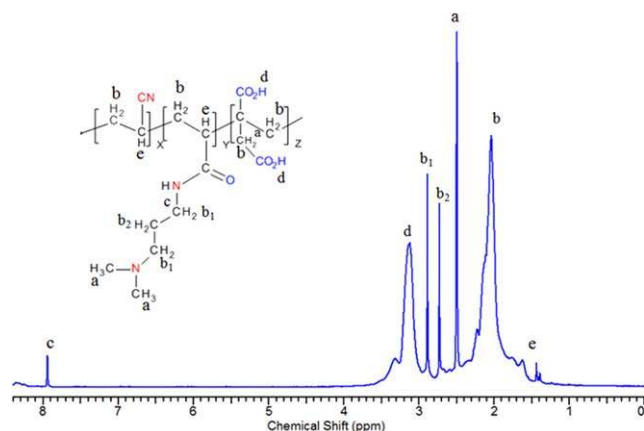
^{13}C-NMR spectra of PAC T01/02 terpolymers are shown in Figure 4 In total, there are eight types of distinct carbons observed in PAC T01/02 terpolymers corresponding to (a) cyano-carbon (CN), (b) methylene(CH_2) carbon in the main polymer skeleton, (c) methine (CH) of acrylonitrile monomer, (d) carbonyl carbon (─C═O), (e) carboxyl carbon (─COOH) of itaconic acid, (f) chemically non-equivalent methylene group of DMPAA, (g) tertiary carbon of itaconic acid, (h) methyl groups attached to tertiary N (3°N) atom of [─N(CH₃)₂] in DMAPP. A strong signal at δ 40 ppm can be assigned to the solvent (DMSO). The methyl carbons attached to tertiary nitrogen resonate at 58.0 ppm whereas, the methylene carbons from acrylonitrile and comonomer are found to have absorption signals between 32 and 36 ppm, which is a complex multiple owing to the coexistence and overlapping of similar monomeric and configurational sequences in detectable amounts. The signals due to methine carbon from acrylonitrile monomer are observed at chemical shift values in the range δ 26.6–27.8 ppm.
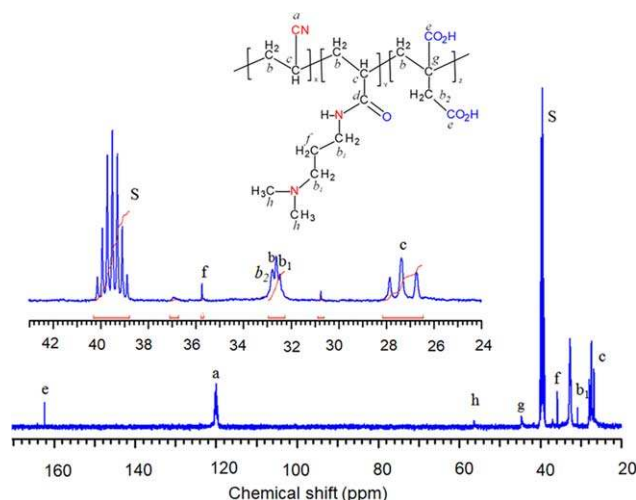
Figure 4. ^{13}C-NMR Spectra of poly(acrylonitrile-ran-3-dimethylamino-propyl acrylamide-ran-itaconic acid). [Color figure can be viewed at wileyonlinelibrary.com]

Other carbon signals from functional groups viz., nitrile carbon, methylene carbon, and carboxyl group appear around chemical shift values (δ) 119.5–120, 32–33.2, and 162–164 ppm, respectively. The tertiary carbon from itaconic acid can be assigned to a NMR signal at δ 44 ppm. The presence of characteristic ^{13}C-NMR signals corresponding to chemical shift values of the respective functional carbons confirms the successful incorporation of comonomers and formation of terpolymer and its structure.

Molecular Characterizations

The molecular parameters of PAC-H01, PAC-C01, and PAC-T01/02 terpolymers, viz. number, weight, viscosity average molecular weights, molecular weight distribution, and bulk density of the dried polymer powder as estimated from SEC, solution viscometry, and bulk density measurements, respectively, are summarized in Table I. 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 SEC with low angle laser light scattering and refractive index detectors (LALLS/RI). Figure 5 represents the traces of SEC-LALLS elution curves, indicating the increase of elution time from @ 7.5 to 8.5 mL as the average molecular weight decreases. Viscosity average molecular weights of the polymers were maintained in the range 1.44–2.23 × 10^5 Da to ensure better processability, and dissolution behavior in the down-stream processes. The weight and number average molecular weight of the PAC-H01, PAC-C01, and PAC-T01/02 are in the range 1.195 × 10^5, 3.8 × 10^4, and 1.53 × 10^5, 4.32 × 10^4, and 1.85–1.88 × 10^5, 3.23–3.84 × 10^4 Da, respectively. The molecular weight distribution was found to be in the range 3.23–3.84. The bulk densities of polymer powder are considered significant from the points of polymer handling and polymer dope preparation. An appropriate range of bulk density of PAN polymer powders is helpful to improve the solubility, stability and homogeneity of polymer dopes used for the precursor spinning operations. The bulk density of PAC-H01 was 0.41 as compared to that of PAC-T01/

02 around 0.31 due to the longer side chain in the case of DMAPP comonomer.

