ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

ELECTROSPUN NANOFIBERS OF ACRYLONITRILE AND ITACONIC ACID COPOLYMERS

M.Sc. THESIS

Selda ŞEN

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Anabilim Dalı : Herhangi Mühendislik, Bilim
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ELEKTROÇEKİM İLE HAZIRLANMIŞ AKRİLONİTRİL VE İTAKONİK ASİT KOPOLİMERİ NANOLİFLERİ

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HAZİRAN 2012

Selda Şen, a M.Sc Student of ITU **Graduate School of Science Engıneering and Technology** student ID 515101025, succesfully defended the **thesis** entitled **"ELECTROSPUN NANOFIBERS OF ACRYLONITRILE AND ITACONIC ACID COPOLYMERS"**, which she prepared after fulfiling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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ABBREVIATIONS

AN : Acrylonitrile
APS : Amonium persulfate
DMA : Dynamic Mechanical Analysis
DMF : Dimethylformamide
DSC : Differential Scanning Calorimetry
FTIR-ATR : Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance
IA : Itaconic Acid
M_v : Viscosity Average Molecular Weight
NMR : Nuclear Magmetic Resonance
r : Reactivity Ratio
P(AN-co-IA) : poly(acrylonitrile-co-itaconic acid)
SEM : Scanning Electron Microscopy
T_g : Glass Transition Temperature
[η] : Intrinsic Viscosity

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ELECTROSPUN NANOFIBERS OF ACRYLONITRILE AND ITACONIC ACID COPOLYMERS

SUMMARY

In this study, acrylonitrile (AN) and itaconic acid (IA) copolymers were synthesized and characterized. Synthesized copolymers were used for nanofiber production by electrospinning method. Electrospun nanofiber mats were treated heat under air atmosphere to be stabilized. The aim of this study is nanofiber production from AN-IA copolymers and discussing the suitablity of the nanofiber as carbon nanofiber precursor by both known characterization methods and applied research.

AN-IA copolymers were sythesized by using ammonium persulfate (APS) as an oxidant in the aqueous medium. Five copolymerization batch were performed with different monomer feed ratios under the same copolymerization conditions.

Firstly synthesized AN-IA copolymer was characterized using Fourier Transform Infrared - Attenuated Total Reflectance spectrometer (FTIR-ATR), Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR), differential scanning calorimeter (DSC), thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The effect of IA content on the spectroscopic and thermal properties of AN-IA copolymers was investigated. Increasing IA content confirmed by spectroscopic methods seriously affects thermal properties which is important for carbon nanofiber production. IA provides a catalytic effect on stabilization process by decreasing initiation cyclization reaction temperature from 202 to 195 ^{o}C.

In the next part of study, elecrospinning from the AN-IA copolymer solutions in dimethyl foramide (DMF) was performed succesfully. Morphology of nanofibers was monitored using Scanning Electron Microscopy (SEM). Bead free nanofibers was produced from AN-IA copolymer solutions under same conditions. Average nanofiber diameter decreases from 878±18 to 376±7 nm according to increasing IA content in copolymers.

The nanofiber mats produced were treated at high temperature under air atmosphere for oxidative stabilization. Stabilizied nanofibers were characterized using FTIR-ATR spectrometer and a new structure was monitored as a result of cyclization reactions. The stabilized nanofibers were also characterized mophologically using SEM. Volume loss occurring after heat treatment calculated based on the nanofiber diameter changes.

Consequently, electrospun nanofibers can be suggested as a carbon nanofiber precursor due to suitability for electrospinning and stabilization process.

AKRİLONİTRİL VE İTAKONİK ASİT KOPOLİMERLERİNDEN ELEKTROÇEKİM YÖNTEMİYLE NANOLİF ELDESİ

ÖZET

Bu çalışmada akrilonitril (AN) ve itakonik asit (IA) kopolimerleri sentezlenmiş ve karakterizasyonları yapılmıştır. Sentezlenen kopolimerler elektroçekim ile nanolif üretiminde kullanılmıştır. Farklı oranlarda IA içeren kopolimerlerinin elektroçekimde nanolif oluşumuna olan etkisi araştırılmıştır. Hazırlanan nanolif matlarına hava ortamında ısıl muamele yapılarak stabilizasyonları gerçekleştirilmiştir. Bu çalışmanın hedefi AN-IA kopolimerlerinden nanolif üretilmesi ve üretilen bu nanoliflerin karbon nanofiber üretimi için uygunluğunun hem bilinen karakterizasyon yöntemleri ile hem de uygulamalı olarak kanıtlanmasıdır.

AN-IA kopolimerleri amonyum persülfat oksidant olarak kullanılarak sulu ortamda, 60 ^{o}C'de sentezlenmiştir. Beş farklı kopolimerin sentezi, aynı koşullar altında farklı monomer besleme oranları ile gerçekleştirilmiştir. Üç saat süren kopolimerizasyon sonucunda suda çökelek halinde kopolimer elde edilmiştir. Kopolimerler etanol ile yıkandıktan sonra vakum etüvünde kurutularak kullanılmıştır.

Öncelikle AN-IA kopolimerlerinin spektroskopik, termal ve mekanik analizleri FTIR-ATR (Fourier Transform Kızılötesi-Azaltılmış Toplam Reflektans) ve NMR (Nükleer Manyetik Rezonans) spektrometre, DSC (Diferansiyel Taramalı Kalorimetre), TGA (Termal Gravimetrik Analiz) ve DMA (Dinamik Mekanik Analiz) cihazları kullanılarak yapılmıştır. Böylece IA içeriğinin, AN-IA kopolimerlerinin spektroskopik ve termal özellikleri üzerine etkisi araştırılmıştır. Kopolimerlerin FTIR-ATR spektrumlarında 1628 and 1730 cm^{-1} bantlarında gözlenen karbonil gerilme piklerinin absorbans değerlerinin, AN ile ilgili olan 2244 cm^{-1} 'de gözlenen -C≡N gerilme pikinin absorbans oranladığında IA besleme artışına paralel bir artış gözlenmiştir. ^{1}H-NMR spektrumlarından hesaplanan kopolimer kompozisyonları ile FTIR-ATR spektrumlarından elde edilen absorbans değerleri ile ilişki kurularak bir kalibrasyon eğrisi türetilmiştir. Kopolimerlerin intrinsik viskoziteleri, Ubellohde viskozimetresi kullanılarak belirlenen spesifik viskozite değerlerinden hesaplanmıştır. Kopolimerlerde IA artışına bağlı olarak intrinsik viskozite değerleri 2,67 ile 0,92 ml/g arasında değişmiştir. DSC ve TGA termal analiz metotları ile kopolimerlerin stabilizasyonu sırasında gerçekleşen halka kapanma, oksidasyon, dehidrojenasyon ve dekompozisyon gibi reaksiyonların sıcaklıkları belirlenmiştir. DSC eğrilerinde gözlenen iki ekzotermik pik halka kapanma ve oksidasyon reaksiyonları ile ilişkilendirilmiştir. AN-IA kopolimerlerinde halka kapanma reaksiyonlarının başlangıç sıcaklığı, IA artışına bağlı olarak 222 ^{o}C'den 195 ^{o}C'ye kadar düşmüştür. TGA eğrilerinde gözlenen iki basamaklı kütle kaybının dehidrojenasyon ve dekompozisyonla ilgili olduğu düşünülmektedir. Dehidrojenasyona kıyasla oldukça büyük kütle kaybınının olduğu dekompozisyonun sıcaklığı kopolimerlerde IA nın etkisiyle 277 ^{o}C'den 257 ^{o}C'ye düşmektedir. Karbon

fiber üretimi için kullanılan polimerlerin dekompoze olması istenilen bir durum değidir. Stabilizasyon sırasında nitril grupları oligomerizasyona girerek halkalar oluştururken, ısının etkisiyle dekompozisyon da görülür. Birbirine pararlel giden iki reaksiyonun sıcaklık farkına baktığımızda IA miktarı arttıkça, kopolimerlerde halka kapanma reaksiyonları başladıktan sonra dekompoziyonun daha geç görüldüğü tespit edilmiştir.Spektroskopik yöntemler ile belirlenen IA içeriğindeki artışın, karbon fiber üretiminde önemli bir aşama olan stabilizasyonu termal özelliklerini geliştirerek ciddi şekilde etkilediği görülmüştür. AN-IA kopolimerlerinden hazırlanan filmlerden belli bir frekansta ısıtılarak ve kuvvet uygulanarak camsı geçiş sıcaklığı (Tg) ölçümleri yapılmışır. PAN'ın yapısına IA girdikçe, Tg değerlerin arttığı görülmüştür.

Çalışmanın sonraki aşamasında, AN-IA kopolimerlerinin dimetil formamid (DMF) içerisinde hazırlanan çözeltilerden elektroçekim yöntemiyle nanolifler hazırlanmıştır. Tüm kopolimerler için çözelti konsantrasyon, besleme hızı ve uzaklık gibi elektroçekim değişkenleri sabit tutularak IA'nın nanolif çapına etkisi araştırılmıştır. Elektorçekim için çözeltiler kütlece % 5 katı içerecek şekilde hazırlanmıştır. Şırıngaya doldurulan kopolimer çözeltisi pompa ile 1 ml/saat debiyle beslenmiştir. Kopolimer çözeltilerinden nanolif üretebilmek için gerekli minimum gerilim (9-10,5 kV) uygulanmıştır. Topraklama hattına bağlanmış metal plaka şırındanın ucundan 19 cm uzağa yerleştirilmiştir. Nanoliflerin morfolojileri taramalı elektron mikroskopu (SEM) ile görüntülenmiştir. AN-IA kopolimer çözeltilerinden aynı koşullar altında boncuksuz ve sürekli nanolifler elde edilmiştir. Ortalama nanolif çapları, IA artışına bağlı olarak 878±18'den 376±7 nm'ye kadar düştüğü görülmüştür. Bu değişim asit gruplarının nanolif oluşumundaki yüklerin transferine olan etkisinden kaynaklandığı düşünülmektedir. Kopolimerlerin intrinsik viskoziteleri ile nanolif çapları arasında bir ilişki olduğu saptanmıştır. İntrinsik viskozitedeki düşüş, nanolif çaplarının azalmasına sebep olmuştur.

Üretilen nanofiber matları bir sonraki aşamada yüksek sıcaklıkta ısı ile muamele edilerek hava ortamında oksidatif stabilizasyon gerçekleştirilmiştir. Stabilize edilen nanofiberlerin renklerinin beyazdan, kırmızı-kahverengi çeşitli renk tonlarına döndüğü gözlenmiştir. Renk tonlarındaki çeşitliliğin kopolimerlerde stabilizasyon sonucu oluşan konjugasyonun derecesi ile ilgili olduğu düşünülmektedir. FTIR-ATR spektrometresi kullanılarak halka kapanma reaksiyonları sonucunda oluşması gereken aromatik yapılardaki C-H bağlarının titreşimlerine ait pikler 805 cm^{-1} dalga sayısında tespit edilmiştir. 2244 cm^{-1} dalga sayısında gözlenen akrilonitrilin karakteristik C≡N gerilme pikinin ısıl işlemden sonra sönümlendiği, 1585 cm^{-1} dalga sayısında oluşan -C=N yapıları ile ilişkilendirilen yeni bir pik oluştuğu gözlenmiştir. Nanofiberler ayrıca SEM ile görüntülenerek morfolojik incelemeleri yapılmıştır. Isıl muamele sonucunda nanofiberlerin çaplarında azalma gözlenmiştir. % 1 IA beslemesi ile sentezlenen kopolimerden üretilen nanoliflerin çapları 878±18 nm'den 629±13 nm'ye düşmüştür. Nanofiberlerin silindirik formda ve çaplardaki azalmanın homojen olduğu kabulü yapılarak, çaplardaki değişim üzerinden yüzde hacim kaybı hesaplanmıştır. En düşük IA içeren kopolimerin hacminde % 48,7 lik düşüş gözlenirken, diğer kopolimerlerde hacim değişimi yüzde 20 ile 30 arasında değişmektedir. IA'nın nanoliflerin termal stabilitesini korumaya yardımcı olduğu, kopolimerlerde yüksek asit miktarı ile yüzde hacim kaybının azalması ile kanıtlanmıştır.

Sonuç olarak, elektroçekim yöntemi ile hazırlanan AN-IA kopolimerlerinin nanofiberlerin karbon nanofiber üretimi için uygun bir başlangıç maddesi olduğu düşünülmektedir. DSC ve TGA sonuçlarından elde edilen kopolimerlerin ısı ile

verdiği reaksiyon sıcaklıklarına bakılarak stabilizasyonda % 3 ve daha fazla IA beslemesi ile sentezlenen kopolimerlerin iyi performans göstereceği öngörülmüştür. Üretilen nanoliflerin hava ortamında ısıl muamelesinden sonra morfolojik incelemeleri yapıldığında %1 den yüksek oranda IA ile sentezlenen kopolimerlerin nanoliflerinde hacim kaybının az olduğu, yani termal stabilitesini koruduğu gözlenmiştir.

1. INTRODUCTION

Polyacrylonitrile (PAN) is an important material for production of both synthetic fibers and high performance fibers, but it is usually modified by copolymerization with small proportions of several vinyl monomers. AN in most cases is copolymerized with comonomers such as vinyl acetate, methyl acrylate, methyl methacrylate, acrylic acid and itaconic acid [1-4].

Polyarylonitrile (PAN) fibers are the most widely used precursor for high-property carbon fibers, the important reinforced materials for advanced composites in many fields, such as aerospace, sports, transportation, and petrochemical industry. PAN as a carbon fiber precursor shows some superiorities such as high carbon yield and flexibility for tailoring of the structure of the final product. PAN based copolymers are generally used in commercial carbon fiber production [5].

Thermal behavior of acrylonitrile homo- and copolymers has always been a subject of great interest to improve precusor for the production of carbon fibers. Thermal stabilization, during which ladder structure is formed to enable PAN fibers infusible and nonflammable, is an indispensable process in the manufacture of carbon fibers. For industrial production, thermal stabilization of PAN fibers is usually performed in a temperature range of 200–300^{o}C under certain stretching force in air. Besides temperature and stretching ratio, the comonomer used in PAN precursor are the other main important factor for the quality of carbon fiber [6].

The rapidly developing electrospinning technique provides a straightforward and cost-effective approach to produce polymeric nanofibers. Electrospinning is a desirable technique to produce micro and/or nanofiber webs of copolymers by applying high voltage to a polymeric solution to create an electrically charged jet. It is fundamentally different from other mechanically driven spinning techniques in that the extrusion force is generated by the interaction between the charged polymer fluid and an external applied electric field. During electrospinning, a conical fluid structure called the Taylor cone is formed at the tip of the syringe. When a critical

value of the electric field is attained, the electrostatic force overcomes the surface tension and a charged jet is ejected from the tip of the Taylor cone. The polymeric jet is then subjected to instability phenomena that stretch and reduce fiber diameter, before being randomly deposited onto a grounded target [7]. PAN has been used as polymer in many electrospinning studies. Based on the morphological studies, average nanofiber diameter has been varied from 200 nm to 1200 nm according to concentration and applied voltage [8-10].

