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Synthesis and Thermal Behavior of Polyacrylonitrile/ Vinylidene Chloride Copolymer

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Abstract: Polyacrylonitrile fiber encompasses a broad range of products based on acrylonitrile (AN) which is readily copolymerized with a wide range of ethylenic unsaturated monomers giving rise to polymers with different characteristics and applications. Such products can be designed for cost-effective, flame and heat resistant solutions for the textile industry, aircraft and automotive markets. In the present work acrylonitrile was copolymerized with vinylidene chloride (VDC) by conventional suspension polymerization process via redox system, with an initial content of 10%/mass of the VDC monomer. The copolymer average molecular weight was obtained by Gel Permeation Chromatography (GPC) and by intrinsic viscosity analysis. To control the polymerization process continuously, qualitative and quantitative analysis of the chloride content in the PAN AN/VDC copolymer structure was accomplished by using X-ray fluorescence and potentiometric titration techniques. A good correlation was found between these two techniques, leading to a straightforward verification of VDC in the polymer structure. The thermal behavior of PAN AN/VDC copolymer was performed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The results showed that VDC monomers exhibited a nearly stoichiometric reaction with acrylonitrile, copolymerizing about 90% of its initial mass. VDC changed significantly the polyacrylonitrile thermal behavior, decreasing the polymer degradation temperature by about 40-50°C.

Keywords: *Acrylonitrile, vinylidene chloride, suspension polymerization, molecular weight, thermal behavior.*

Introduction

Mankind is constantly searching for technological developments based on innovative materials that are stronger, lighter, safer, environmental friendly and sustainable. New generation fibers having superior properties such as high strength, high temperature resistant and flame retardant, are a class of products of remarkable importance in the development of innovative textile product.

Several types of polymers have specific properties for flame resistance, flame retardancy and flameproofing behavior. Varga[1] and Masson[2] mentioned that fibers of low combustibility can be created by developing a base material that can generate a significant amount of charred solid residue, prevent flame spread and simultaneously produce a minimum of inflammable volatiles. In general, polyamide, polyesters and acrylic thermoplastic fibers, which contain highly reactive halogenated atoms in the polymer backbone, such as chloride or bromide, fulfill these requirements[2,3]. Table 1 gives examples of some commercial halogenated monomers which can be copolymerized with acrylonitrile to obtaining flame resistant fibers or flame retardant fibers based on a polyacrylonitrile backbone.

The measurement of relative flammability of polymer materials can be ascertained by determining the Oxygen Index, often referred to as the Limiting Oxygen Index (LOI). In general, LOI values for flammable fibers are <25%, whilst flame retardant fibers are 25-28% and flame resistant fibers have LOI values in excess of 28%[1,4,5]. Flameproof fibers are completely unaffected by heat and have LOI >50%[4,5]. Acrylic fibers, when heated at medium temperatures (200 – 300°C) shrink and burn, followed by a small amount and slowly spreading flame, which in turn decrease the possibility of accidental ignition. On the other hand, modacrylic fibers are preferred as flame retardant fibers[1-3]. Modacrylic fiber is a copolymer of acrylonitrile, vinyl chloride or vinylidene chloride in ratio of 60:40 weight basis, and has LOI about 30%[1].

Acrylic fibers encompass a broad range of diverse applications. The major reason for this is that acrylonitrile (AN) is readily copolymerized with a wide range of ethylenic unsaturated monomers giving rise to polymers having different characteristics and applications[6,7]. Vinylidene chloride (VDC) is one of the options, among other monomers, suitable for copolymerization with

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Table 1. Commercial halogenated monomers suitable for flame retardant materials[2,3].

Monomers	Chemical structure	% mass of halogen
Vinyl chloride (VC)	CH_2=CHCl	56.7% Cl
Vinylidene chloride (VDC)	CH_2=CCl_2	73.1% Cl
Vinyl bromide (VBr)	CH_2=CHBr	74.7% Br

AN, which can give rise to polymer fibers having flame retardant and flame resistant characteristics, similarly to oxidized polyacrylonitrile (PAN) fibers. Particularly, vinylidene chloride monomer has a limited thermal stability, therefore, easily degrades and consequently helps conversion of the PAN polymer backbone in a thermally stabilized material[3-5,8,9].

Besides, acrylic fiber can also be oxidized giving rise to non-flammable flameproofing materials which are cost-effective, flame and heat resistant solutions for the textile, industrial, aircraft and automotive markets[4,5]. Oxidation of acrylic fibers takes place in air at relatively low temperatures (200 to 300°C). The acrylic polymer backbone undergoes, during oxidation, a number of physical and chemical changes due to a variety of exothermic chemical reactions, including cyclization, dehydrogenation, oxidation, crosslinking and fragmentation[10-14]. Therefore, acrylic fiber is then converted thermically to a stable thermoset structure capable of withstanding high temperatures, becoming a flameproof fiber.

The polyacrylonitrile (PAN) polymers are commercially obtained by suspension or aqueous dispersion polymerization process, in the presence de catalysts such as ferric cation and anion persulfate and bisulfite[2,4]. The polymerization occurs when the formation of a complete polymeric molecule starting from an acrylonitrile monomer takes place by addition of free radicals from the same monomer or from different monomers. The polymer chain formed grows due to the high reactivity double bond[4,15]. According to Masson[2] and Morgan[4], the redox system generates free radicals in an aqueous acid medium, pH 2 to 3.5, at relatively low temperature, 40-60°C. The most common redox system consists of an oxidizer (potassium persulfate or potassium chlorate), a reducing agent (sodium bisulfite, sulfur dioxide or sodium metabisulfite) and a catalyst (ferrous iron)[15-17].