Thermal Studies on Differential DSC Exotherms

As described previously, major part of carbon fiber production involves thermal processes in the temperature region of 140–2450 °C; in particular the TOS of precursor in the range 180–270 °C. The studies on heat evolution, reaction time, and degradation behavior during the TOS reveal the nature of thermal rearrangement, and thermal process parameters to be adopted for a particular PAN precursor during the CF manufacture.

DSC thermograms are very useful in analyzing and predicting the green and thermal treated precursors with respect to changes in the nature and extent of isotherms. DSC exotherms proved to be useful in designing the thermal stabilization experiments for novel precursor chemistries. In the present investigation, new polymers synthesized were subjected to extensive thermal analysis in both nitrogen and air atmospheres. Figure 6(a–d) represent the DSC exotherms of PAC-H01, PAC-C01, PAC-T01, and PAC-T02 in nitrogen atmosphere respectively. The shape and size of the DSC exotherms change as number of monomeric components in the polymer increases. Data related to DSC exothermic curves are presented in Table III, where the characteristic temperatures of the peak are also illustrated. The subscripts i, p, and f refer to the initial, peak, and end temperatures, respectively. The subscript i denotes start of the exothermic reaction temperature. The onset temperature is the temperature at which the first deviation from linearity of the sample baseline is observed. The extrapolated onset temperature, T_i, is defined as the intersection between the tangent to the maximum rising slope of the peak and the extrapolated sample baseline. According to the DSC data presented in the Table III, The PAC-H01 homopolymer shows a sharp single exothermic peak, starting at an initiation temperature of 302 °C, and peak temperature (T_{pk}) ca. 308 °C, followed by the thermal reaction ending at 314 °C. This exothermic reaction is accompanied by the release of heat $\Delta H = 542$ J g^{-1}, with heat evolution rate 7.5 J g^{-1} s^{-1}. In case of PAC-CO1 copolymers cyclization
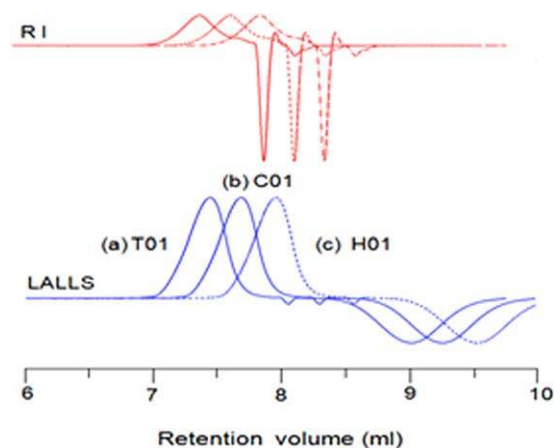