Carbon nanofibers are also a good candidate for composite applications, beside they have been originally used in other applications as filters, high temperature catalysts, heat management materials in aircraft and semiconductor device. Fabrication process of carbon nanofibers contains nanofiber production of polyacrylonitrile (PAN) precursors, stabilization of nanofibers at 200-400°C in the air and follows carbonization process in inert atmosphere at high temperature (>1000°C) [11]. To produce carbon fibers with diameters in the nanometer range, the electrospinnig method has been used by various researchers effectivelly [11-13]. In these studies, commercial PAN was prefered as precursor mostly. After carbonization process, electrospun PAN based nanofibers showed good electrical and mechanical properties related to uniform and continuous fiber formation. The electrical conductivities of the carbonized web could have been improved modifing electrospinning process and carbonization process. Aligned nanofibers carbonized at 1000 and 2200 ^{o}C shows electrical conductivities 180 and 800 S/cm which were measured paralel to bundle axis [11].

The electrospun PAN nanofibers possess high degrees of macromolecular orientations and substantially reduced concentration of structural defects, and the ultra-small diameters may also mitigate the formation of structural inhomogeneities, particularly sheathcore structures, during the thermal treatments [14-16]. Electrospun carbon nanofibers are produced through a top-down nano-manufacturing process; they are low-cost, continuous, and also easy to align, assemble, and process into applications.

Itaconic acid as comonomer used in PAN production has been an important material for both commercial applications and scientific research. There are several studies about reaction kinetics, rheology and thermal properties of AN-IA copolymer. In this study, PAN has been modified with different proportions of IA comonomer.

Synthesized AN-IA copolymers were used to produce nanofibers by electrospinning technique first time in literature. To obtain the effect of IA on nanofiber or carbon nanofiber production several characterization methods was performed. Nanofibers of AN-IA copolymers were produced using electrospinning technique and their acceptability as carbon nanofiber precursor was discussed

2. THEORETICAL PART

2.1 Polyacrylonitrile

The morphology of PAN is unique [17]. Due to strong repellent dipole–dipole interactions between intramolecular neighboring nitrile groups in parallel position, the polymer backbone is forced into an irregular helical conformation. Strong attractive dipole–dipole interactions between antiparallel nitrile groups.

Free radical polymerization of vinyl monomers containing carbon – carbon double bonds has been widely used in industry to manufacture a variety of polymeric materials such as PAN. The generally accepted free radical polymerization mechanism involves three kinetic steps in sequence, namely, initiation, propagation, and termination Monomer concentration, initiator concetration and temperature are main parameters effecting polymerization rate [18].

The polymerization of AN is different from the other vinyl polymerization reactions characteristically [19]: AN is soluble in most organic solvents and in water (the azeotrope with water contains 88% of AN). However, PAN is insoluble in most common organic solvents, in water, and in its monomer. For this reason, the polymerization reaction often becomes heterogeneous even at low conversions and monomer concentrations, and the borders between emulsion and suspension polymerization are not well defined. Heterogeneous AN polymerization shows autoacceleration when an insufficient amount of a surfactant is used. Furthermore, there is obviously no consensus among the authors reporting on AN polymerization as far as use of the terms solution polymerization, dispersion polymerization, and precipitation polymerization is concerned, especially in aqueous systems.

Due to the disadvantages of solution polymerization, heterogeneous polymerizations are used in free-radical polymerization. There are four basic heterogeneous polymerization processes: suspension polymerization, emulsion polymerization, dispersion polymerization, and precipitation polymerization. The following

discussions focus on the precipitation polymerization of acrylonitrile and acrylonitrile based copolymers.

2.2 Acrylonitrile Based Copolymers

Free radical polymerization can be conducted with mixtures of two monomers to form copolymer products with two different structures in the polymer chain. Composition and order of each mer are controllerd by the ratios between the tendency to homopolymerize and to cross-polymerize r_1 and r_2.

$$A + A^* \longrightarrow AA^*, \quad k_{11} \qquad \textbf{(I)}$$

$$A + B^* \longrightarrow AB^*, \quad k_{12} \qquad \textbf{(II)}$$

$$B + B^* \longrightarrow BB^*, \quad k_{22} \qquad \textbf{(III)}$$

$$B^* + A \longrightarrow BA^*, \quad k_{21} \qquad \textbf{(IV)}$$

Reactions (I) and (III) are identical to homopolymerization. The parameters r_1 and r_2 are defined as the ratio between the kinetic constant for homopolymerization and that for cross-reaction [18].

$r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$

Acrylonitrile-based copolymers produced free radical polymerization are widely used in the production of acrylic fibers. Polyacrylonitrile fibers suffer from poor hygroscopicity and low dye uptake because of a high degree of ordering, a lack of segmental mobility as a result of a compact structure, and a high glass-transition temperature (T_g). Therefore suitable comonomers are used in acrylic fiber precursor production with AN to overcome these shortcomings [20]. Comonomers used in the manufacturing of acrylic fibers can be either neutral or ionic.

Neutral comonomers, such as methyl acrylate, methyl methacrylate, and vinyl acetate, modify the structure of polyacrylonitrile; the resulting reduction in compactness of the fibers increases the diffusion of the dyes. Polar, nonionizable

comonomers, such as ketones, ethers, and alcohols, increase dye adsorption by enhancing nonionic interactions with the dyes [4,21-22]

On the other hand, the use of ionic acidic comonomers containing sulfonic, phosphoric, or carboxylic acid groups influences both the rate of diffusion and the uptake of cationic dyes. Acidic comonomers not only improve the hygroscopicity but also help in the cyclization of the nitrile group to form a ladder structure during oxidation of acrylic fibers for carbon fiber production [23].

Block copolymers of PAN with polymethacrylonitrile as one component are of potential interest in the development of high-tech devices such as lithography due to their polarity, solubility and high plasma etching resistance properties. Block copolymers can be prepared by means of special techniques like anionic living polymerization [24].

Polymerization of acrylonitrile with different comonomers have been carried out bulk, solution and emulsion polymerization techniques successfully [25-27]. Water-phase precipitation polymerization has been a preferable technique for AN based polymer synthesize to achieve high molecular weight, which is important for mechanical properties of polymer [28,29]. Acrylonitrile which is a partially water-soluble monomer is added to the medium, a small fraction of acrylonitrile dissolved in the continuous aqueous phase where initiator is present. The initiation step of polymerization occurs in aqueous phase. Then, chain growth starts and continues in water until polymer precipitate. After the precipitation, the polymerization transfers from homogeneous phase to heterogeneous phase. The polymerization is carried out both in water and at the surface of the micro-particles precipitated from the water. In this process, the possibility of chain termination and chain transfer are low, therefore, the molecular weight and the yield of the polymer increases. In Figure 2.1 representation of polymerization taking place in the fluid phase, on the surface of the polymer particle, or throughout the interior of the particle was seen. No surfactant is required to stabilize the particles, so that precipitation polymerization can be considered for the synthesis of high-purity polymers for sensitive applications, e.g., cosmetics and food additives. Dispersion polymerization is a very similar process, except that a surfactant is used to stabilize the polymer particles [30].

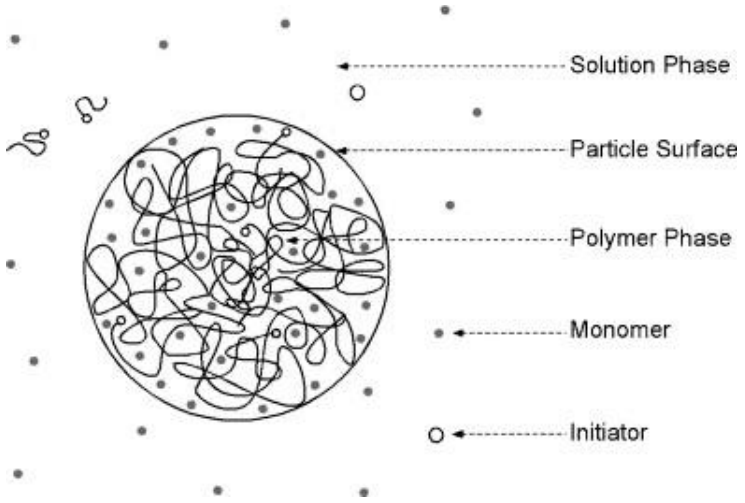


Figure 2.1 : Representation of a precipitation polymerization system [30].

2.3 Acrylonitrile – Itaconic Acid Copolymers

The selection of a suitable comonomer is an important step, which has been a important of study. IA is the most commonly used comonomer among acidic monomers.

The conversion of PAN precursor fibers to carbon fibers involves an intermediate step of stabilization reaction at 180–400°C. During stabilization, the polymer undergoes physical and chemical changes as a result of of nitrile groups to form an aromatized structure known as a ladder polymer. The acid monomers play a catalytic role in the cyclization process which stabilizes the polymer backbone before carbonization [31].

Grassie and McGuchan showed the strong initiating effect of acrylic, methacrylic, and itaconic acid and acrylamide on the exothermic nitrile group oligomerization [32]. As the acid content increases, the DSC exotherm becomes less intense and broader with lower initiation and peak temperature. The methacrylic and itaconic acid copolymers show more complex and broad exotherms than the AN-AA copolymer. In N_2 atmosphere, the initiation temperatures 220, 200 and 190 ^{o}C were found for AN-AA, AN-MAA and AN-IA copolymers respectively. Among these acidic monomers IA improves thermal process most effectively.

It is widely accepted that in PAN the cyclization of nitrile groups only can be initiated at a higher temperature through a free radical mechanism, while in P(AN-co-IA) the cyclization can be initiated by the carboxylic groups of IA units at a lower

temperature through an ionic mechanism Figure 2.1 [33]. As shown in second reaction, the hydroxyl oxygen of –COOH in IA unit has made a nucleophilic attack on the carbon atom of an adjacent nitrile group and induced it to cyclize. The major reason for the superiority of IA over other acidic comonomers is the presence of two carboxylic groups, which provides more opportunities to induce the nitrile group to cyclize following the ionic mechanism.

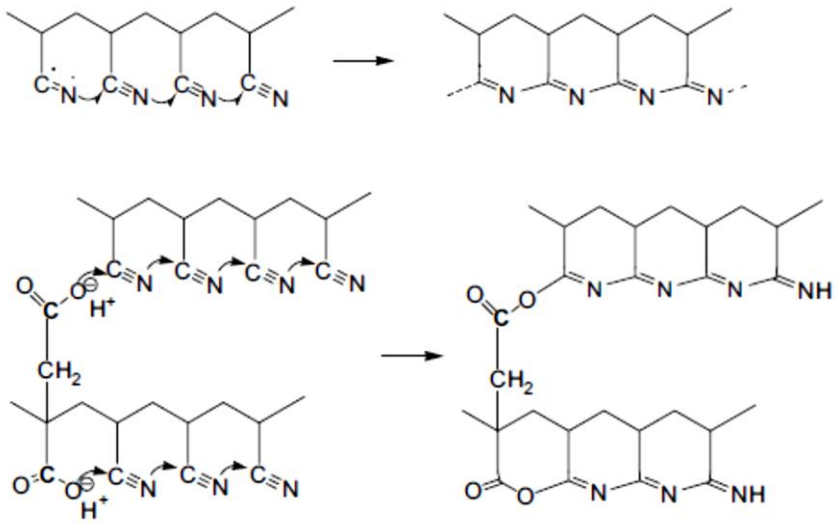


Figure 2.2 : Cyclization in PAN initiated through a free radical mechanism and AN-IA copolymer initiated through an ionic mechanism [33].

The effect of itaconic acid as a comonomer and additive on the exothermic reaction of acrylonitrile copolymers has been studied by Tsai et al [34]. As the itaconic acid content increases from 0.5 to 3.5 mol % in the copolymer, the exothermic peak becomes complex with several distinct maxima. Further, the initiation of nitrile oligomerization was also confirmed with itaconic acid as an additive. The rate of cyclization, however, would depend on the sequence distribution of the comonomer in the acrylonitrile copolymers.

The copolymerization of AN/IA in the aqueous deposited polymerization system initiated by the single water-soluble initiator-APS was performed [35]. Polymerization temperature and polymerization conversion are the important parameters to affect the monomer reactivity ratios of AN and IA in the aqueous deposited copolymerization system. The monomer reactivity ratios of AN/IA at 60 °C are 0.64 (r_{AN}) and 1.37 (r_{IA}) calculated from Kelen–Tüdõs method, 0.61 (r_{AN}) and 1.47 (r_{IA}) calculated from Fineman–Ross method. At lower polymerization conversion (<5%), the reactivity ratios of AN and IA remains stable. If the

polymerization conversion is more than 5%, the monomer reactivity ratio of AN increases, IA decreases.

The copolymerization of AN/IA by the solution polymerization method with dimethylformamide (DMF) was investigated [36]. The presence of IA comonomer in this system caused retardation of copolymerization. Triethylamine (TEA) was added to polymerization medium to overcome the retardation at enhanced concentrations of IA in the feed. Presence of TEA is conducive for overcoming the retardation observed for the copolymerization of AN/IA pair when the concentration of IA in the feed exceeds 10–15 mol%. Synthesis of PAN containing higher concentrations of IA is facilitated by the presence of TEA in the medium.

Copolymerization of AN with IA in DMF and DMF/water mixture was investigated at enhanced concentrations of the latter [27]. The copolymerization of IA/AN is associated with a marked penultimate unit effect for radicals terminated in AN as a result of the copolymer composition analysis. IA radicals have very little reactivity towards its own monomer unit. AN radical has a greater preference to the IA unit than its own monomer. The copolymerization resulted in the enrichment of IA in the polymer at extremely low concentrations of it in the feed and the subsequent decrease on increasing further its concentration in the feed. Presence of water marginally retards the reactivity of IA and the overall polymerization rate. IA retarded the polymerization rate significantly.

Porous AN/IA copolymers were synthesized by suspended emulsion polymerization with potassium peroxydisulfate (KPS) as an initiator, poly(vinyl alcohol) (PVA) as a dispersant agent, and Span80 as an emulsifier [26]. Suspended emulsion polymerization took place basically by an emulsion mechanism with the formation of the radicals in the water phase, the radicals being captured by the existing particles inside that water phase.The final AN/IA copolymers formed with agglomerates of primary particles had a porous structure, low particle density, and uniform particle size and did not agglomerate easily between the particles. The average particle size decreased and the size distribution became wide with increasing water/monomer mass ratio. With increasing KPS concentration, the average particle size decreased, and the size distribution became narrow. With increasing the concentration of PVA, the average particle size increased, and the size distribution became narrow.