The mechanism of polymerization of the AN is quite complex, because a lot of variables must be controlled to meet high polymer yield. In a redox system, for example, the catalyst concentration, temperature and pH range of the reacting system directly affect the polymeric chain growth. In the present work a continuous redox polymerization system was used in the copolymerization reaction of acrylonitrile (AN) with vinylidene chloride (VDC). The resulting PAN AN/VDC copolymer was characterized by Gel Permeation Chromatography (GPC) and intrinsic viscosity. Besides, Energy Dispersive X-ray Fluorescence (ED XRF) and potentiometric titration were used to evaluate the homogeneity of copolymerization and VDC concentration in the final product. The thermal behavior of the copolymer was analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

Experimental

Materials

A PAN copolymer was obtained by suspension polymerization. The composition of the PAN copolymer was 90%/mass of the acrylonitrile (AN) monomer and 10%/mass of vinylidene chloride (VDC), which is designated as PAN AN/VDC in this work. The AN was provided by Radicifibras (SP/Brazil) with purity >99.0% and the VDC was provided by Sigma-Aldrich with 99.9% purity. The aqueous solutions of sodium bisulfite and potassium persulfate were supplied by Radicifibras (SP/Brazil) in the ratio 3:1 concentration of sodium bisulfite and potassium persulfate[2]. The aqueous solutions was used as received. The EDTA was provided by Quimlab (SP/Brazil) with purity > 99.0% and dimethylformamide (DMF) was purchased by BASF with 99.5% purity. The polymerization process was carried out in five cycles of 8 hours each. In order to achieve process homogeneity, samples from the five cycles, named A, B, C, D and E were taken and characterized.

Suspension Polymerization-Redox System

The PAN AN/VDC copolymer was obtained in a polymerization pilot plant, as shown in Figure 1. The aqueous suspension polymerization starts by concurrent dosing of the AN, VDC and demineralized water (1) in a premixing tank (2) using peristaltic pumps. This mixture is transferred by means of a centrifugal pump to a polymerization reactor of 20 L (3). Polymerization is initiated by feeding an aqueous solutions of sodium bisulfite ($NaHSO_3$), which is a reducing and initiator agent for the reaction, potassium persulfate ($KHSO_4$), which is an oxidizer and initiator agent for the reaction, and a redox catalyst composed of a 1 ppm aqueous solutions of Fe^{2+} ion as $FeSO_4$[4]. The reactor was filled with demineralized water and the sodium bisulfite/potassium persulfate solution up to 2/3 of its full volume (4). The polymerization starts at a pH between 2.7 and 3.0, at 60°C constant temperature. The reaction is undertaken in a carefully controlled acid environment, because the bisulfite ion and the Fe^{3+} ion formed by oxidation are soluble[4]. Several works reported the used reaction temperature at 60°C for polyacrylonitrile copolymer polymerization[18-20].

After overflowing the suspension, an aqueous slurry of polymer particles is obtained and mixed with tetrasodium ethylene diamine tetraacetic acid (EDTA) to stop redox radical initiation and stop the polymerization[2]. Unreacted monomers, through a countercurrent flow of steam from the bottom of the column (5), are condensed (6) to reuse in the polymerization process. The aqueous suspension is collected in a reservoir and transferred for later steps (washing, filtration and drying)[2,15-19].

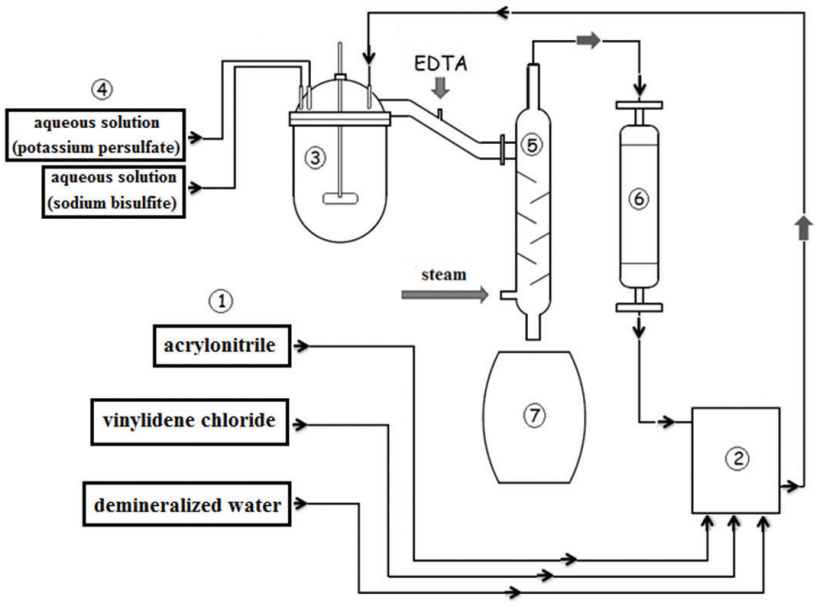

Figure 1. Schematic diagram of aqueous suspension polymerization reactor for polyacrylonitrile.