Figure 5. Traces of SEC-LALLS elution curves (a) VHP and (b) VCP polymers in dimethylformamide. [Color figure can be viewed at wileyonlinelibrary.com]
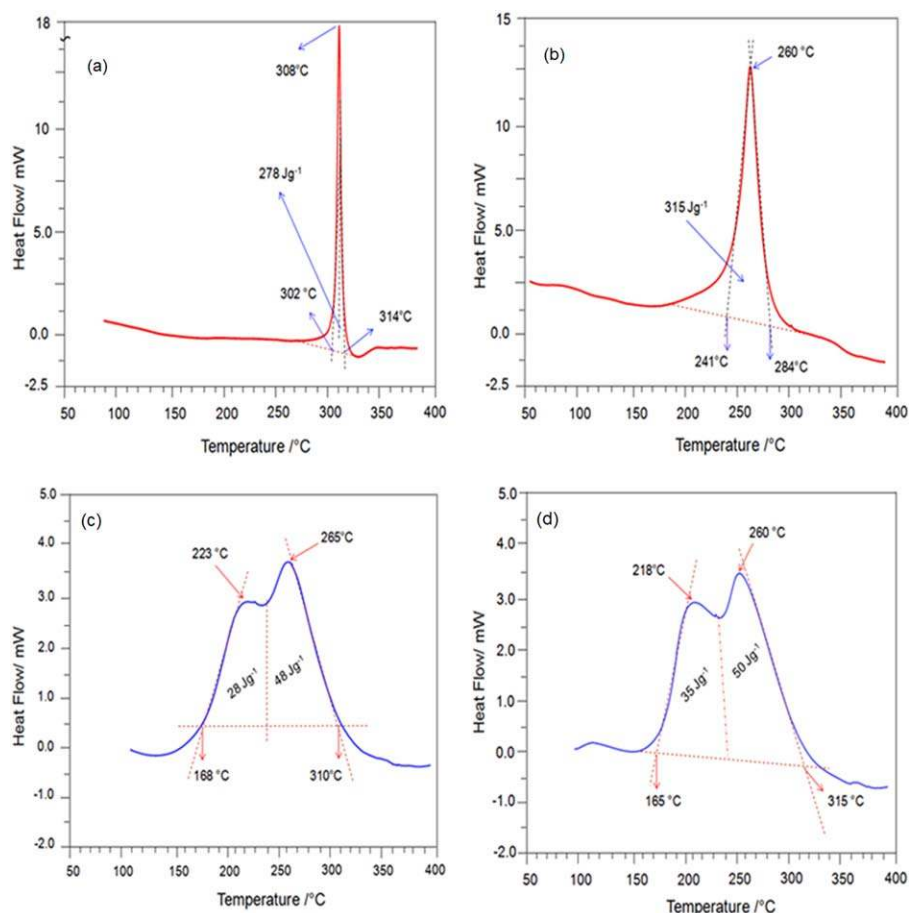
Figure 6. DSC Exotherms of (a) PAC-H01, (b) PAC-C01, (c) PAC-T01, and (d) PAC-T02 in nitrogen atmosphere. [Color figure can be viewed at wileyonlinelibrary.com]

exotherm starts at 241 °C, and closes at 284 °C with evolved heat of 315 J g^{-1} at a heat release rate 1.2 J g^{-1} s^{-1}, which shows a very distinct exothermal characteristic different from PAC-H01. In contrast to the PAC H01/C01 terpolymers180-27-T01/02, showed a characteristic broad exotherms having two distinct peaks with an average differential temperature 75 °C; total evolved heat of 76 J g^{-1}, at an average heat release rate 0.10 J g^{-1} s^{-1}.

The presence of characteristic doublet peaks as observed in DSC exotherms of PAC-T01/02 can be attributed to the two distinctive thermal reactions viz., cyclization through oxidative-crosslinking via ionic mechanism of DMPAA with pendant nitrile functional groups and nitrile oligomerization. The structural proximity of functional groups in DMPAA promote the oxidative-crosslinking/cyclization through intramolecular amidation and effectively facilitates the formation of thermally stable carbon networks. Amine and amide moieties of the DMPAA react with adjacent nitrile group to form a conjugated cyclic structure similar to naphthyridine rings. This is an auto-catalyzed polymerization reaction wherein nitrile groups zipper themselves up via an original amidation reaction to give a linear chain of naphthyridine ring systems. This clearly demonstrates

Table III. DSC Data of PAC-H01, PAC-C01, and PAC -T01/02 Polymers in Nitrogen

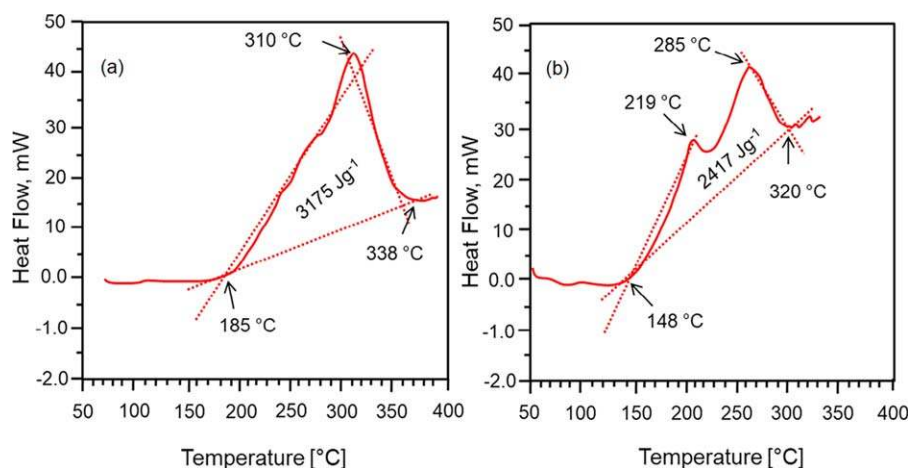| Polymer code	η_{iv} (dL/g)		T_i (°C)	T_f (°C)	ΔT (°C)	T_p (°C)	ΔH (J/g)	$\Delta H/\Delta t$ (J g^{-1} s^{-1})
PAC-H01	1.74		302	314	12	308	542	7.5
PAC-C01	2.02		241	284	43	260	315	1.2
PAC-T01	2.32	P$_1$	168	231	63	223	28	0.07
		P$_2$	234	310	76	265	48	0.10
PAC-T02	2.38	P$_1$	165	234	69	218	36	0.08
		P$_2$	236	315	79	260	50	0.11