2.4 Electrospinning Method for Nanofiber Production

Electrospinning technique was originally developed by Zeleny (1914) to prepare interconnected webs of fibers from polymer solutions or melts. It is a process that applies a high voltage to create electrically charged jets of a polymer solution. The jets within the electric field are directed toward the grounded target, during which they dry to form fibers [37]. This technique has been recognized as an effective way to fabricate polymeric nanofibers with diameter ranging from several micrometers down to tens of nanometers. Among various polymers, acrylonitrile-based homo- and co-polymers were most recently fabricated into nanofibrous materials with reinforcing, superhydrophobic and catalytic properties [38]. Electrospinning uses electrostatic forces to produce fine fibers from polymer solutions or melts and the fibers thus produced have a thinner diameter and a larger surface area than those obtained from conventional spinning processes. Furthermore, a DC voltage in the range of several tens of kVs is necessary to generate the electrospinning [38].

The minimum equipment requirements for demonstration of simple electrospinning in the laboratory are as follows:

- A viscous polymer solution or a melt and a feeding equipment.
- An electrode that is maintained in contact with the polymer solution.
- A high-voltage DC generator connected to the electrode.
- A grounded or oppositely charged surface to collect the nanofibers.

2.4.1 Parameters affecting electrospinning process

The electrospinning process is solely governed by many parameters, classified broadly into solution parameters, process parameters, and ambient parameters. Solution parameters include viscosity, conductivity, molecular weight, and surface tension and process parameters include applied electric field, tip to collector distance and feeding or flow rate [39,40].

In electrospinning process, the solution must gain sufficient charges such that the repulsive forces within the solution are able to overcome the surface tension of the solution. Subsequent stretching or drawing of the electrospinning jet also depends on the ability of the solution to carry charges, in other words the conductivity of

solution. Generally, the electric conductivity of solvents is very low (typically between 10^{-3} to 10^{-9} ohm^{-1} m^{-1}) as they contain very few free ions, if any, which are responsible for the electric conductivity of solution. The presence of acids, bases, salts and dissolved carbon dioxide may increase the conductivity of the solvent. The electrical conductivity of the solvent can be increased significantly through mixing chemically non-interacting components. Substances that can be added to the solvent to increase its conductivity includes mineral salts, mineral acids, carboxylic acids, some complexes of acids with amines, stannous chloride and some tetraalkylammonium salts. For organic acid solvents, the addition of a small amount of water will also greatly increase its conductivity due to ionization of the solvent molecules [41]. This increase in the conductivity can help production of beadless fibers just because stretching of the solution has increased and to some degree fiber diameter decrease can be observed [42]. Cetiner and et al. have used electrospinng technique to produce conductive composites from polypyrole that had been polymerized in AN-VAc copolymer matris. The nanofiber diameters and surface morphology show changes according to conductivty of polymeric material [43].

During the electrospinning process most of solvent evaporates while the jet and the nanofibers are moving to the grounded electrode. The solvent evaporates and forms a mist during continuous spinning. One of the several reasons for electrical discharge of the stored charge through the atmosphere surrounding the fibers may be the dielectric breakdown of the solvent. Corona parameters such as breakdown voltage and corona current depend on the dielectric properties of the gas medium, notably permittivity. Molecular structure and processes such as molecular excitation, ionization and the specifics of charge carrier interactions have an impact on charge transfer from one ionized molecule to another, which can be expressed in terms of the conduction of the gas surrounding the charged fibers. These chemical alterations may affect the outcome of the electrospinning process in terms of fiber surface modification, fiber diameter distribution, etc. It is clear that solvent evaporation and charge chemistry are major process factors in electrospinning [44].

During electrospinning, electrical charges develop into the polymer solution (or melt), but some portion of the charge on the fiber surface may ionize the moisture in the surrounding air and thus, lose its own charge. However, solvent does not carry any charge to the surrounding while evaporating [44].

The viscosity of electrospinning solution is a significiant factor effecting the process. The solution viscosity depends on molecular weight, polymer chain entanglement, concentration, and temperature. Molecular weight of a polymer is directly related to viscosity of the solution. Generally, when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than solution of the same polymer but of a lower molecular weight. One of the conditions necessary for electrospinning to occur where fibers are formed is that the solution must consists of polymer of sufficient molecular weight and the solution must be of sufficient viscosity. As the jet leaves the needle tip during electrospinning, the polymer solution is stretched as it travels towards the collection plate. During the stretching of the polymer solution, it is the entanglement of the molecule chains that prevents the electrically driven jet from breaking up thus maintaining a continuous solution jet. As a result, monomeric polymer solution does not form fibers when electrospun [45].

The polymer concentration in solution is a parameter to change the viscosity of the solution [41]. Increasing solution concentration shows almost same effect as using higher molecular weight polymer. Polymer chain entanglement of the polymer solution is improved in either case. At higher concentrations, viscosity of the solution becomes higher and it prevents the jet having larger bending instabilities. This causes small deposition on the collecting media for fibers and the resultant fiber diameter is thickened. At low viscosities, there will be less amount of chain entanglement in polymer solution. The forces from surface tension become dominant and bead formation occurs along the string of electrospun fibers. At high viscosities, jets can be stretched fully and beadless fibers can be obtained. High viscosity values also provoke splitting of jets into smaller fibers. Moreover, pumping of the polymer solution becomes difficult and drying of the solution on the tip of the pipette can be observed [42].

2.4.2 The applications of electrospun nanofibers

The Donaldson Company was the first to realize the commercial value of electrospinning taking advantage of the enormous availability of the specific surface of electrospun fibers and the ultrafine nature of the fibers. They introduced the Ultra-Web® cartridge filter (Figure 2.3) for industrial dust collection in 1981 [46] and

more recently the Hollingsworth & Vose Company introduced the Nanoweb® for automotive and truck filter applications [47].

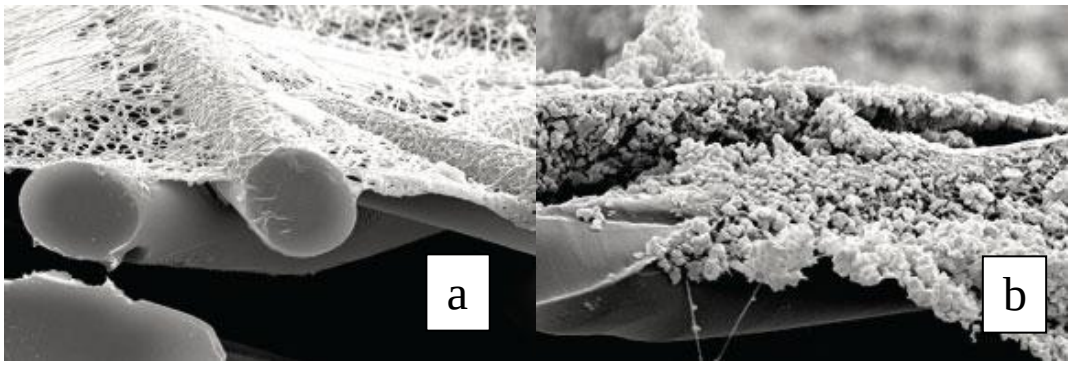


Figure 2.3 : (a) Clean Ultra-Web® cartridge filter, (b) After dust particles collected on the surface of Ultra-Web® cartridge filter [46]

On the basis of the papers presented in the Polymer Nanofiber Symposium held in New York at the American Chemical Society [48], one can categorize the potential applications of electrospun fibers into (1) biomedical applications (tissue engineering scaffolds, wound care, superabsorbent media, drug delivery carrier, etc.), (2) electronic applications (electronic packaging, sensors, wearable electronics, actuators, fuel cells, etc.), (3) industrial applications (filtration, structural toughening/reinforcement, chemical/bio-protection, etc.)

Polymeric conductive membranes produced by electrospinning technique have potential for applications such as, electrostatic dissipation, corrosion protection, electromagnetic interference shielding, photovoltaic device, fabrication of tiny electronic devices or machines such as Schottky junctions, sensors and actuators etc., as the rate of electrochemical reactions is proportional to the surface area of the electrode [49,50].

Conductive nanofibrous membranes are quite suitable for use as porous electrodes in developing high performance batteries and polymer electrolyte membrane fuel cells (PEMFCs) due to its high porosity and inherent large total surface area. Polymer batteries have been developed for cellular phones to replace conventional, bulky lithium batteries. The components of polymer batteries are a carbon anode, a lithium cobalt oxide cathode, and a polymer gel electrolyte. Conductive nanofibers offer noteworthy properties of polymer batteries, for example, less electrolyte leakage, high dimension flexibility, and high energy density per weight [51]. However, there is still a need to improve energy density per weight of polymer batteries to increase their market share.

Recently, carbon nanofiber webs have been prepared [52,53] through the electrospinning technique and evaluated on the application of these materials in electrical energy-storage systems. Researchers, therefore, have been investigating methodologies to develop carbon nanofiber webs as a novel electrode material for electric double layer supercapacitor showing high performance by increasing spesific surface area.

3. EXPERIMENTAL PART

3.1 Materials

Acrylonitrile (99.5>%) was provided by the Aksa Acrylic Chemistry Company. Itaconic acid (99.5>%) was purchased from Sigma Aldrich. Ammonium persulfate (APS), (99.5>%), dimethylformamide (DMF) and ethanol were all Merck reagents. All these reagents were used without further purification.

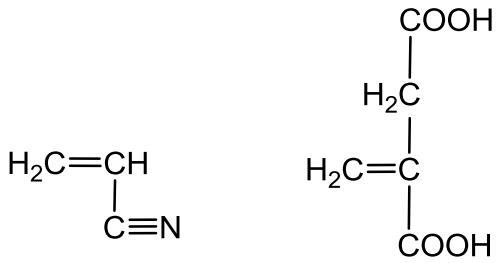


Figure 3.1 : Chemical structure of AN an IA monomers

3.2 Copolymerization of AN with IA

Copolymer of AN-IA was synthesized by free radical polymerization using APS as an oxidant in the aqueous medium. Copolymerization was carried out in a two necked flask attached a condenser equipped with a stirrer seen in Figure 3.2. 10 g monomer mixture was stirred with distilled water for 30 minutes. 0.3 g APS dissolved in 30 mL distilled water was added to monomer mixture. The ratio of APS to monomers in feed is 3 % (wt). The monomer feed ratios used in this experiments were 99:1, 97:3, 95:5, 93:7 and 91:9 (AN:IA). During copolymerization the temperature was kept at 60 ^{o}C. After 3 hours adding oxidant, copolymerization was finished by stopping heater. The precipitated polymer was obtained in excess ethanol, filtered and dried at 50 ^{o}C under vacuum for 4 hours.

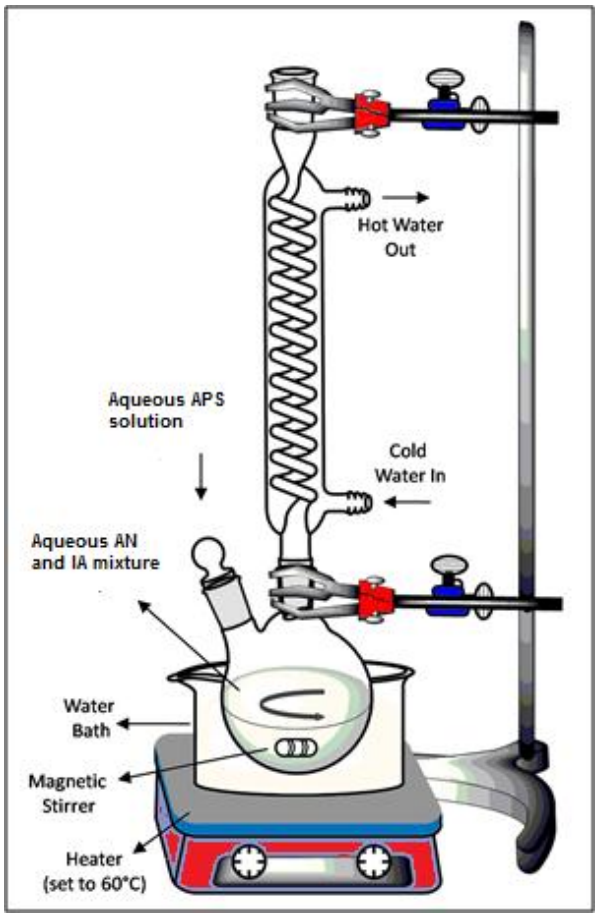


Figure 3.2 : Experimental setup of copolymerization

3.3 Electrospinning of P(AN-co-IA) Copolymers

The copolymer solutions were prepared with 5 %wt concentration in DMF at room temperature to produce nanofiber mats. The electrospinning apparatus includes a syringe pump (NE-500 model, New Era Pump Systems, Inc., USA) with feeding rate from 5.5 μL/h to 400 mL/h, high voltage DC power supplier generating positive DC voltage up to 50 kV DC power supply (ES50 model, Gamma High Voltage Inc., USA) and a grounded alumium collector which is covered with aluminum foil. Solution was loaded into a syringe having 12 mm diameter and positive electrode was clipped onto the dispensing needle having 0.8 mm outer diameter. The feeding rate of the polymer solution was controlled by syringe pump and solutions were electrospun horizontally onto the collector. The voltage of power supply was kept 9 – 10 kV. Polymer solution was fed with 1 ml/h flowrate. The flat collector was put 19 cm away from the needle. Figure 3.3 shows the experimental setup of electrospinning process which was used .

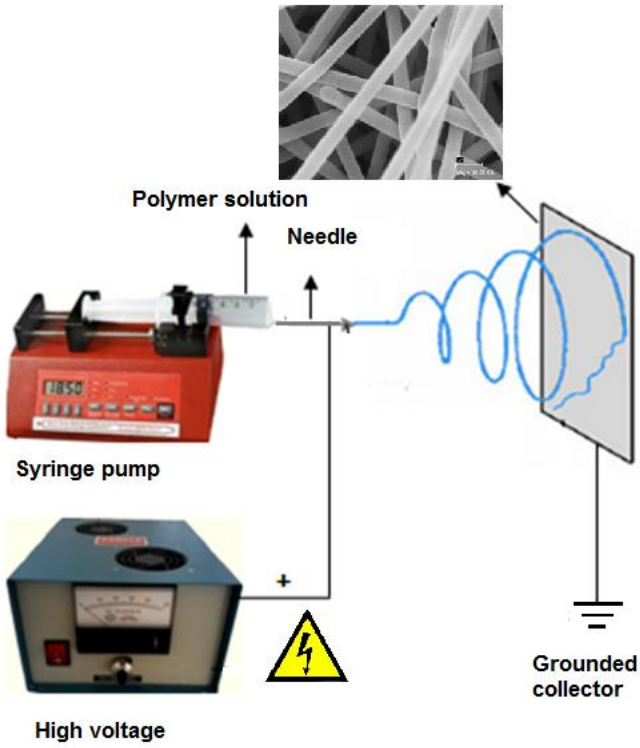


Figure 3.3 : Experimental setup of electrospinning.