Gel Permeation Chromatography (GPC)

PAN AV/VDC GPC analysis was performed on a Waters system by an isocratic pump model 600E and speed of the mobile phase (dimethylformamide/lithium bromide) of 1 mL/min at pressure of 2 kPa. The samples were injected by a Rheodyne injector with loop of 100 µL. A MCT/Waters CHM oven, with a pre-column (50 × 7.5 mm) and two PLgel columns (300 × 7.5 mm) in series, having nominal particle size of 10 mm and pores of the MIXED-B type (M_w range from 500 to 10,000,000 g/mol) were used. The columns temperature was maintained at 60°C. A differential refractometer HP (HP Model 1047A) was used to measure differences in refractive index (RI) and Viscotek OmniFace integrator, which converts RI analog signals into digital signals, and interprets and calculates information collected from to RI detector.

The calibration was performed using standard polyethylene oxide (PEO). Seven PEO polymers standards were used for obtaining the calibration curve, as shown in Figure 2.

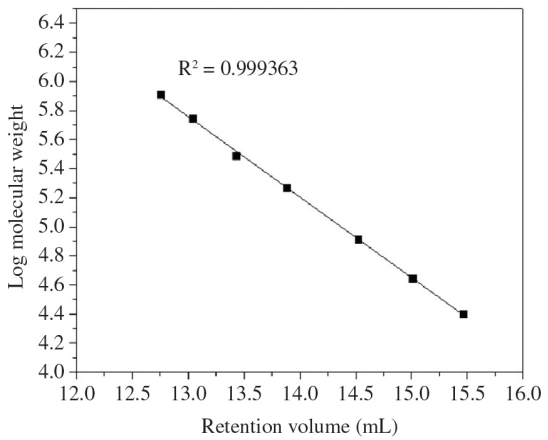

Figure 2. Calibration curve for the seven PEO standards.

Determination of intrinsic viscosity and the viscometric molecular weight

The simplest relative method for measuring molecular weight is viscosity. In the case of acrylic fiber production viscosity related molecular weight is used as a control method for polymer quality. Although widely used, viscosity is not an absolute method to measure molecular weight, since it depends on other properties, such as temperature, polymer morphology, size and shape of the solvent molecules[21-24]. Solution viscosity is basically a measure of the size or extension in space of polymer molecules, and is empirically related to molecular weight for linear polymers[2].

The viscometric molecular weight (M_v) of the PAN AN/VDC polymer was obtained from measurement of intrinsic viscosity using DMF as solvent. Measurements were performed using a torque Brookfield viscometer, with spindle 1, speed of 100 rpm at 20°C. The intrinsic viscosity [η] can be calculated by Kraemer equation (1) and viscometric molecular weight by the Mark-Houwink-Sakurada relation (2)[2,21].

$$\frac{\ln \eta_r}{c} = [\eta] + k[\eta]^2 c \quad (1)$$

where (ln η_r)/c is the inherent viscosity, η_r is the relative viscosity ($\eta_{solution}/\eta_{solvent}$), c is the concentration, k is the Kraemer constant and [η] is the intrinsic viscosity.

$$[\eta] = kM_v^{\alpha} \quad (2)$$

where k and α are constants related to the interaction between polymer/solvent/temperature and M_v is the

viscometric molecular weight. The polymer intrinsic viscosity was determined using results of inherent viscosity as a function of solution concentration of the PAN AN/VDC in DMF.

Determination of chloride content

X-Ray Fluorescence (XRF) analysis was performed in order to verify chloride presence in the PAN AN/VDC copolymer chain. A PANalytical, Epsilon 3-XL was used. The X-ray tube operates with energy of 5.0 kV and current of 2500 μA. The analysis was done in air atmosphere and samples were exposed to X-ray for 60s.

In order to quantify the chlorine presence, titration chemical analysis was used. PAN AN/VDC copolymer samples were mixed with sodium metal in a 1:5 mass proportion. The high ratio of sodium metal was used to guarantee the complete release of chlorine out from the polymer chain. After mixing, the mixture was heated until complete melting and diluted in 100 mL of water. Prior to dilution in water, 25 mL of ethanol was added in the polymer/sodium mixture in order to eliminate the unreacted sodium, avoiding a wanted explosive reaction between water and alkaline metals. Finally, it was placed 10 mL of nitric acid in the dilute solution to titration with silver nitrate ($AgNO_3$)[25]. Thus, the chloride content in the PAN AN/VDC copolymer can be calculated according to Equation 3.

$$\%chloride = \frac{V.c.E}{m}.100 \quad (3)$$

where V is the volume (mL) of silver nitrate used in the titration, c is the silver nitrate concentration (c=0.01 mol/L), E is the chlorine equivalent weight (Eq=0.035453) and m is the polymer sample mass (g) used in the analysis.

Thermal analysis

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were performed to evaluate the thermal behavior of the PAN AN/VDC copolymer.

DSC analysis was performed in a DSC-60 model Shimadzu equipment. Indium and zinc were used as calibration standards. The samples were placed in an aluminum pan with samples in the range of 2.5 and 3.0 mg. The samples were heated from 50 to 450°C, at a heating rate of 10°C/min. All the scans were performed in duplicate in air atmosphere.