Figure 7. DSC Exotherms of (a) PAC-C01 and (b) PAC-T01/02 in air atmosphere. [Color figure can be viewed at wileyonlinelibrary.com]

the catalytic effect of functional comonomers in PAN terpolymer, a low-temperature thermal stabilization process with delayed heat release rate.

However, in carbon fiber production, the oxidative stabilization process is conducted in presence of oxygen containing air atmosphere in a temperature range 180–270 °C. Therefore, in order to understand the DSC exotherm characteristics in presence of oxygen, DSC experiments of the polymers as-synthesized were performed in air atmosphere as well. The DSC Exotherms of PAC-C01 and PAC-T01/02 in air atmosphere are shown in Figure 7(a,b). As presented in the Table IV, PAC-H01 released heat energy of ca. 4124 J g^{-1}, an order of magnitude higher than that in nitrogen atmosphere at a heat release rate of 3.97 J g^{-1} s^{-1}·PAC-C01 exhibited a distinct shoulder and peak at 254 and 310 °C, respectively. The total exothermic energy release was ca. 3175 J/g. While PAC-T01/02 show an average cyclization initiation temperature ca. 150 °C, bimodal peaks with temperatures P$_1$: 219 °C, P$_2$: 284 °C with very slow heat release of 2.0–2.8 J g^{-1} s^{-1}.

As previously described, thermal stabilization process in particular, is very crucial to obtain the high-tensile grade carbon fibers, which is also a time-consuming process taking up to several hours depending on the precursor tow size, process temperature, precursor chemistry, and stabilization equipment's operating line speeds. One of the possibilities to bring down the CF price is to reduce the cost of thermal stabilization process by

increasing operational line speeds. The stabilization of acrylic fibers of acrylonitrile homo and copolymers in an oxygen-containing atmosphere involves essentially two major thermal reactions: firstly, an oxidative crosslinking 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 order to remove the heat accumulated at the surface precursor tows during this process, several heat dissipation mechanisms have been proposed, especially for polymer precursors with very high rate of heat release.

PAC C01/T01/02 co/terpolymers with improved/low-temperature stabilization properties promise accelerated stabilization behavior too. Figure 8 shows the influence of comonomers in varying amounts on the stabilization time of newly synthesized acrylonitrile-based polymers. As compared to the conventional PAN homopolymer (PAC-H01), PAC-C01 is structurally modified with the addition of IA, a known cyclization initiator which acts through an ionic mechanism[18]; with inclusion of IA, DSC exotherms of PAC-C01 become less intense and broader with lower initiation and peak temperature as evident from Figure 8 As we move from the top to bottom in Figure 8, that is, PAC-H01 to PAC T01/02, the overall rate of heat release (δH/

Table IV. DSC Data of PAC-H01, PAC-C01, PAC-T01/02 Polymers in Air

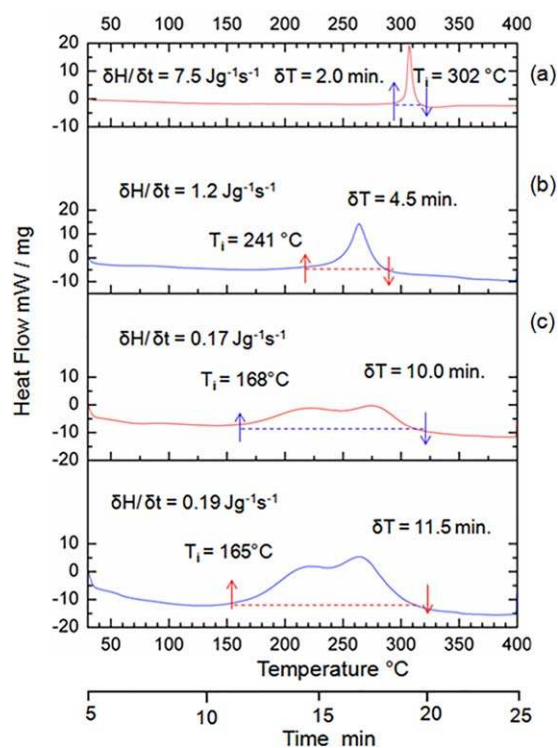| Polymer code	η_{iv} (dL/g)		T_i (°C)	T_f (°C)	ΔT (°C)	T_{peak} (°C)	ΔH (J/g)	$\Delta H/\Delta t$ (Jg^{-1} s^{-1})
PAC-H01	1.74		214	387	173	324	4124	3.97
PAC-C01	2.02		185	338	153	310	3175	3.4
PAC-T01	2.32	P$_1$	148	231	83	219	442	0.87
		P$_2$	235	320	85	285	942	1.8
PAC-T02	2.38	P$_1$	152	234	72	221	438	1.01
		P$_2$	235	328	93	274	895	1.6