3.4 Stabilization of P(AN-co-IA) Nanofibers

The stabilization was carried out by heating p(AN-co-IA) nanofiber mats from the room temperature to 220 ^{o}C with 1 ^{o}C/min heating rate, followed by holding the temperature at 220 ^{o}C for 14 h to allow the stabilization to complete. The heat treatment performed in a Memmert Ufe 400 oven.

3.5 Characterization

The structure of the copolymers was characterized by means of ^{1}H NMR spectroscopy and Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy. FTIR analysis of P(AN-co-IA) copolymers were performed with FTIR-ATR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal).

^{1}H NMR spectroscopy analysis of AN-IA copolymers was performed using a Agilent VNMRS 500 MHz spectrometer. NMR samples were prepared by dissolving the copolymers in deuterated dimethyl sulfoxide (DMSO-d_6).

Intrinsic viscosity [η] of the copolymers was measured in dimethylformamide (DMF) solution using an Ubbelohde viscometer in a water bath at 30 ± 1°C.

The DSC and TGA measurements were carried out using Mettler Toledo instruments in Aksa Acrylic Chemical Company laboratuaries. The DSC samples were scanned at a heating rate of 10 °C min^{-1} under air atmosphere from ambient temperature to 400 °C. TGA samples were heated with a heating rate of 10 °C min^{-1} from ambient temperature to 800 ^{o}C under air atmosphere.

DMA measurements of polymer films were performed using TA Q800 instrument by applying multifrequency-strain test method. The film samples were casted from copolymer solutions in DMF to glass surface at room temperature. The casting films were annealed at 80 ^{o}C under vacuum for 24 hours. Tg measurements using DMA run in tension clamps, at a frequency of 1 Hz and a ramp rate of 3°C/min from ambient temperature to 175 ^{o}C.

Morphology of electrospun nanofibers were characterized using Scanning Electron Microscope (Carl Zeiss EVO MA 10) and the samples for the SEM measurements are coated with gold (Ion Sputter Metal Coating Device, MCM-100). The thickness of gold coating was about 30 nm. Diameters of nanofibers were calculated using Adobe Acrobat 9 Pro Extended software.

4. RESULTS AND DISCUSSION

4.1 Copolymer Characterization

The results of the copolymerization of AN-IA and feed ratio of monomers as weight and mole percentage for various experiments are listed in Table 1. The conversions of copolymerization calculated gravimetrically are high enough for an effecient polymerization.

Table 4.1: Copolymerization of AN-IA.

	Monomer feed ratio (wt%)		**Monomer feed ratio (mole%)**		**Conversion %***	**[η] (dL/g)**
	IA	**AN**	**IA**	**AN**		
C(IA-1%)	1	99	0.41	99.59	87.8	2,67
C(IA-3%)	3	97	1.25	98.75	65.5	2,41
C(IA-5%)	5	95	2.10	97.90	80.7	1.94
C(IA-7%)	7	93	2.98	97.02	86.5	1,07
C(IA-9%)	9	91	3.88	96.12	83.3	0,92

*Calculated gravimetrically

Based on Devasia's study on viscosity properties, high molecular weight AN-IA copolymers have led to the problem of the rectilinearity of the concentration dependency of reduced viscosity [54]. Viscosity experiments worked using definite concentrations showing rectilinearity, thereby demonstrating the polyelectrolyte behavior caused by ionogenic groups in the copolymer, which at a higher dilution in DMF may undergo greater ionization. For C(IA-%7) reduced viscosity (η_{sp}/C) versus concenration (C) from 1.05 to 0,85 g/dL was plotted and the linear regression line was displayed to obtain intrinsic viscosity in Figure 4.1. The viscosity average molar mass (Mv) of C(IA-7%) was calculated as 7.49×10^5 according to Mark Houwink Sakurada equation [55].

$$[\eta] = 2.86 \times 10^{-4} M_v^{0.733}$$

Intrinsic viscosity of AN-IA copolymers calculated shows a drop by increasing IA content (Table 4.1). According to Bajaj study, the copolymers having higher IA

content shows lower intrinsic viscosity, too [56]. The intrinsic viscosity or the molecular weight of the polymer controls the solid concentration of the dope, the fiber morphology, and the density [57].

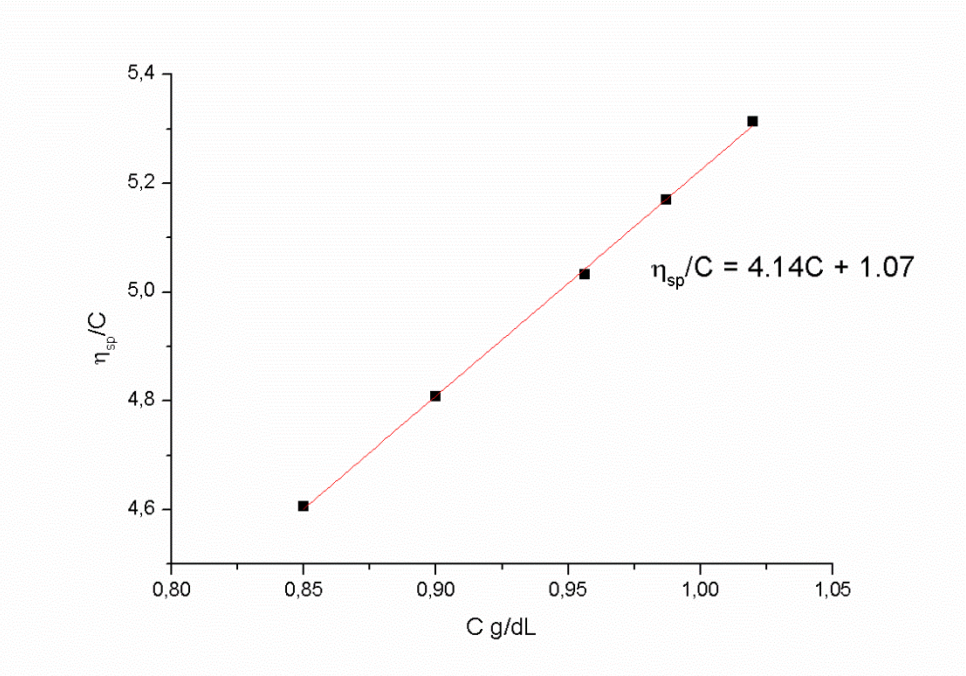


Figure 4.1 : Plot for C(IA-7%) η_{sp}/C versus C in DMF at 30 ^{o}C.

4.1.1 FTIR-ATR Spectroscopy

The FTIR-ATR spectra of PAN homopolymer and P(AN-co-IA) copolymer are shown in Figure 4.2 and it was recorded in the absorbance mode. The characteristic peak of C≡N stretching of AN repeating unit is observed as a strong absorption peak at 2244 cm-1 in both PAN and its copolymer. The peak at about 1735 and 1628 cm^{-1} related to the carbonyl stretching vibration of the carboxylic acid was appeared in the spectrum of AN- IA copolymer . The characteristic peak of aliphatic -CH_2- stretching is at 2940 cm-1. There is also a strong band at 1454 cm-1 related to bending vibration of -CH in -CH_2. The band at 1076 cm-1 is ascribed to the -CH bending mode in CH. These results are in agreement with literature[31,58,59].

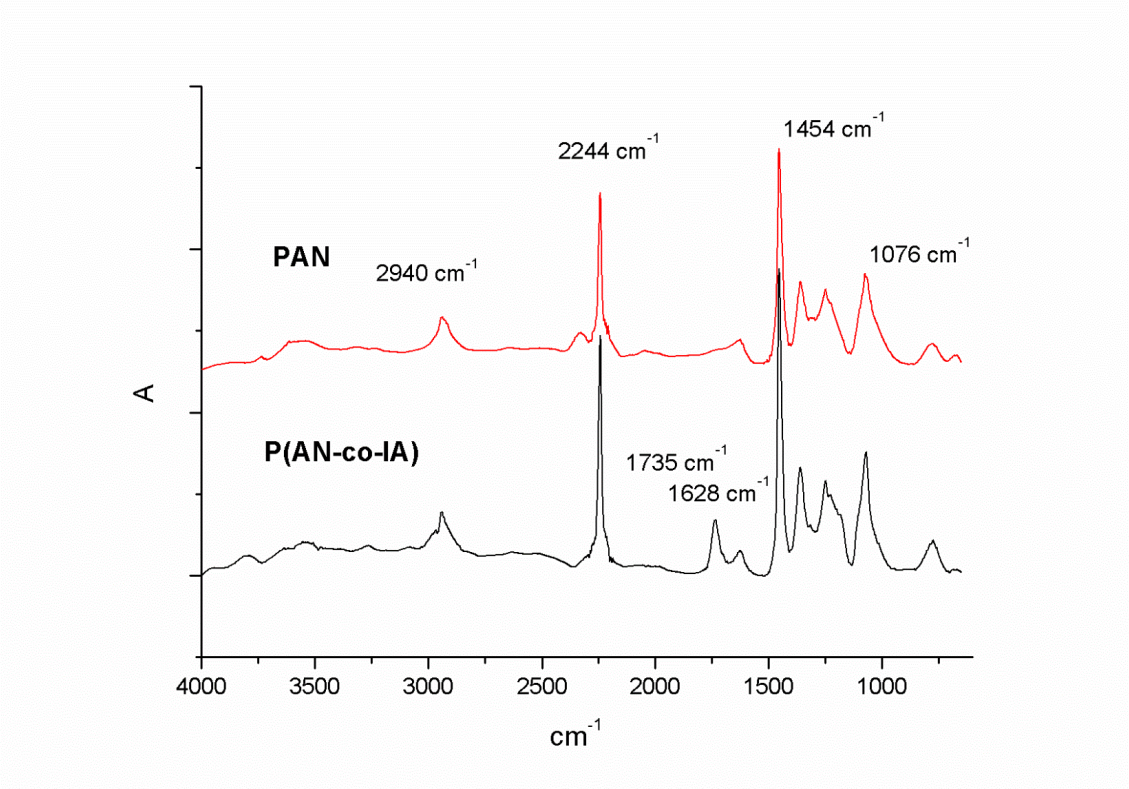


Figure 4.2 : FTIR-ATR spectra of PAN and AN-IA copolymer.

In Figure 4.3 FTIR-ATR spectrums of AN-IA copolymers which synthesized with different proportions of IA were presented in absorbance mode. The peak of carbonyl stretching in copolymers is shifted from 1737 to 1732 cm^{-1}, corresponding to increase in IA feed.

The relation between AN and IA units in copolymers composition was founded by comparing the strong bands at 2244 cm^{-1} due to C≡N stretching vibration and 1628 and 1730 cm^{-1} due to C=O stretching vibrations. Absorbance ratio of the characteristic peaks of carboxylic acid to C≡N stretching vibration of AN units was plotted versus IA feed ratios (wt%) in Figure 4.4. The absorbance ratios shows an increasing trend in copolymers which had feeded high IA.

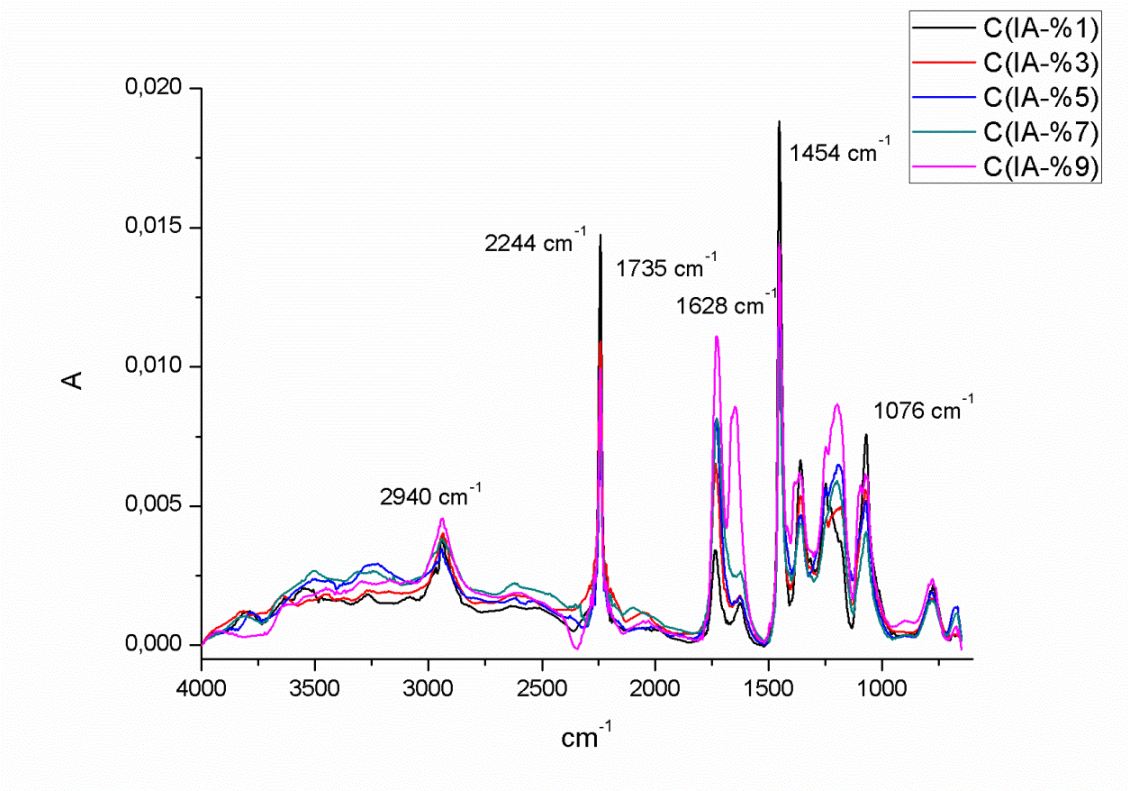


Figure 4.3 : FTIR-ATR spectras of AN-IA copolymers

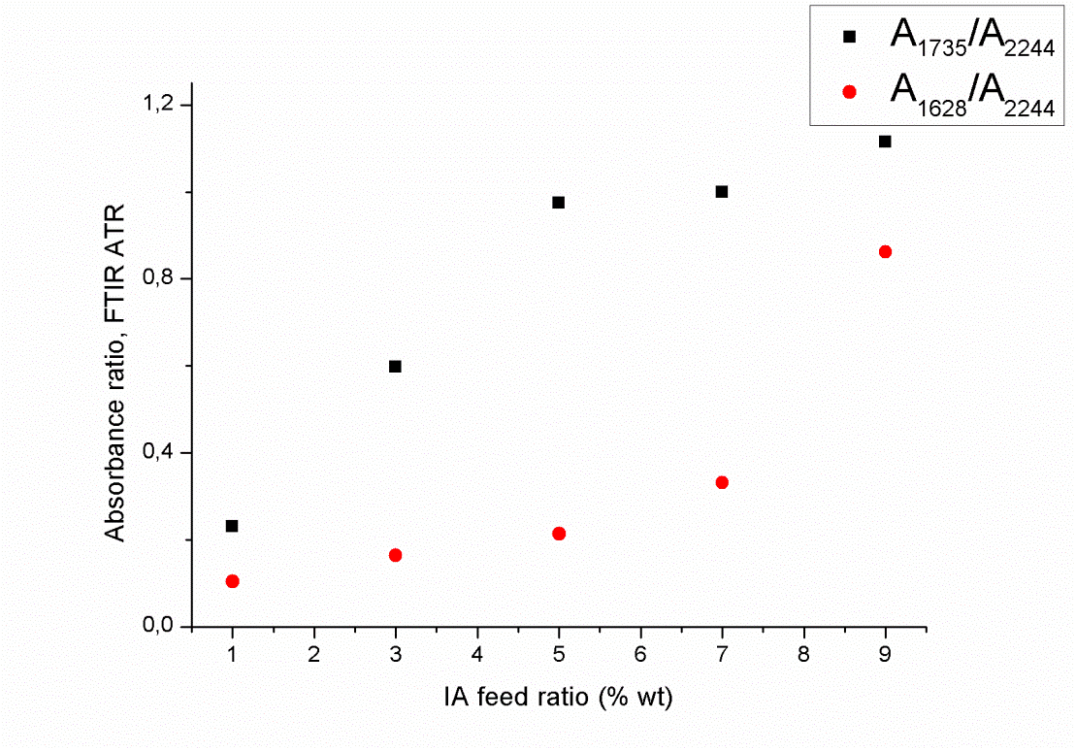


Figure 4.4 : The relation between the absorbance ratios and the initial feed ratio of AN-IA copolymers based on the FTIR-ATR results