TGA analysis was performed in a TGA 7HT model Perkin Elmer equipment. A 100 mg 316 stainless steel was used as calibration standard. The samples were placed in a platinum pan with samples in the range of 12 and 15 mg. The samples were heated from 30 to 900°C, at a heating rate of 10°C/min. All the scans were performed in duplicate, under synthetic air with flow of 20mL/min.

Results and Discussion

Molecular weight by GPC

Gel permeation chromatography was used to measure the molecular weight distributions for the polymers under study. Results for number average molecular weight (M_n), weight average molecular weight (M_w) and polydipersity index (M_w/M_n) of PAN AN/VDC are shown in Table 2. It is observed that molecular weight M_n gives rise to a lower change in relation to the molecular weight M_w, during the five cycles of the polymerization process. Statistically data are obtained from polyacrylonitrile polymers having different molecular chain lengths through GPC analysis[2,21]. The molecular weight M_n values were between 20,000 and 25,000 g/mol, having average of 23,260±1,794 g/mol. Whereas, the molecular weight M_w exhibit a more significant change, ranging from 73,000 to 100,000 g/mol, having average of 90,580±11,065 g/mol.

The polydispersity index does not have a single value for the synthetized polyacrylonitrile polymer, as shown in Table 2, since the molecular weight M_w and the molecular weight M_n exhibits different values. According to Masson[2] the polydispersity of the acrylic polymers is a function of the method of polymerization and typical values for free-radical polymerization (redox system) range from 2 to 3, though some commercial processes can yield higher polydispersity index values. Table 2 shows that a higher polydispersivity was achieved in relation to other works reported in the literature[2,18]. During PAN AN/VDC synthesis a higher concentration of initiators can possibly create an excess of free radicals. As the amount of monomers in the reaction system is the same, a higher proportion of free radicals could result in a dispute for a same amount of monomers can hinder chain propagation. Besides, the control of parameters that influences the polymerization is more difficult for the amount of PAN AN/VDC synthesized in the pilot plant (20 L). Anyway, the polydispersity indexes are still within the addition polymers polydispersity range, which is between 2 and 5[21].

In the case PAN fibers, raw materials (monomers, co-monomers and catalyst) and synthesis conditions (temperature, residence time, pH and catalyst concentration) have a strong impact on polymer molecular weight. In fact, molecular weight defines final mechanical properties after fiber processing, related to spinning and

Table 2. Molecular weight obtained by GPC coupled to the RI detector.

Samples	M_n (g/mol)	M_w (g/mol)	M_w/M_n
Polymer A	20,600	73,000	3.54
Polymer B	22,800	98,400	4.32
Polymer C	23,100	94,500	4.09
Polymer D	25,200	86,900	3.45
Polymer E	24,600	100,100	4.07
Average	23,260±1,794	90,580±11,065	3.89±0.38

draw ratio[18,26]. Qin[26], for instance, reported for a PAN fiber obtained by the synthesis between acrylonitrile, methyl acrylate and itaconic acid, a tensile strength of 348 MPa and 381 MPa, and a Young´s Modulus of ~2.5 GPa, using a stress ratio of 5.0, related to a molecular weight (M_n) of 97,000 and 169,000 , respectively. So, a variation in the M_n of 72,000 led to a difference of only 33 MPa on tensile strength. In this work, the M_n was found to be much lower (~23,000) than the ones reported by Qin[26] and lower mechanical properties are expected from the PAN fiber, a part from any other process condition.

Intrinsic viscosity and viscosity average molecular weight M_v

Measurements of solution viscosity were made by an appropriate spindle system, under controlled torque, besides precise temperature control for a particular polymer/solvent system. These are key issues for adequately measuring viscosity parameters. As it can be seen in Table 3, during viscosity test, the torque efficiency reduces as a decrease in the solution concentration of the polymer/solvent system occurs. A reduction on polymer concentration from 0.03 to 0.005 g/mL, reduced the solution viscosity of the polymers A, B, C, D and E to ~0.60 mPa.s.

The results showed that viscosity of the polymeric solutions are within a narrow range, which is a result of a polymer/solvent interaction mechanism. However, several studies reported that at low polymer concentration in the solution, and thus it is diluted, it makes feasible to extrapolate to infinite dilution[2,21-24]. According to Etxabarren[23], in most cases the concentration dependence is not relevant in applications which the polymer concentration tends to a weight or volume fraction close to unity. In solutions with dilution to infinity, the interactions between the polymer chains disappear and excluded volume effects related to the molecular segments become negligible[24]. Therefore, it is possible to determine the intrinsic viscosity under these considerations.

The relative viscosities ($\eta_{solution}/\eta_{solvent}$) obtained experimentally are then processed in inherent viscosity. Inherent viscosity ($(\ln \eta_r)/c$) was plotted as a function of concentration for polymers A, B, C, D and E and intrinsic viscosity was obtained by extrapolating the solution concentration to infinitive dilution, as shown in Figure 3. The limit which the dilution is infinite is known as intrinsic

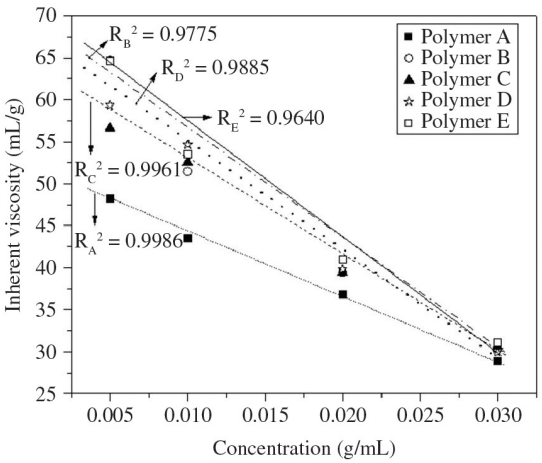

Figure 3. Inherent viscosities as function of the solution concentration for PAN AN/VDC polymers.