Figure 8. Influence of comonomer content on stabilization time of (a) PAC-H01, (b) PAC-C01, and (c) PAC -T01/02 polymers at a heating rate 10 °C/min. [Color figure can be viewed at wileyonlinelibrary.com]

δt) during this process reduces with lowering of stabilization initiation temperature.

The broad heat-releasing pattern shows the possibilities of operating the thermal stabilization process at higher line-speeds, thereby improving the productivity, quality of carbon fibers at reduced cost. Table V presents residual nitrile content, critical temperature, and specific gravity of the oxidized acrylic fiber corresponding to the desirable level for thermal stabilization process. The critical temperature (T_c) of TOS process decreases as the DMPAA content increases. PAC-T01 exhibits T_c of 210/215 °C whereas that of PAC-H01 is 270 °C, demonstrating the influence of the functional monomer, DMPAA in reducing the temperature of TOS process corresponding to a conventional specific gravity level of 1.34–1.35.

The thermal energy that must be supplied in order to stabilize the precursor tow is related to the specific heat capacity (C_p) of the precursor fiber, total mass (Dtex), and temperature difference (ΔT) of the precursor and oven atmosphere. The differential temperature of heating the precursor tow depends on the specific heat capacity of the precursor polymer(C_p), linear density of the precursor tow to be heated i.e., mass of the precursor tow per unit length (MPUL in gram), and thermal energy (Q) that must be supplied. This can be expressed in terms of eq. (4).

$$[H] = [\delta L / \delta S] \int_{T_i}^{T_f} \sum_{i=1}^{i=f} C_p dT \tag{4}$$

where C_p is the specific heat capacity of the polymer precursor; the specific heat reflects the heat absorbing tendency of the materials. It is usually observed that specific heat changes very moderately in the range of practical processing and design temperature of polymeric materials. However, semi-crystalline polymers like PAN display a discontinuity in the melting point of crystallites represent the heat that must be supplied. In the present investigation, specific heat capacities of acrylonitrile based homo, co, and terpolymers incorporated with certain functional monomers were estimated using DSC on standard Al_2O_3 (sapphire) in the temperature range 25–450 °C. The heat capacity curves as in Figure 9(a–c) show the variation of specific heat capacity of homo, co, and terpolymers due to the inclusion of functional monomers. In case of PAN, C_p increases linearly from 1.23 up to 2.13 J g^{-1} °C between 25 and 240 °C, followed by a discontinuity in heat capacity till 318 °C. Whereas in case of P(AN-DMAPP), the discontinuity in the specific heat values starts from 2.14 J g^{-1} °C and again back to 2.01 J g^{-1} °C. This can be attributed to several thermal transitions occurring in the polymeric structure.

Estimation of Kinetic Parameters of Thermal Oxidative-Stabilization Process

As discussed in previous articles, TOS of acrylonitrile based copolymers proceeds in two stages, viz., cyclization of pendant nitrile functionalities to a stable linear ladder type aromatic structure followed by dehydrogenation leading to oxidation reactions.[35,36] In order to further confirm the low-stabilization behavior of PAN terpolymer under the investigation, DSC experiments of PAC-H01 and PAC T01/02 were conducted in

Table V. Residual Nitrile Content Corresponding to the Optimum Thermal-Oxidative Stabilization Levels