4.1.2 Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR are used to specify the composition of AN-IA copolymers which is shown as chemical structure in Figure 4.5. ^{1}H NMR spectrum of AN-IA copolymer coded C(IA-1%) is seen in Figure 4.6. The signal at 2.2 – 1.85 ppm is related to -CH_2 protons of both AN and IA (a). The signals of -CH proton of AN (b) were observed at 3.25 – 3.09 ppm. The other peaks seen in the ^{1}H-NMR spectrum are related to solvent, DMSO-d_6. NMR results are in agreement with literature [58].

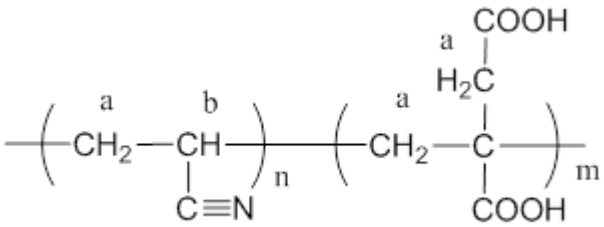


Figure 4.5 : Chemical structure of AN-IA copolymer indicated protons.

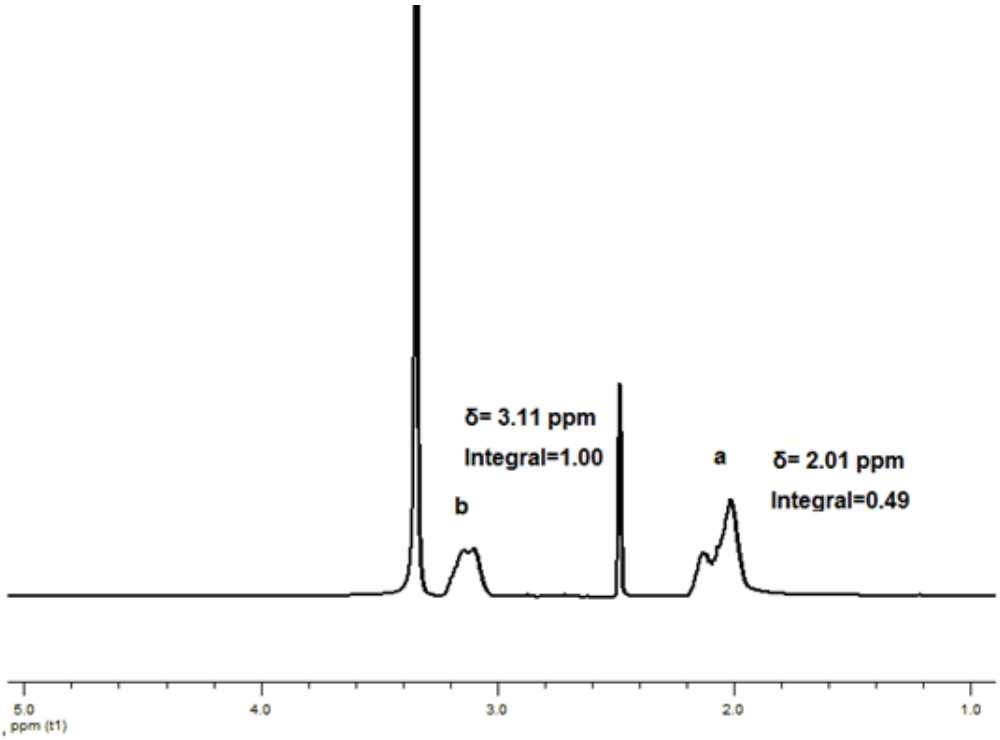


Figure 4.6 : ^{1}H NMR spectrum of AN-IA copolymer coded C(IA-1%).

The copolymer compositions calculated from the ratio of the integrals of the peaks related to a and b protons. IA content in the copolymers as molar percentage and also absorbance ratios determined from FTIR ATR spectrums are listed in Table 4.2.

High IA content of copolymers can be explained by reactivity ratios that r_{IA}=1.37 is higher than r_{AN}= 0.64 [35].

Table 4.2 : Determination of copolymer compostion.

	IA feed ratio (mole%)	IA content (mole %)*	Absorbance ratio**
C(IA-1%)	0.41	1.00	0.23
C(IA-3%)	1.25	1.92	0.60
C(IA-5%)	2.10	2.23	0.97
C(IA-7%)	2.98	3.14	0.99
C(IA-9%)	3.88	4.09	1.11

*Calculated from NMR spectrums

** Determined from FTIR ATR spectrums A_{1735}/A_{2244}

NMR spectoroscopy is a certain way to determine copolymer compositions, but it is time consuming because of sample preparation. Copolymer characterization by FTIR spectroscopy, especially in ATR mode is a very practical way. Therefore, a calibration curve was fitted using FTIR ATR absorbance ratios and IA content (% mole) calculated from NMR results (Figure 4.7).

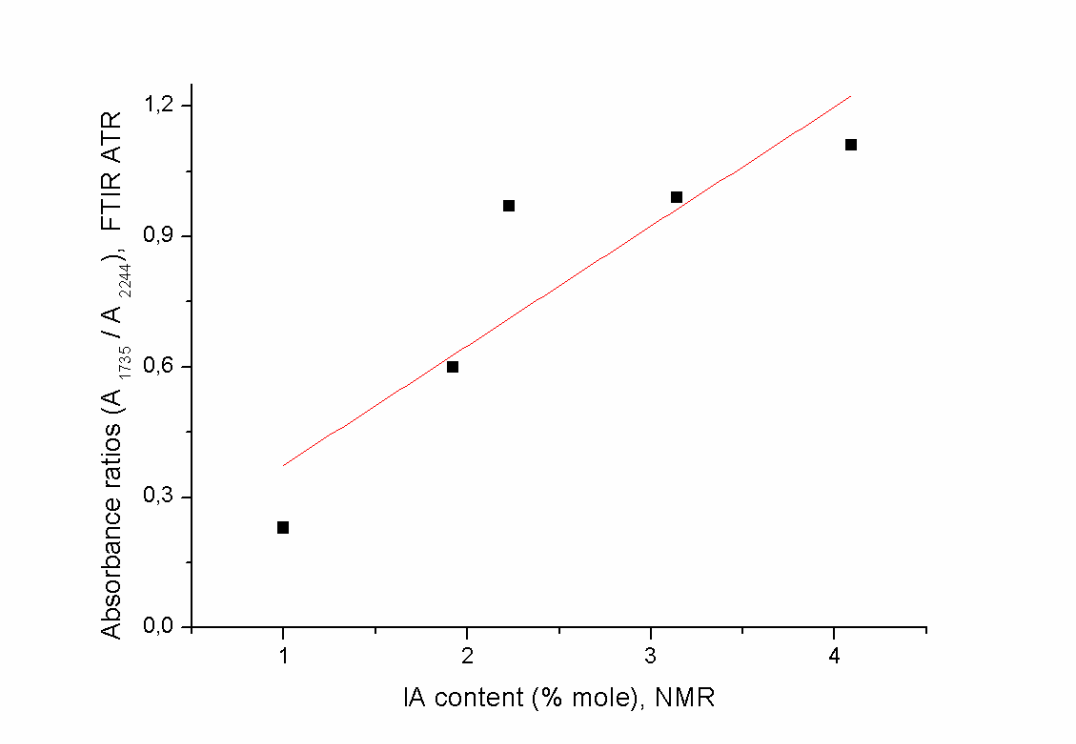


Figure 4.7 : Calibration curve fitted based on absorbance ratios and IA content (% mole) calculated from NMR results

4.1.3 Differential scanning calorimetry (DSC)

The DSC curves of AN-IA copolymers all show a doublet exothermic peak between 200 and 300 ^{o}C (Figure 4.8). Based on the DSC studies, PAN homopolymer exhibits a single sharp peak centered at 310 ^{o}C which is known that it is related the cyclization reactions in the PAN homopolymer following a free radical mechanism at high temperature. Carboxylic acid groups in AN-IA copolymers can initiate the cyclization reactions at a lower temperature through an ionic mechanism [60]. First exothermic peak at the lower temperature is associated with the ionic cyclization reactions which are described in Figure 4.8. As for C(IA-1%), it appears as a shoulder at about 222 °C. With IA content increasing, initiation temperature (T_i) decreases from 222 to 195 ^{o}C.

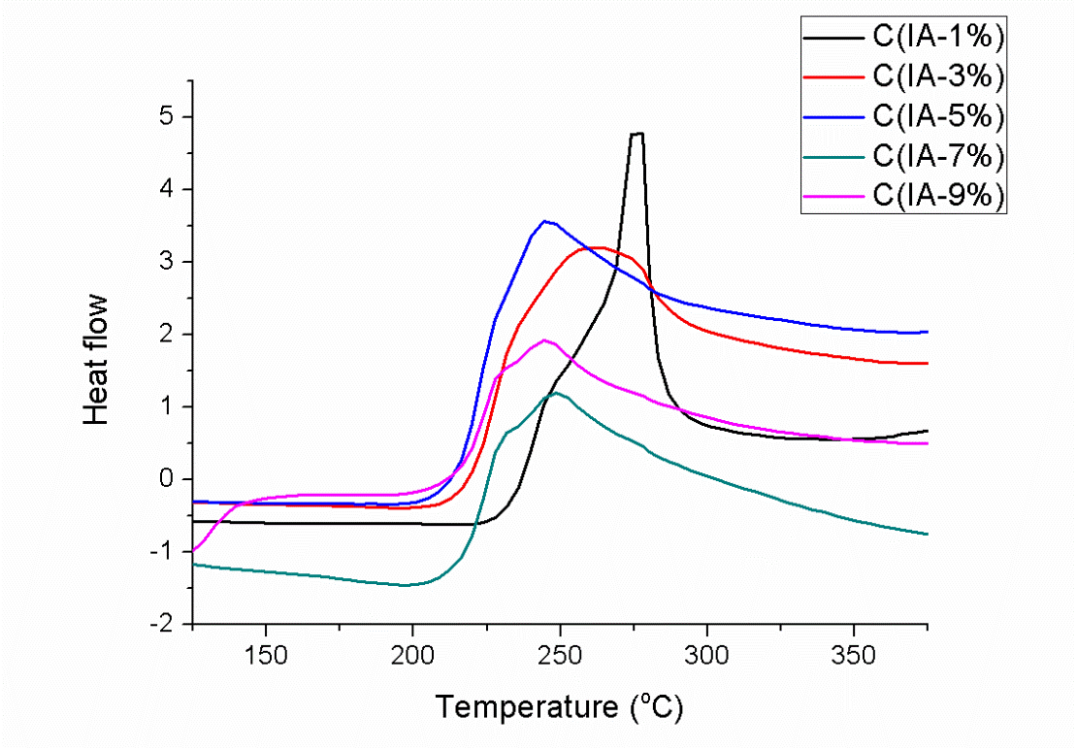


Figure 4.8 : DSC curves of AN-IA copolymers with different IA contents at a heating rate of 10°C min^{-1}

The ionic cyclization reactions are initiated by elimination of hydrogen ion (Figure 4.9). The hydroxyl oxygen of –COOH in IA units has made a nucleophilic attack on the carbon atom of neighbour nitrile group and induce it to cyclize. Cyclization reactions lead to the development of ladder structures by oligomerization of nitrile (C≡N) groups. Oligomerization is terminated by addition of hydrogen ion [61].