Table 3. Viscosities of PAN AN/VDC polymers at various concentrations.

Samples	Concentration (g/mL)	$\eta_{solution}$ (mPa.s)	$\eta_{relative}$	$\eta_{inherent}$ (mL/g)	Torque efficiency (%)
Polymer A	0.030	1.31	2.38	28.923	14.0
	0.020	1.15	2.09	36.880	12.3
	0.010	0.85	1.55	43.532	9.1
	0.005	0.70	1.27	48.232	7.5
Polymer B	0.030	1.36	2.47	30.177	14.5
	0.020	1.21	2.20	39.423	12.9
	0.010	0.92	1.67	51.446	9.8
	0.005	0.76	1.38	64.680	8.1
Polymer C	0.030	1.38	2.51	30.664	14.7
	0.020	1.21	2.20	39.423	12.9
	0.010	0.93	1.69	52.527	9.9
	0.005	0.73	1.33	56.625	7.8
Polymer D	0.030	1.35	2.45	29.931	14.4
	0.020	1.22	2.22	39.834	13.0
	0.010	0.95	1.73	54.654	10.1
	0.005	0.74	1.35	59.346	7.9
Polymer E	0.030	1.40	2.55	31.144	14.9
	0.020	1.25	2.27	41.049	13.3
	0.010	0.94	1.71	53.596	10.0
	0.005	0.76	1.38	64.680	8.1
DMF solvent		0.55			5.9

$\eta_{relative} = \eta_{solution}/\eta_{solvent}$.

viscosity. The intrinsic viscosities will be higher in better solvents because of greater interactions and greater polymer chain extensions (viscosity is proportional to the hydrodynamic volume of the chain in solution)[22].

From values of intrinsic viscosity, k and α constants, the viscosity average molecular weight M_v were obtained by Mark-Houwink-Sakurada relation, shown in Equation 2. The k and α parameters are empirical constants which depends on the temperature and nature of the polymer/solvent interaction[2,21,24]. For example, in monodisperse solutions, which have a single particle size, the constant α equals 1, thus $M_v=M_w$. However, most of the solutions obtained are polydisperse in practice and the constant α can range from 0.5 to 1, and is generally between 0.6 and 0.8[2,24].

The polyacrylonitrile/DMF solvent/temperature system was used in the present work at 20°C. The Mark-Houwink-Sakurada k and α constants relating M_v to the intrinsic viscosity have been determined by a number of researchers[21,24]. Particularly for polyacrylonitrile, these values can be found in various solvents in Masson's work[2]. The Table 4 shows intrinsic viscosity and viscosity molecular weight M_v. The M_v values were between 27,000 and 40,000 g/mol, having average of 35,980±4,977 g/mol. According to literature, the viscosity molecular weight (M_v) have values in between the number molecular weight (M_n) and weight molecular weight (M_w) which are consistent with values obtained in this work, i.e., $M_n \leq M_v \leq M_w$[21].

Chloride content in the polymer structure

The molecular structure of PAN copolymers is composed mostly of carbon, nitrogen and hydrogen. These elements are considered to be light and are not usually analyzed by X-ray fluorescence. However, chlorine can be detected qualitatively and quantitatively by the emission intensity of its electronic transition Kα in 2.62 keV. As it can be seen in Figure 4, the X-ray fluorescence spectrum shows an intense peak having maximum at 2.60 keV, confirming the presence of chlorine in the PAN AN/VDC copolymer.

The amount of VDC monomer that reacts with AN to form PAN AN/VDC copolymer was quantified by titration chemical analysis with $AgNO_3$ and chloride group content can be determined. The results are showed in Table 5. It was found a chloride content in the PAN AN/VDC copolymer of 6.53±0.26%.

The vinylidene chloride ($C_2H_2Cl_2$, 96.94 g/mol), is monomer with two chloride elements in its backbone, and thus the chloride represents 73.1%/mass of the VDC monomer (Table 1). For this reason, the chloride content (6.53±0.26%) obtained by titration corresponds to 8.93±0.36% of VDC in the PAN AN/VDC copolymer backbone. This result shows that a nearly stoichiometric reaction takes place when vinylidene chloride reacts with acrylonitrile in a suspension polymerization system. A 90% AN/10% VDC composition resulted in approximately 9% VDC in the copolymer backbone. Figure 5 shows a theoretical representation of the PAN AN/VDC copolymer obtained by bisulfate/persulfate redox system.

X-ray fluorescence is a faster analysis than titration chemical. Therefore, it can be used to monitor polymerization processes and polymer homogeneity. The chloride content in the PAN AN/VDC copolymer is directly proportional to the fluorescence intensity of the corresponding assignment line to the electronic transition Kα, as can be seen in Figure 6. Thus, the chloride content is directly proportional to fluorescence intensity, and can be determined using polymer samples having known concentrations of chloride in the range to be analyzed.