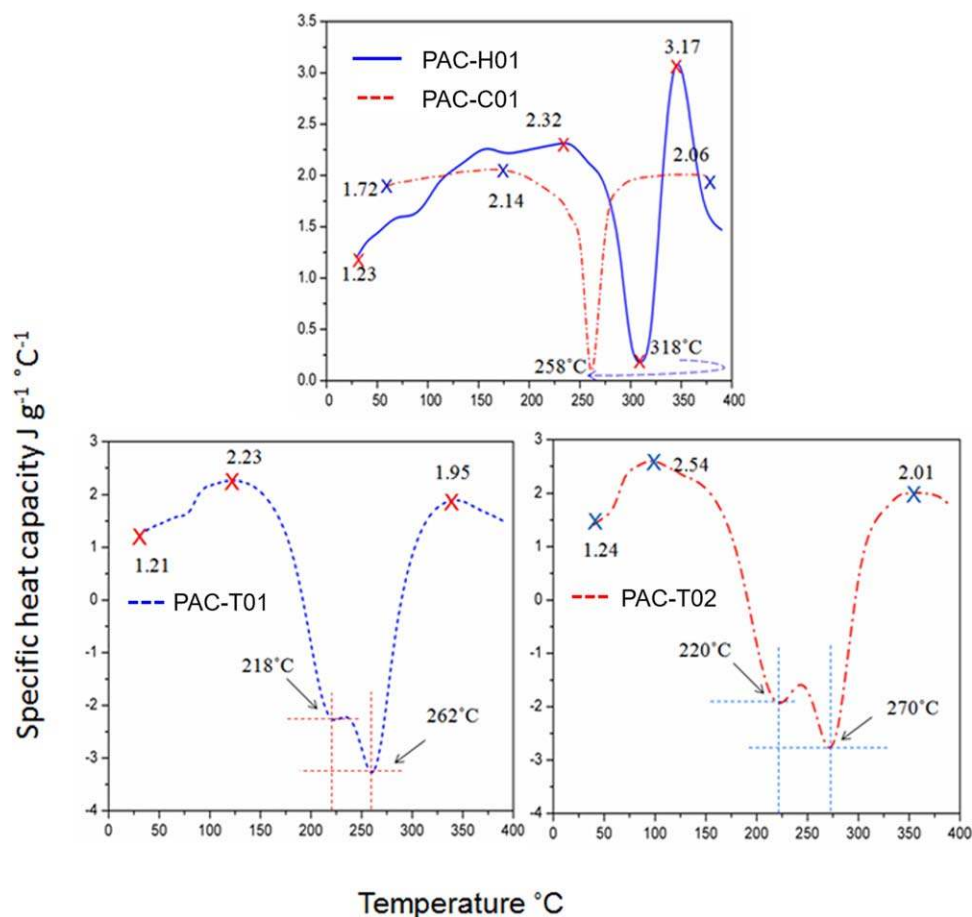| Polymer code	Functional comonomer content (wt %)		Critical temp (T_C) (°C)	Heat release rate (T_C) (J g^{-1} s^{-1})	Specific gravity (g cm^{-3})	D_a/D_b (2242 ± 10) (cm^{-1})	Residual nitrile content (%)
	DMAPA	IA					
PAC-H01	0.0	0.0	270	2.8	1.34	0.37	37
PAC-C01	3.0	0.0	265	2.2	1.34	0.34	34
PAC-T01	3.0	2.0	210	0.82	1.35	0.34	34
PAC-T02	4.0	2.0	215	0.82	1.34	0.34	34

Figure 9. Influence of comonomer on the specific heat capacity of acrylonitrile-based co/ter polymers. [Color figure can be viewed at wileyonlinelibrary.com]

both air and nitrogen atmospheres at different heating rates (5, 10, 15 °C/min). The cyclization reaction accompanied by oxidation with different heating rates resulted in strong exothermic peaks in DSC analysis in air atmosphere. The Kissinger thermal kinetic method was adopted for the estimation of kinetic parameters of cyclization and thermal oxidation reactions in air atmosphere. From the resolved thermal exotherms, the effect of the differential heating rate on the thermal behavior of PAC-

H01 and PAC T01/02 can be easily observed. As the heating rates are changed from 5 to 15 °C/min, the exothermic peaks wholly shifted to a higher temperature. The peak temperatures were 302.5, 312, and 319.8 °C, respectively, and the exothermic peaks became stronger and stronger. This is because the polymer has had enough time to fully react. The thermal effects and thermal inertia of the reaction increased with an increase in heating temperature. The two successive peaks in Figure 10
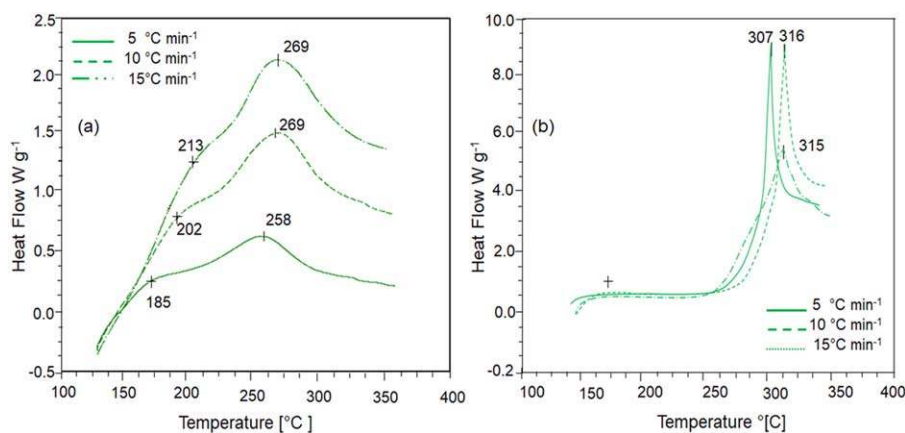