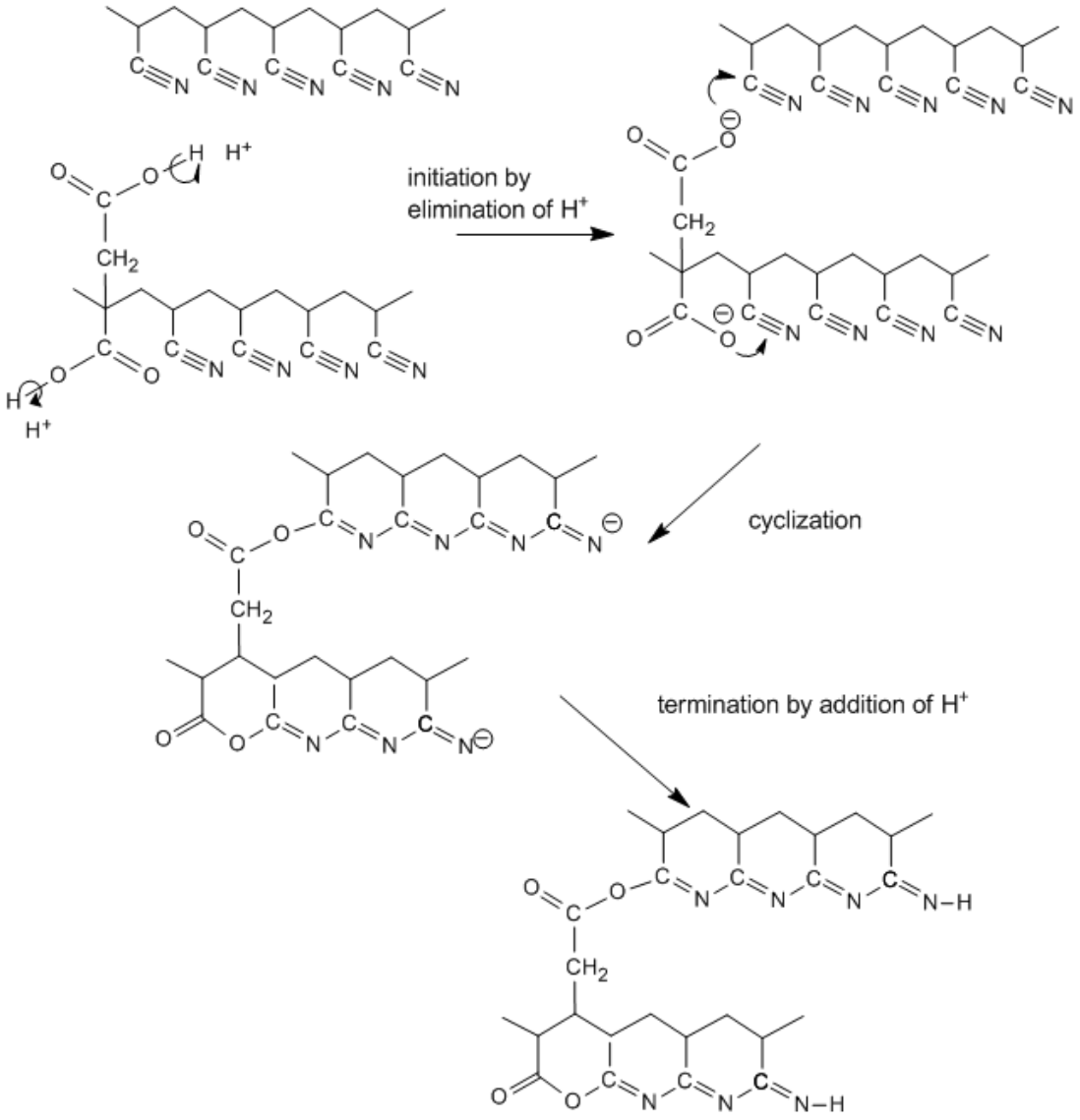


Figure 4.9 : Cyclization mechanism of AN-IA copolymers

According to the literature [61], the first exothermic peak at the lower temperature side is assigned to cyclization reactions including hydrogenation and oxidation, and the second peak is attributed to the secondary oxidative reactions. Summary of stabilization parameters obtained from DSC exoterms is presented in Table 4.3. All the stabilization parameters shows a significant decrement, which implies IA is effective to control the exothermic behavior and improve the stabilization treatment. The relation between stabilization parameters and IA feed ratio (wt%) is shown in Figure 4.10.

Table 4.3 : Summary of stabilization parameters obtained from DSC exoterms.

Sample	T_i (°C)	$T_{peak\ 1}$ (°C)	$T_{peak\ 2}$ (°C)
C(IA-%1)	222.8	249.6	276.6
C(IA-%3)	204.3	236.4	257.9
C(IA-%5)	199.3	227.9	245.8
C(IA-%7)	198.2	231.4	247.1
C(IA-%9)	195.5	227.6	246.3

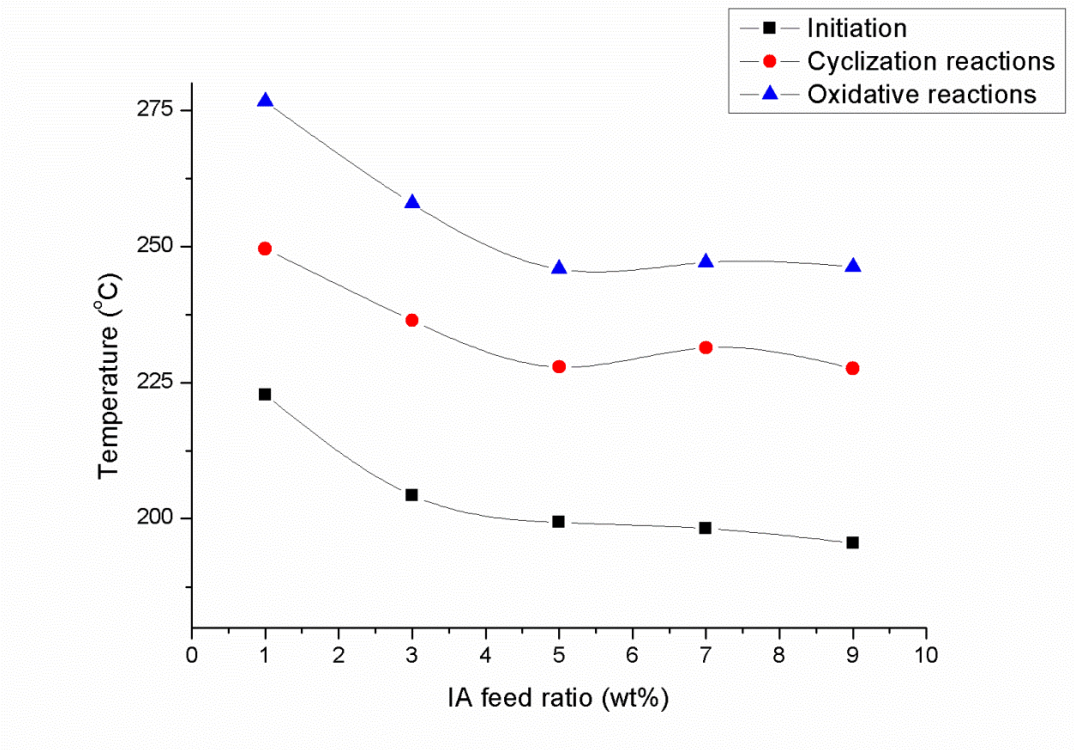


Figure 4.10: Relation between stabilization parameters and IA feed ratio (wt%).

4.1.4 Thermal gravimetric analysis (TGA)

The thermal behaviour of AN-IA copolymers with varying IA content were compared under air atmosphere at a heating rate of 10 °C min^{-1} shown in Figure 4.11. The weight loss seems to be divided into two steps basically [62]. The first step is starting at about 230 - 250 °C which may be mainly due to the dehydrogenation and carboxylation reactions presented in Figure 4.12, because the nitrile cyclization reactions theoretically do not cause any weight loss.

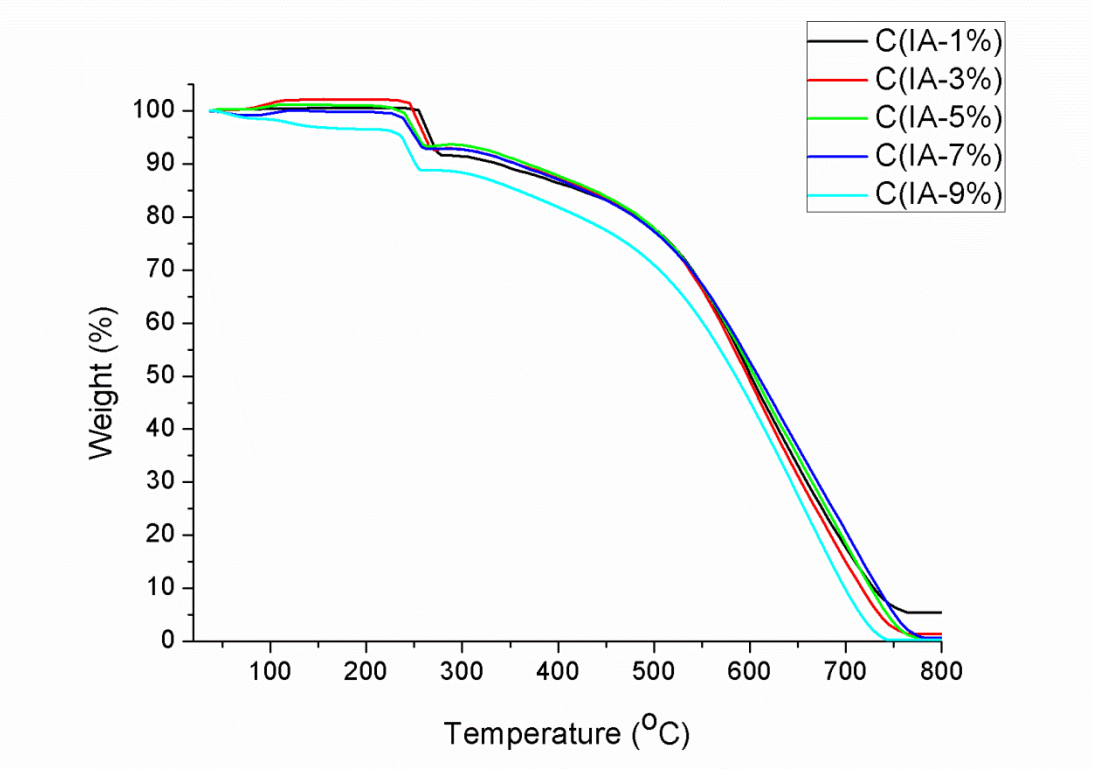


Figure 4.11: TG curves of AN-IA copolymers under air atmosphere at a heating rate of 5 °C min^{-1}.

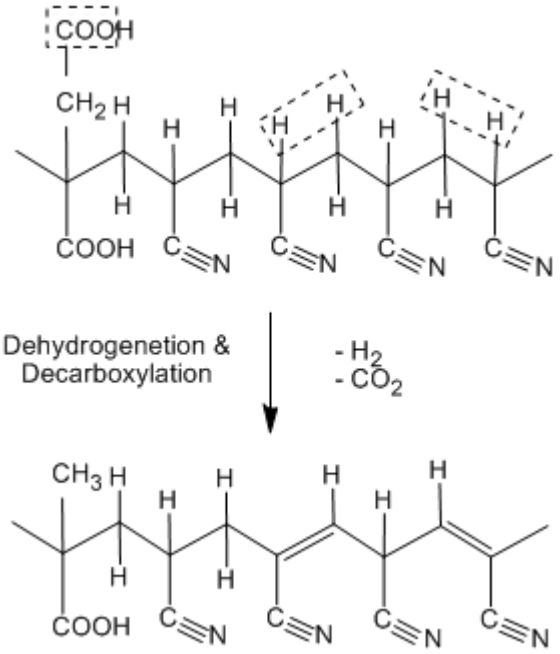


Figure 4.12: Dehyrdrogenetion and de carboxylation reactions.

However, the rate of weight loss in the second step is quiet large, which could be attributed to the occurrence of oxidative reactions, causing fragmentation of polymer

chains and evolution of gas fragments such as HCN, NH_3,CO_2, H_2O [63]. The starting temperature of second step can be assumed as decomposition temperature between 277 and 257 ^oC.

Ionic cyclization occurring at low temperature improves stabilization, but IA also causes to decrease in decomposition temperature (T_d). The difference between T_d obtained from TGA and T_i obtained from DSC is listed in Table 4.4 and plotted in Figure 4.13. For C(IA-1%) copolymer, the temperature difference is lowest. Higher IA content is useful for prevent decomposition during cyclization, although the copolymers with higher IA content have low decomposition temperature.

Table 4.4 : Thermal decomposition temperature of AN-IA copolymers.

Sample	T_{step1}	T_d	T_d-T_i
C(IA-%1)	254.2	277.8	55
C(IA-%3)	245.2	268.8	64.8
C(IA-%5)	239.8	262.5	63.2
C(IA-%7)	238.1	262.1	63.9
C(IA-%9)	232.7	257.7	62.2

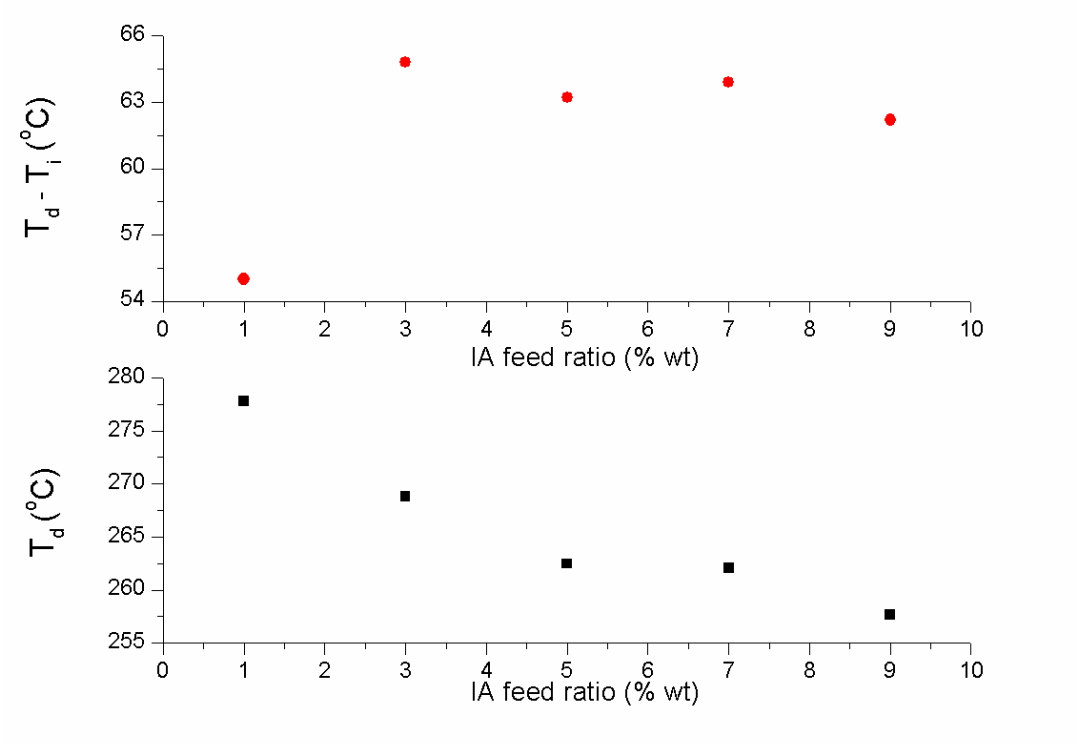


Figure 4.13 : The relation between T_d and T_d-T_i with IA feed ratio (% wt).

4.1.5 Dynamic mechanical analysis (DMA)

The determination of Tg using differential scanning calorimetre has been difficult due to the strong exothermic reaction, minor transitions like Tg cannot be seen [62]. The Tg of AN-IA copolymers was obtained from the temperature corresponding to the maximum of the tan delta curves determined with multifrequency – strain test method (Figure 4.14) using DMA instrument. In this test method, storage modulus (E') and loss modulus (E'') are measured by applying heat and force at a frequency to the film samples. Storage and loss modulus are elastic and viscous response of material respectively. The ratio of E''/E'is called damping factor (tan delta). Tg values of the copolymers decreases, with increasing IA content, while tan delta increases (Table 4.5). The Tg and damping factor of copolymers shows an increasing trend, by increasing the amount of IA adding the copolymer. IA comonomer which is crystalline with a melting point 167-168 ^{o}C [64], cannot cause an softening effect on PAN naturally.