Thermal behavior of the PAN AN/VDC

PAN polymers start an exothermic thermal behavior at temperatures about 200ºC. This exothermic mainly takes place owing the cyclization reactions of nitrile groups, dehydrogenation, crosslinking and oxidative reactions, when treatment is performed at oxidative atmosphere[10-14].

DSC curves of the PAN AN/VDC copolymer, compared with PAN homopolymer, are shown in

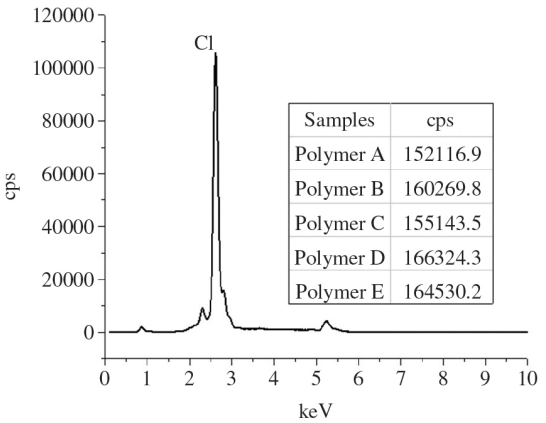

Figure 4. X-ray fluorescence of the PAN AN/VDC polymers. Only a single spectrum is shown due to similarities between them, which respective results are showed at the embedded table.

Table 4. Intrinsic viscosity and M_v for PAN AN/VDC polymers.

Samples	$\eta_{intrinsic}$ (mL/g)	M_v (g/mol)
Polymer A	51.673	27,713
Polymer B	67.867	39,306
Polymer C	62.254	35,189
Polymer D	65.697	37,702
Polymer E	68.790	39,993
Average	-	35,980±4,977

Table 5. Results of PAN AN/VDC titration with $AgNO_3$ (0.01mol/L).

Samples	Chloride content (%)	% of VDC in the copolymer
Polymer A	6.20	8.48
Polymer B	6.51	8.89
Polymer C	6.38	8.72
Polymer D	6.86	9.38
Polymer E	6.72	9.19
Average	6.53±0.26	8.93±0.36

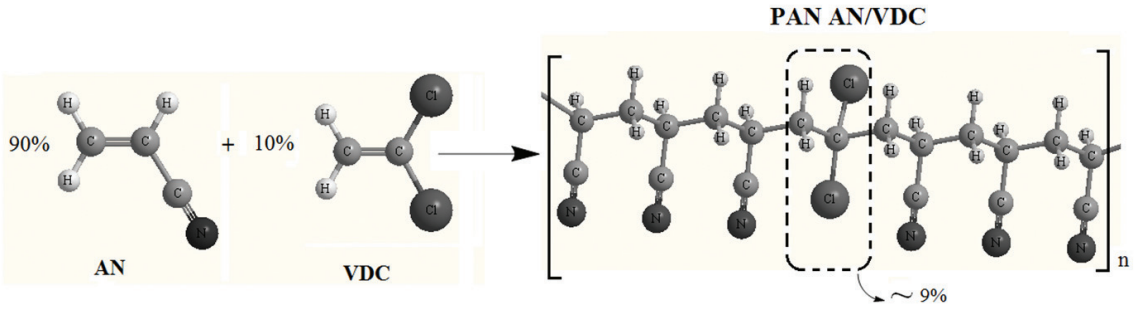

Figure 5. Probably PAN AN/VDC backbone.

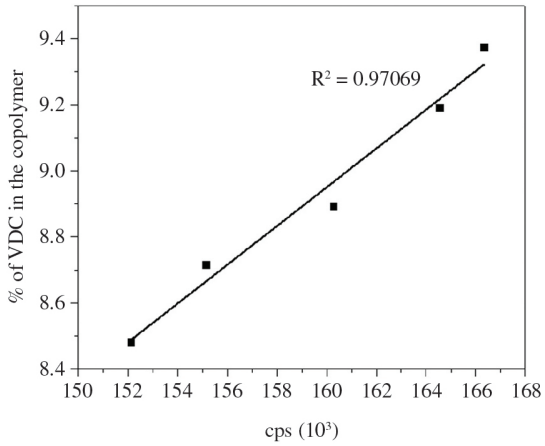

Figure 6. Chloride content as a function of fluorescence intensity.

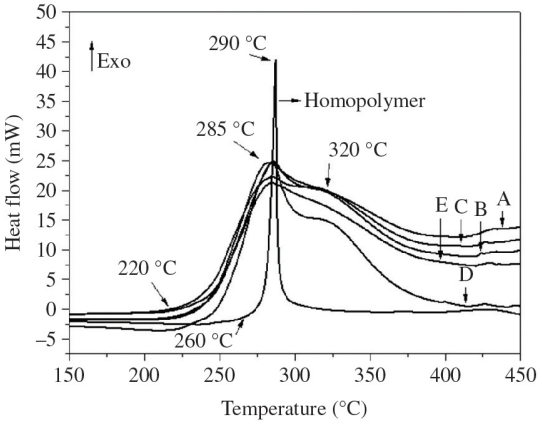

Figure 7. DSC curves of the PAN AN/VDC samples and PAN homopolymer heated at 10°C/min under air atmosphere.