Figure 10. DSC exotherms of (a) PAC-H01 and (b) PAC- T01/02 in air at different heating rates. [Color figure can be viewed at wileyonlinelibrary.com]

Table VI. Thermal Oxidative Stabilization Kinetic Parameters as Estimated from Kas Method

Polymer code	Heat up rate (φ) °C/min	Peaks (°C)		Activation energy (E_a) (kJ/mol)		Arrhenius constant (A) (min^{-1})	
				Cyclization	Oxidation		
PAC-T01/02	5	185.1	257.9	23.3	71.0	30.199	14,57,730.54
	10	202.2	269.7			45.05	19,66,516.16
	15	213.3	269.8			56.5	29,40,901.93
PAC-H01	5	298.0		167.4		6.3 × 10^{14}	
	10	307.0				7.05 × 1014	
	15	315.4				6.4 × 1014	

were assigned to cyclization and thermal oxidation reaction, respectively. The temperature corresponding to first and second peaks were used for the estimation of cyclization and oxidation reactions, respectively. The activation energy can be determined from the slope of the plot of $\ln(\varphi/T_{2pk})$ against $1/T_{pk}$ as shown in Figure 11. Table VI presents the activation energy (E_a) of cyclization and oxidation as observed clearly in case of PAC-T01/02 whereas PAC-H01. The values of E_a for PAC-H01 are about 170 kJ/mol. The activation energy of PAC-T01/02 is found be 95 kJ/mol, much lower than that of PAC-H01, due to the incorporation of dimethyl amino propyl acrylamide, a very

functional monomer for low-temperature thermal stabilization reaction.

Thermal Stability Analysis Using TGA-DTA

The thermal stability, mass loss behavior of PAC-T01/02 was investigated in the range 50–500 °C using a thermogravimetry analyzer coupled with differential thermal analyzer. These analyses were performed to confirm the distinct low-temperature stabilization behavior exhibited by PAC-T01/02 through their DSC exotherms. TG-DTA curves of PAC-T01/02 are shown in Figure 12(a,b). It was observed that both terpolymers exhibited
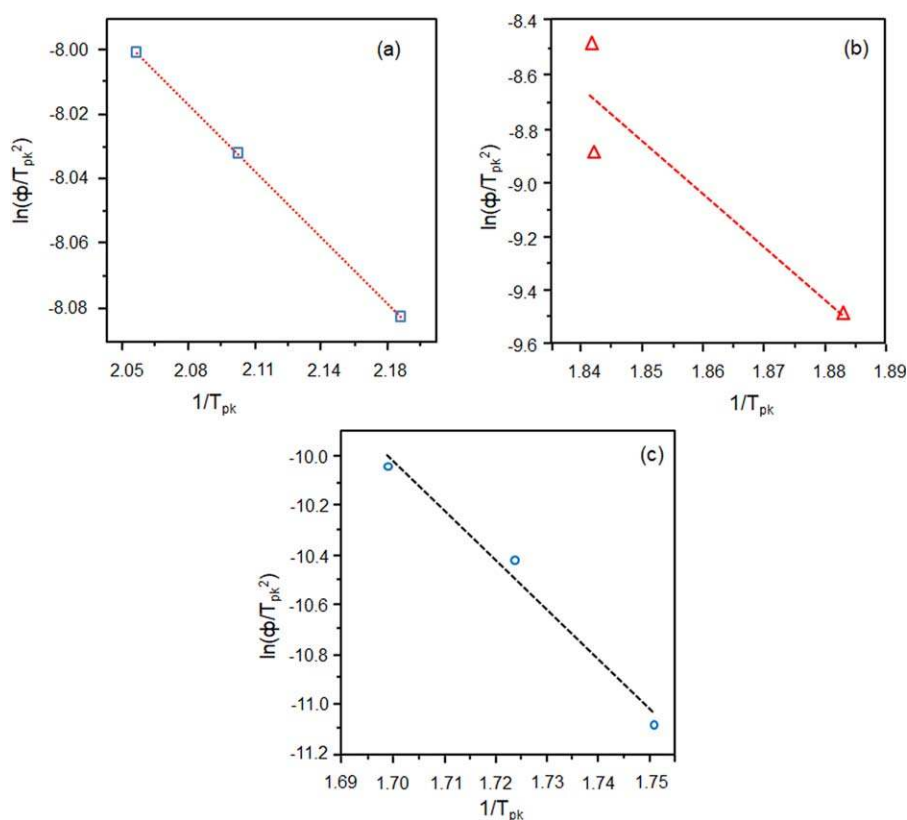