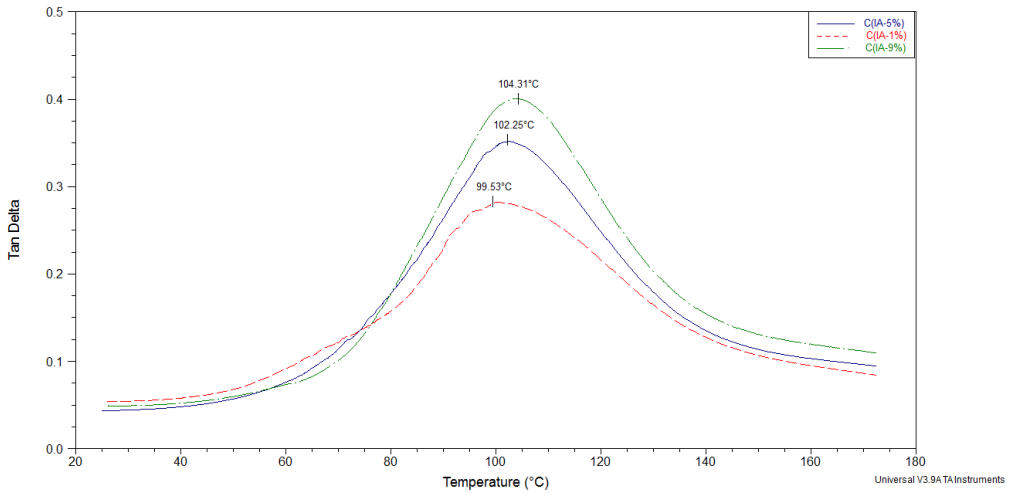


Figure 4.14 : Tan delta curves of AN-IA copolymers; C(IA-1%), C(IA-5%) and C(IA-9%).

Table 4.5 : DMA results of AN-IA copolymers.

Sample	T_g (^{o}C)	Tan delta
C(IA-%1)	99.53	0.28
C(IA-%5)	102.25	0.35
C(IA-%9)	104.31	0.40

4.2 Morphology of Elecrospun Nanofibers

Electrospinning solutions were prepared from AN-IA copolymers having different itaconic acid content in DMF. All the solutions had same concentration (5 wt%). Electrospinning parameters (distance and flowrate) were also kept constant. Required minumun voltage to create spinning jet was applied to the solution, for the C(IA-1%) solution it was 10.5 kV and 9 kV was enough for the other solutions. The effect of itaconic acid on nanofiber diameters was investigated in this part of study. In Figure 4.15 and 4.16, SEM images of electrospun nanofibers with 20,000 magnitude are seen. Based on the SEM images, bead free nanofibers were produced from all the copolymer solutions.

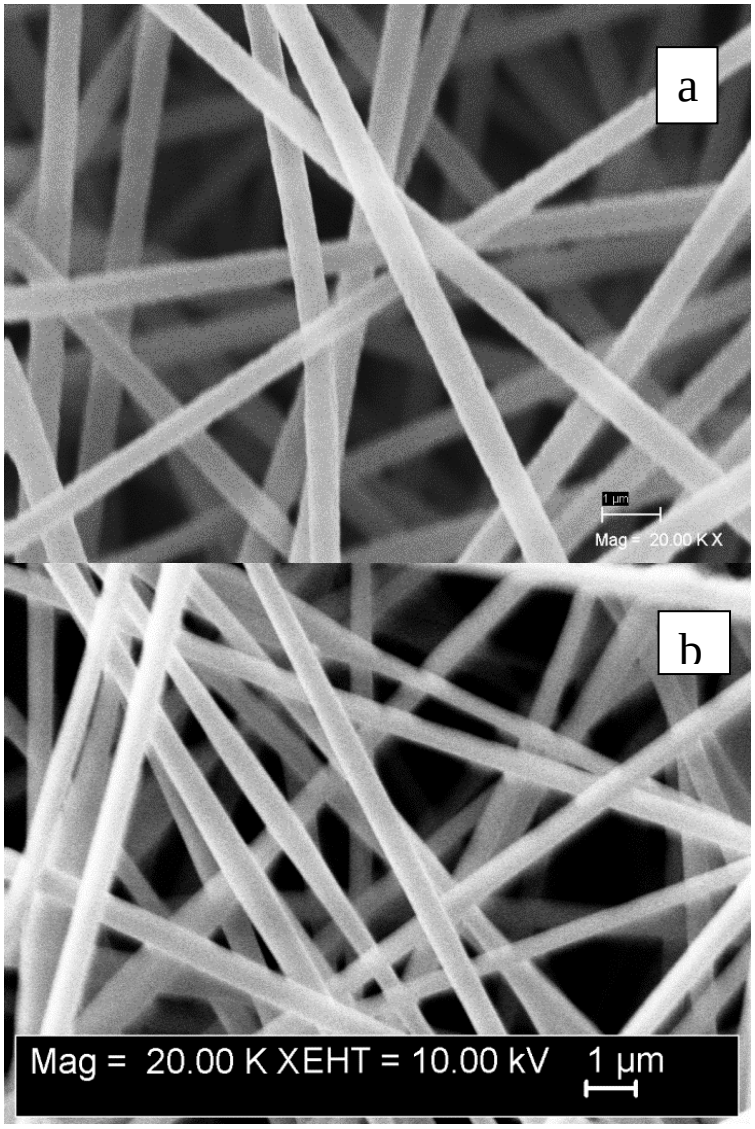


Figure 4.15 : SEM images of electrospun nanofibers with 20,000 magnitute; (a) C(IA-1%), (b) C(IA-3%).

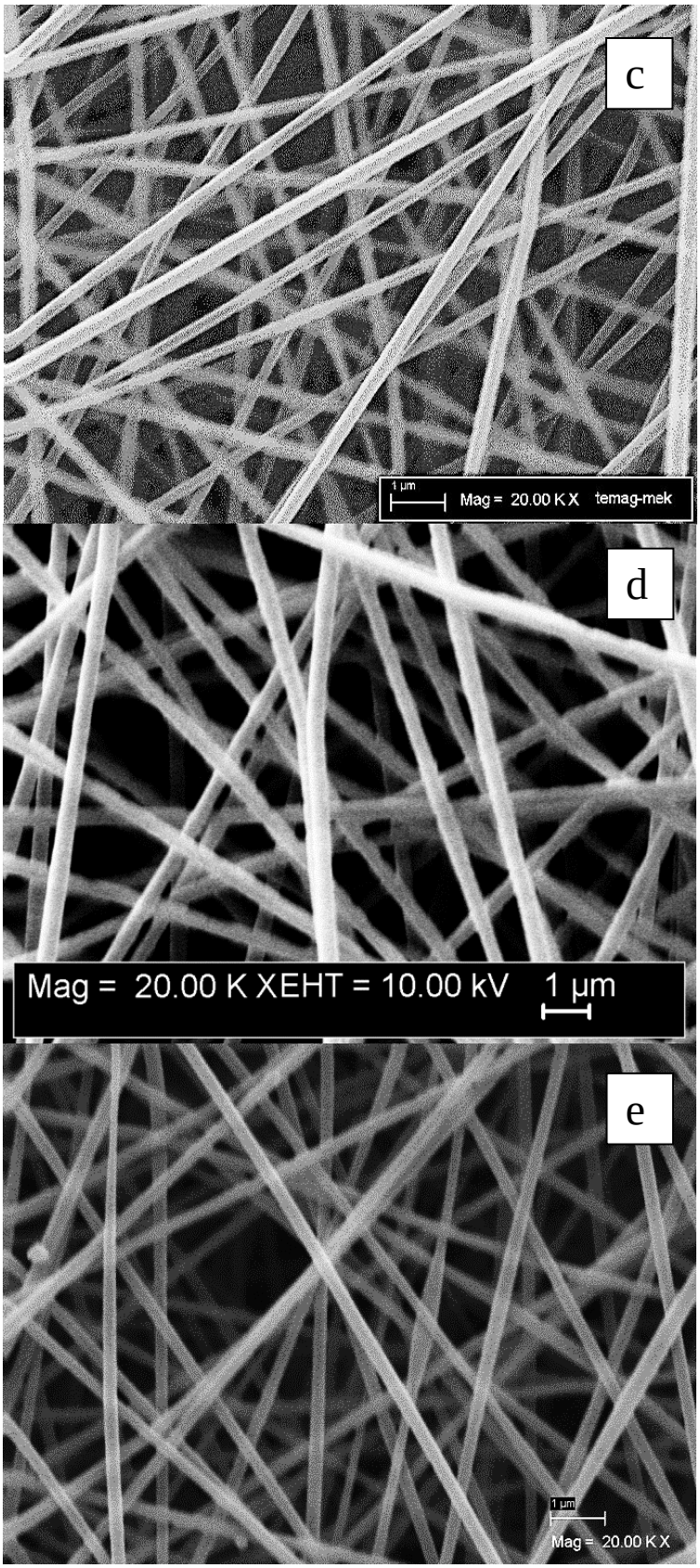


Figure 4.16 : SEM images of electrospun nanofibers with 20,000 magnitute; (c) C(IA-5%), (d) C(IA-7%) and (e) C(IA-9%).

About 20 nanofiber was measured from the SEM images of nanofiber mats with x20,000 magnitute to obtain average nanofiber diameter which was presented as box plot in Figure 4.17. C(IA-1%) sample which has the lowest IA content exhibited the highest average nanofiber diameter, 878±18 nm. The average nanofiber diameter decreases corresponding with IA content in copolymers. Decrement in standart deviation of nanofibers shows that uniformity of nanofibers is improved by increasing IA content.

Table 4.6 : Nanofiber diameters obtained from SEM images.

Sample	Ave. nanofiber diameter (nm)	Standart deviation (nm)
C(IA-%1)	878	18
C(IA-%3)	747	24
C(IA-%5)	704	13
C(IA-%7)	508	10
C(IA-%9)	386	7

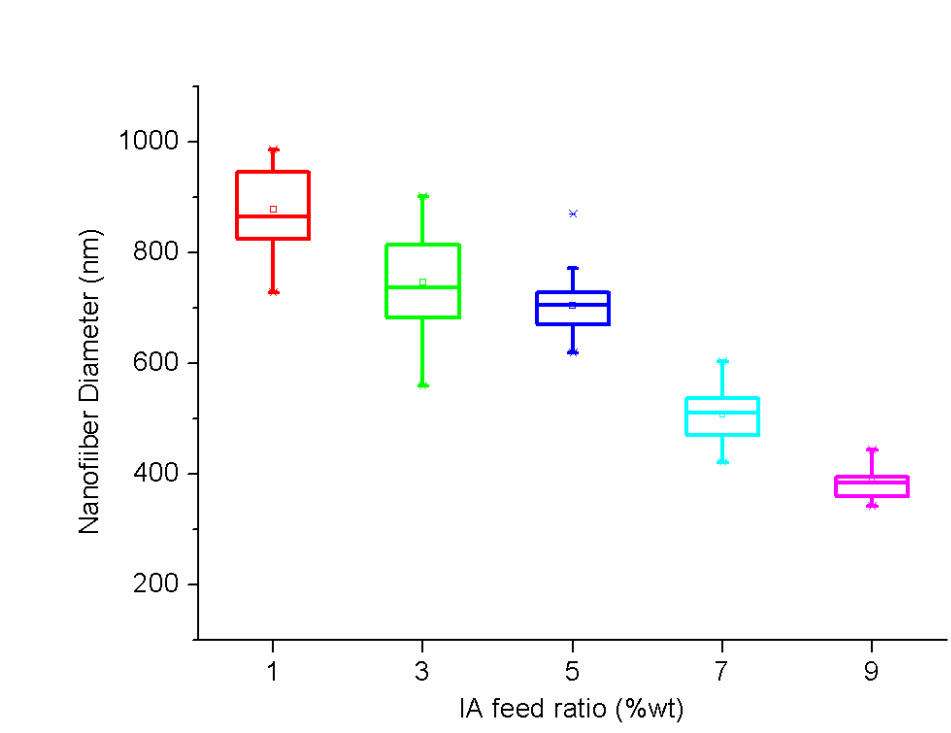


Figure 4.17 : Nanofiber diameter range for AN-IA copolymer.

The nanofibers transport charge across the distance between the charged needle and the grounded collector in electrospinning process. During the electrospinning process the electric current due to ionic conduction of charge in the polymer solution is so small that is considered negligible [44], so the only mechanism of charge transport is

the flow of polymer from the syringe to the collector plate. Thus, an increase in the IA contents of copolymers might reflect an increase in the electrospinning current from the capillary tip to the grounded target when all other variables are held constant.

The intrinsic viscosity of AN-IA copolymers are varied from 2.67 to 0.92 dL/g. Electrospun nanofibers prepared from the solutions having same solid concentration exhibit nanofiber diameters paralel to the decrement in the intrinsic viscosities. The relation betweeen nanofiber diameters and intrinsic viscosities are shown in Figure 17. In our previous study, the effect of vinyl acetate content of AN-VAc copolymers on nanofiber diameters has been investigated. Increasing VAc content of copolymers resulted in decreasing nanofiber diameter which is related to low intrinsic viscosity [65].

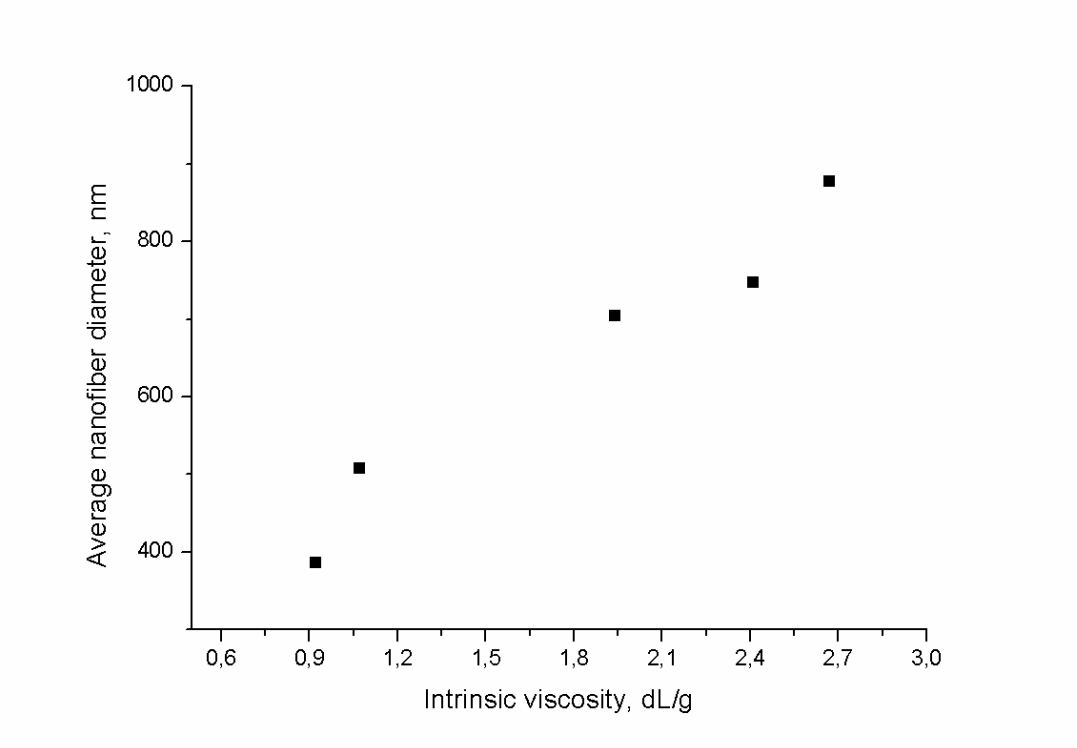


Figure 4.18 : Relation between nanofiber diameter and intrinsic viscosity.