Figure 7. The parameters obtained from the exotherms are the temperature of initiation (T_i), the temperature of termination (T_f) and their difference ($\Delta T = T_f - T_i$), the first peak temperature (T_{p1}), the second peak temperature (T_{p2}), and the released heat (ΔH), which are listed in Table 6.

The results show that approximately ~9% of VDC monomer in the polymer backbone, reduces the initial temperature of exothermic reactions by ~40°C in relation to the PAN homopolymer, increasing PAN polymer instability. It can be observed that all PAN AN/VDC copolymer samples show a thermal behavior rather similar, initiating exothermic reactions at ~220°C with a peak at ~285°C, whereas the PAN homopolymer is initiated at a temperature of ~260°C with a peak of ~290°C.

As shown in Figure 7, only one sharp exothermic peak in PAN homopolymer can be identified. The cyclization reactions are initiated through a free radical mechanism, leading to a large amount of heat to be released in a shorter period of time. This results in the breakage of molecular chains, making the reaction difficult to control in the conversion of PAN polymer into a thermally oxidized polymer[27,28,29]. On the other hand, the exothermic event of the PAN AN/VDC copolymers during heat treatment is broader and proceeds gradually. Besides, it is interesting to note that although the exothermic reactions of the PAN AN/VDC copolymers starts at lower temperatures, the peak temperature of the exothermic reactions are similar (~5°C difference). The cyclization reactions are highly exothermic and for PAN homopolymer and PAN AN/VDC copolymers. Therefore, such reactions for these polymers proceeds at high speed at temperatures in between 280 and 290°C.

According to Grassie[30] all the chloride comonomers degrade at lower temperatures than the acrylonitrile units. Chlorinated polymers, when heated, easily release hydrochloric acid (HCl), which is related to dehydrochlorination reaction[8,31,32]. Further self-catalyst reaction results in a release of other HCl molecules, given rise to a cascade reaction, which quickly degrades the whole polymer[2,21,30].

The Figure 8 shows a schematic illustration of how the dehydrochlorination reactions can take place. At temperatures above 180°C, the first HCl molecule can possibly be eliminated (intramolecular reaction), which results in a chain having double bond formation and can also generate free radicals in the backbone polymer[31,32]. DSC curves also show a weaker exothermic event, around 320°C, which may be related elimination of the second HCl molecule that could be expected to be intermolecular[30]. According to Oh[31] nearly all chloride subjected to decomposition was transformed into HCl. Although there is some evidence that HCl elimination generates free radicals, there is no evidence that these free radicals directly influence the cyclization reactions of nitrile group. Formation of free radicals as well as oxidation reactions, are prone to occur in the formation of intermolecular cross-links.

Table 6. Parameters for DSC curves of PAN homopolymer and PAN AN/VDC.

Samples	T_i (°C)	T_f (°C)	ΔT (°C)	T_{p1} (°C)	T_{p2} (°C)	ΔH (kJ/g)
Homopolymer	260	300	40	290	-	1.28
Polymer A	222	382	160	284	322	3.42
Polymer B	222	394	172	283	322	3.37
Polymer C	223	381	158	286	322	3.01
Polymer D	218	406	188	285	323	3.69
Polymer E	220	392	172	285	-	3.52