Figure 11. Plot of $\ln(\varphi/T^2_{pk})$ against $1/T_{pk}$ for activation energy in thermal oxidative-stabilization of (a) PAC-T01, (b) PAC-T02, and (c) PAC-H01. [Color figure can be viewed at wileyonlinelibrary.com]
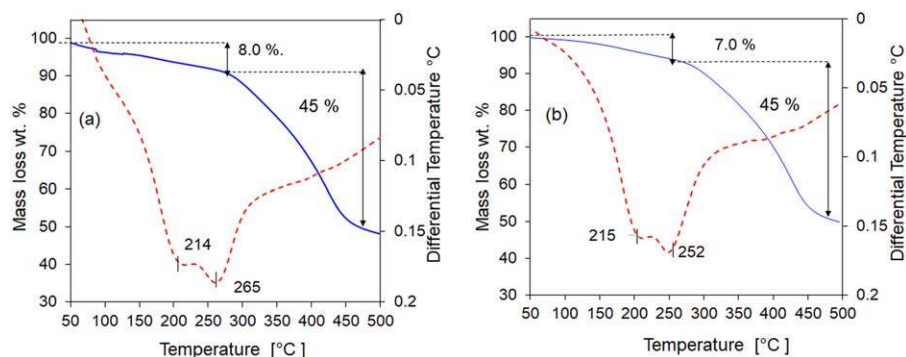
Figure 12. TGA-DTA curves of (a) PAC–T01 (b) PAC–02 terpolymers. [Color figure can be viewed at wileyonlinelibrary.com]

almost similar thermal degradation behavior except a very slight difference in their DTA peaks corresponding to major mass loss around 215 and 260 °C due to different kinds of thermochemical reactions. The thermal degradation was almost gradual up to 220 °C; mass loss was found to occur ca. 8% wt, and begins to lose the mass rapidly after this temperature. The overall mass loss of terpolymers was found to be around 50% wt at 450 °C, confirming the DSC data and, indicating their suitability as precursor polymer for low-temperature stabilization behavior.

CONCLUSIONS

Novel PAN-based carbon fiber precursor terpolymers with low-temperature stabilization characteristics viz., Poly(acrylonitrile-ran-3-dimethylaminopropyl acrylamide-ran-itaconic acid), poly(acrylonitrile-*co*-3, dimethylaminopropyl acrylamide) was synthesized using solution polymerization process. Their chemical structure functional groups identification and bonding networks were established using FTIR-ATR and ^{1}H, ^{13}C-NMR techniques, respectively. Viscosity, number, and weight average molecular weights were estimated with, solution viscometer, size exclusion chromatograph and found to be in the range 1.44–2.23 × 10^5 Da, 3.8–5.74 × 10^4 Da, and 1.19–1.88 × 10^5 Da, respectively. PAC T01/02 terpolymers exhibited distinctive broad bimodal DSC exotherms consisting of two peaks at a temperature difference of ca. 54 °C, while that of copolymer (PAC-C01) was unimodal with low initiation and end temperature as compared to that of acrylonitrile homopolymer. Extensive DSC analysis of as-synthesized acrylonitrile-based terpolymers, copolymer in nitrogen as well as air atmosphere showed a very low thermal stabilization initiation temperature in the range 160–170 and 145–150 °C, respectively, proving to be more effective in reducing the initiation temperature of stabilization process. PAC-C01/T01/02 co/terpolymers were found to have the low-temperature stabilization characteristics with distinctively low-heat release rate in the range 0.19–0.17 and 1.9 J g^{-1} s^{-1} The thermal stability and mass loss behavior of AN terpolymers with DMAPP and ITA was studied using TG-DTA and found to give a char yield of ca. 48% wt. The energy of activation corresponding to bimodal peaks identified as cyclization and oxidation were found to be 23.3 and 71.0 kJ/mol, respectively. These kinetic energy values of P(AN-DMAPP-IA) are much lower than the conventional PAN homo and co-polymers. Specific heat capacity measurements confirmed and complemented the

results of thermal analysis and proved that the incorporation of DMPAA comonomer has contributed towards the low-temperature stabilization behavior of terpolymers as cost-effective polymer precursors for carbon fiber production.

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