4.3 Characterization of Stabilized Nanofibers

Electrospun nanofibers of AN-IA copolymers were treated with heat at 220 ^{o}C under air atmosphere to investigate physical and chemical changes occuring on the copolymers. The main reason for choosing 220 ^{o}C as the final temperature for stabilization is DSC results showing that the initiation reactions start at about 220 ^{o}C.

The first observation is that the color of nanofiber mats turned to brown-red from white visibly after the heat treatment. The mechanism of coloration is not fully understood, but the different shades of brown-red seen in stabilized nanofiber mats can imply variation in conjugation degree between AN-IA copolymers. The photograph of stabilized nanofiber mats is shown in Figure 4.19.

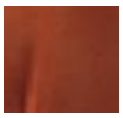
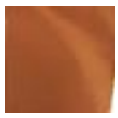
Sample	C(IA-1%)	C(IA-3%)	C(IA-5%)	C(IA-7%)	C(IA-9%)
Color of stabilized nanofiber					

Figure 4.19 : The photograph of stabilized nanofiber mats.

4.3.1 FTIR-ATR Analysis of stabilizied nanofibers

FTIR analysis of stabilized nanofibers of AN-IA copolymers shows that the strong CN stretching band at 2243 cm^{-1} shown in precursor fully disappeared after stabilization process (Figure 4.20). CN band centered at the wavenumber of 1585 cm^{-1} and C-H band in the =CH- structure centered at the wavenumber of 1370 cm^{-1} had significantly high intensities. This indicates the formation of cyclic conjugation leading to a tetrahydropyridine-type ladder structure, as shown in Figure 4.8. Additionally, the emerging band centered at the wavenumber of 805 cm^{-1} indicated that aromatic structures started to form in the stabilized P(AN-co-IA) nanofibers and this band was attributed to the vibration motion of C-H bond in aromatic structures. The observed FTIR bands in stabilized copolymers agree with previous workers approximately[31].

It was reported that the cyclization of PAN macromolecules could be initiated by the functional groups of carboxyl and/or hydroxyl through the reduction of activation energy for the reaction [60]. IA units in the precursor of electrospun nanofibers could effectively initiate the cyclization and further induce the aromatization, as and this was evidenced by the FTIR ATR. The well-stabilized PAN nanofibers possessed regularly oriented ladder structures, which can further facilitate the formation of ordered graphitic structures in carbon nanofiber. [12].

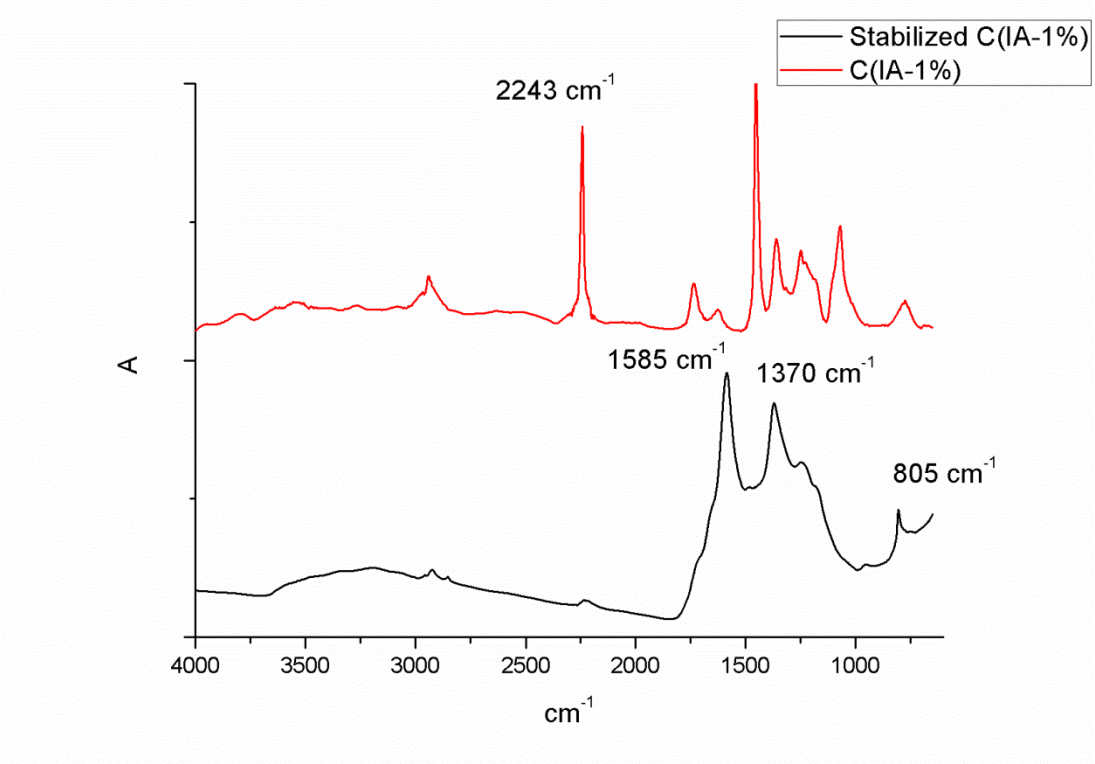


Figure 4.20 : FTIR-ATR spectrum of stabilized C(IA-1%) and its precursor.

4.3.2 Morphology of stabilized nanofibers

SEM images of nanofibers of C(IA-5%) copolymer before and after heat treatment are seen in Figure 4.21. Obviously, diameters of nanofibers decreased as a result of reactions and thermal decomposition during heating process. If it is assumed that nanofibers are cylindrical and volume loss occurs homogeneously, volume loss percentage can be correlated with the difference between squared nanofiber diameters before and after heat treatment.

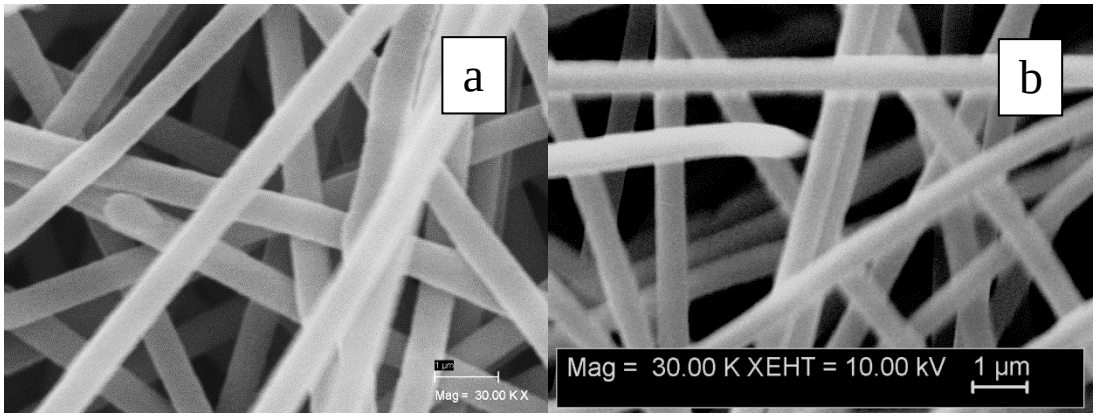


Figure 4.21 : SEM images with 30,000 magnitute; (a) C(IA-5%) precursor, (b) Stabilized C(IA-5%) nanofibers

SEM images of the other stabilized nanofibers were shown in Figure 4.21. The average nanofiber diameter was obtained measuring about 20 nanofiber from the SEM images with x20,000 magnitute. Volume loss (%) calculated and average nanofiber diameter were presented in Table 4.7. Volume loss for the nanofibers produced from the copolymer having the fewest IA content is highest, 48,7. The other stabilized nanofibers had a volume loss between 31.3 and 21.3, it can imply the copolymers produced feeding IA more than 3 % (wt) is more effective in stabilization without volume loss.

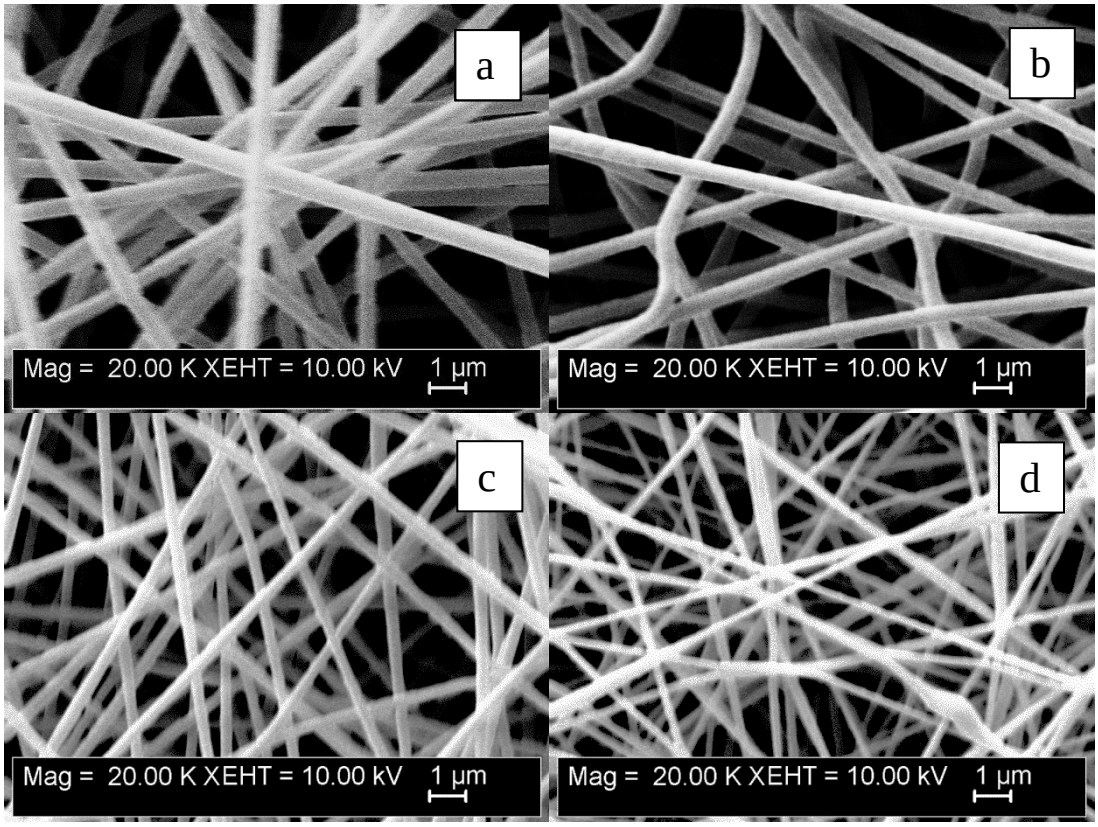


Figure 4.22 : SEM images with x 20,000 magnitute of stabilized nanofibers; (a) C(IA-1%), (b) C(IA-3%), (c) C(IA-7%) and (d) C(IA-9%).

Table 4.7 : The diameters of stabilized nanofibers

Sample	Ave. nanofiber diameter (nm)	Volume loss %
C(IA-%1)	629±13	48.7
C(IA-%3)	619±9	31.3
C(IA-%5)	738±11	21.3
C(IA-%7)	434±7	27.0
C(IA-%9)	341±6	21.9

5. CONCLUSION

AN-IA copolymers were sythesized in aqueous medium changing the monomer feed ratios. Copolymerizations were achieved with high conversion owing to water-phase precipitation polymerization. Increasing IA concentration in copolymerization results in low intrinsic viscosity. IA content of copolymers were determined using FTIR ATR and NMR spectroscopies. The absoption bands at 1628 and 1730 cm-1 due to C=O stretching vibrations in carboxylic acid showed an increase comparing to the characteristic peaks of to C≡N stretching vibration of AN in copolymers which had feeded higher IA. ^{1}H-NMR results also supports AN-IA compositions in copolymers.

IA content confirmed by spectroscopic analysis seriously affects thermal properties which is important for carbon nanofiber production. Based on the DSC studies, IA provides an catalytic effect on stabilization process by decreasing initiation cyclization reaction temperature from 202 to 195 ^{o}C. Oxidative reactions are also decreased because of increasing acid content. TG analysis shows two reactions based on weight loss. Thermal decomposition reactions relasing HCN, NH_3,CO_2, H_2O gases starts at second step. The copolymers having high IA content shows decomposition at lower temperatures. DMA was used to determine Tg values appling force and heat to the casting films. IA comonomer having crystalline structure couldn't shows an improving effect on segmental mobility of macromolecule chains, Tg values increases.

In the next part of study, elecrospinning from the AN-IA copolymer solutions in dimethyl foramide (DMF) was performed successfully. Morphology of nanofibers was monitored using SEM. Bead free nanofibers were produced from AN-IA copolymer solutions under same conditions. Average nanofiber diameter decreases from 878±18 to 376±7 nm according to increasing IA content in copolymers.

The nanofiber mats produced were treated at high temperature under air atmosphere to investigate physical and chemical changes occurring on the copolymers. The color of nanofiber mats turned to different shades of brown-red from white visibly after the

heat treatment. It degree between AN-IA copolymers. Stabilized nanofibers were characterized using FTIR-ATR spectrometer and a new structure was monitored as a result of cyclization reactions. The stabilized nanofibers were also characterized morphologically using SEM. Volume loss occurring after heat treatment calculated based on the nanofiber diameter changes. The nanofibers produced from the copolymer having the smallest IA content showed highest volume loss, 48,7 %. The other stabilized nanofibers had less volume loss, it can imply the copolymers produced feeding IA higher than is more effective in stabilization without volume loss. These results also can be associated with the results obtained from thermal analysis. According to DSC and TGA results the copolymers were synthesized with IA feed higher than 1 % (wt) have to show good stabilization performance.

Consequently, electrospun nanofibers of AN-IA copolymers can be suggested as a carbon nanofiber precursor due to suitability for electrospinning and stabilization process.

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