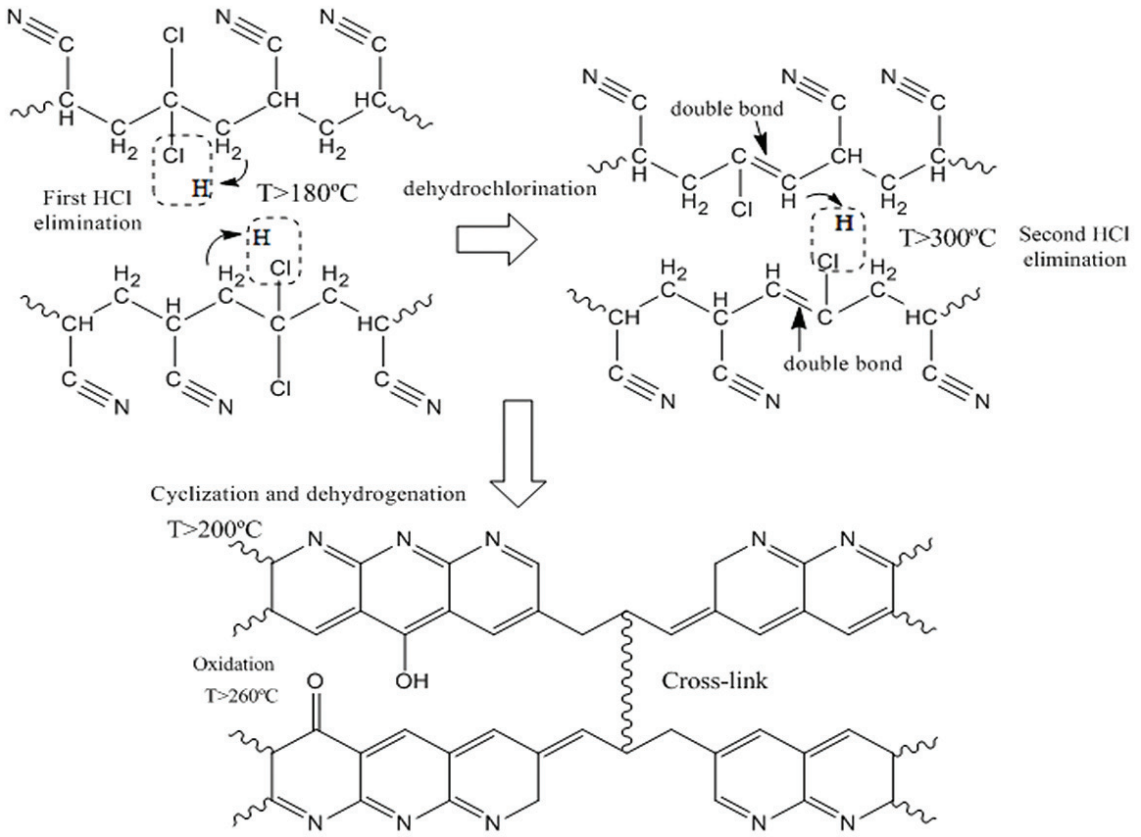

Figure 8. Proposed reaction scheme during thermal degradation of PAN AN/VDC copolymer up to 400°C.

The thermal degradation behavior of the PAN homopolymer and PAN AN/VDC copolymer were monitored by TGA analysis, heated at 10°C/min from ambient temperature to 900°C under synthetic air (20 mL/min). The relevant data from TGA and DTG curves are shown in Table 7. It is observed that thermal decomposition of PAN AN/VDC samples occurs in two steps and there are no significant differences in degradation point between samples. The first step corresponds to a temperature range around 215°C and 400°C, related to a slow rate of weight loss and which is the same temperature range of exothermic reactions DSC curves showed in Figure 7. During this step the PAN AN/VDC copolymers exhibit nearly 15% weight loss. As the cyclization reactions do not cause any weight loss, this event can be attributed not only to HCl release, as well as to H_2O, CO, CO_2, CH_4, NH_3 and HCN, which are released during the stage of the PAN thermal degradation[28,33-35].

PAN homopolymer also showed two well-defined steps of degradation. However, the first step starts the temperature about 40°C higher than PAN AN/VDC samples and show approximately 10% weight loss in a short temperature range, between 260°C and 300°C.

The thermal degradation stage takes place up to ~ 400°C. Beyond the cyclization and dehydrogenation, dehydrochlorination reactions also occur during the oxidation phase, in which the cyclized PAN polymer reacts with oxygen. This changes the PAN chemical composition, but keeps the carbonic rings. The presence of oxygen plays a significant role during the treatment step to transform PAN fibers into oxidized PAN fibers. Oxygen is desirable because it results in the formation of some oxygen containing groups (such as OH and C=O) in the backbone of the ladder PAN polymer[4,10,28,29]. These groups help gas release and, as a consequence, overall weight change during this step is small. However, at

Table 7. Data from TGA/DTG curves of PAN homopolymer and PAN AN/VDC copolymer.

	Step 1			Step 2					
Samples	T_i (°C)	T_{MV1} (°C)	% WL_1	T_{MV2} (°C)	% WL_2	T_{MV3} (°C)	% WL_3	T_f (°C)	% WL_T
Homopolymer	262	285	5.9	306	10.7	665	65.4	820	97.9
Polymer A	219	244	6.7	312	14.3	625	59.7	783	99.2
Polymer B	218	241	7.9	299	13.5	627	65.6	757	98.0
Polymer C	215	238	6.7	304	13.1	688	70.5	830	99.0
Polymer D	215	241	6.8	306	13.2	619	61.2	763	98.9
Polymer E	217	242	6.8	315	14.8	658	68.8	786	99.0

T_i = Initial degradation temperature. T_f = Final degradation temperature. T_{MV} = Temperature at the maximum velocity of the weight loss. % WL= Weight Loss in percentage.

temperatures above 400°C (second step), chain scission of carbonaceous backbone and carbonization of the unstable char occurs, leading to a significant weight loss, especially if stabilization is not complete.

Conclusions

PAN copolymer with vinylidene chloride was obtained by conventional suspension polymerization process via redox system. From five polymerization batches in the pilot plant a polymer having an average molecular weight M_n of 23,000 g/mol and an average molecular weight M_w of 90,000 g/mol were found, related to a viscosity average molecular weight of 36,000 g/mol, resulting in a polidispersivity of 3.9.

The X-ray fluorescence and potentiometric titration techniques were effective in the polymerization process monitoring, allowing to control the polymerized chloride content in the PAN copolymer. The VDC monomer exhibited a nearly stoichiometric reactivity with acrylonitrile monomer revealed by the copolymerization of approximately 90% of the initial mass. A good correlation between XRF and titration was found. This helps the monitoring of incorporation of VDC in the polymer backbone during processing by making it fast and easy by XRF.

The DSC and TGA results showed that no expressive differences were found on thermal stability of the PAN AN/VDC polymers, despite a variation of 1,800 g/mol in the M_n and 11,000 g/mol in M_w (Table 2). However, there is significant difference between the thermal behavior of PAN homopolymer and the PAN/VDC copolymer. Only 9%/mass of VDC monomer in the PAN polymer backbone leads to a reduction of 40°C in the onset of degradation temperature. So, less energy and time are needed during transform the PAN/VDC polymer to a thermally stabilized structure.

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