Thermal Analysis of Acrylonitrile/Acrylic Acid Copolymer Dendrigrafted with Citric Acid

Somaye Akbari, Mohammad Haghighat Kish, Mohammad Karimi, and Ali Akbar Entezami

Abstract—Thermal analysis of acrylonitrile/acrylic acid P(AN/AA) copolymer films containing 5%, 10%, and 20% acrylic acid dendrigrafted with citric acid (CA) is examined using differential scanning calorimetry (DSC) with various heating rates, thermogravimetry (TGA) and derivative thermogravimetric analysis (DTG). Also, the effect of carboxylic acid on thermal stabilization of the P(AN/AA) copolymers, when the carboxylic acid groups are in the bulk and when they are on the surface of the films dendrigrafted with CA, were studied using FTIR analyses.

It is demonstrated that inclusion of carboxylic acid considerably enhances the rate of thermal degradation. The apparent activation energy ($E_a$) for overall cyclization and oxidation reactions is calculated using Kissinger’s method. The results reveal that carboxylic acid, when used as a dendrigraft, influences the cyclization and oxidation process in a different way in comparison with when they are in the bulk. The activation energy of the first generation dendrigrafted P(AN/AA) copolymer was lower than that of the copolymer and the forth dendrigraft generation.

Keywords: acrylonitrile/acrylic acid copolymer, activation energy, dendrigraft, stabilization, thermal analysis

I. INTRODUCTION

Thermal behavior of polyaCRYlonitrile (PAN) and its copolymers has been studied extensively by a number of researchers because of their wide applications in textile industry and in high performance carbon fiber productions [1-4]. Mainly due to the unacceptable properties of PAN homopolymer, using small amounts of acidic co-monomers facilitates its processing and broadens its applications [5-8].

By heating PAN homo and copolymers above 39°C, the materials initially undergo a number of transitions, then at about 150 °C thermal instabilities begin. Using conventional techniques, PAN homo and copolymers do not show a melting point due to their tendency for degradation before melting [9-11]. The lack of melting point is attributed to the structure adopted by the polymer chains and the interactions between the pendant nitrile groups originated from the asymmetry of electrons arrangement in the C≡N group in a moderately strong electrical interaction. For temperatures above 150 °C, PAN and its copolymers undergo a number of chemical and physical changes including shrinkage, cyclization, dehydrogenation, oxidation, cross-link formation, and fragmentation [1-3,12].

PAN and its copolymers in the thermal stabilizations temperature range (=150-300°C) undergo certain reactions resulting in ensuing prominent DSC exothermic curves [13-15]. These reactions lead to formation of an infusible stable ladder structure (cyclization) [16]. In the presence of air, these reactions show much broader exotherms compared to those that occur in the presence of inert atmosphere which exhibit doublet peaks. It is believed that the large primary peak in the air atmosphere is the result of both cyclization and oxidation reactions [17-20] while the single DSC peak observed in nitrogen atmosphere is mainly due to the cyclization reaction. Furthermore, several authors have reported that the inclusion of acidic comonomer facilitates the exothermic reaction during thermal stabilization [7,21]. Consequently, the effects of acrylic, methacrylic, and itaconic acid on the cyclization process have also been examined by some investigators [22-23]. The findings revealed that when the acidic content increase, the exotherm becomes less intense. In addition, the initiation of the exotherm peak starts at a lower temperature due to cyclization through a radical mechanism for PAN homopolymer, while in the presence of acidic co-monomer the cyclization initiates through an ionic mechanism. The findings revealed that when acidic content increase, the exotherm becomes less intense and the lower broader initiation peak due to the cyclization temperature due to cyclization through a radical mechanism for PAN homopolymer, while in the presence of acidic co-monomer the cyclization initiates through an ionic mechanism [7,22].

There are other methods for thermal modification of PAN-based carbon fibers; for instance, polyaCRYlonitrile was modified with ammonium itaconic acid via copolymerization [24]. The influence of surface modification of acrylic copolymer on the thermal stabilization and degradation is concerned in the present work. Among various modifications, the dendrigraft structure is considered as a class of highly branched macromolecules belonging to the dendritic polymer family [25]. Hyperbranched polymers including dendrimers have recently attracted special interest because of their great potential in a number of applications resulting from high degree of chemical functionality, precise molecular sizes, and the presence of nano-scale cavities within their structures [26-28].

In the previous works [29-31], the formation of citric acid (CA) dendrigrafted on the P(AN/AA) samples
containing various amounts of acrylic acid (AA) in the form of powder, film, wet-spun and electrospun fibers having considerably different specific surface area was examined in detail. The present work deals with the effect of carboxylic acid on the thermal degradation of P(AN/AA) copolymer films in the bulk during copolymerization process as well as thermal degradation of dendrigraft modifications. Furthermore, the apparent activation energies for stabilization reactions are determined by the use of differential isoconversional and Kissinger method from DSC data according to the recommendation results of the ICTAC Kinetics Committee [32-33]. They have mentioned that only multiple temperature program methods should be used for computation of reliable kinetic parameters.

II. EXPERIMENTS

A. Materials

Acrylonitrile (AN) and dimethylformamide (DMF) from Fluka were purified by distillation before use. Sodium metabisulfate, acrylic acid (AA), sodium bicarbonate, citric acid (CA) and dicyclohexylcarbodiimide (DCC) were purchased from Merck (Germany) and used as received. Potassium persulfate from Merck was purified by recrystallization in methanol. 1,4-Dioxane and tetrahydrofuran (THF) were purchased from Lab-Scan and used as received.

B. Preparation of P(AN/AA) Copolymer Film

Dendrigraft was synthesized according to the procedure described in the previous work [29]. In brief, the carboxylic acid of P(AN/AA) copolymer films was activated with DCC in a mixture of THF and dioxane (50:50 v/v) at room temperature for 3 h. The mol fraction of DCC was taken in accordance with the mol fraction of AA in P(AN/AA) copolymer films. The film was then removed and washed with pure dioxane and allowed to hang free at room temperature. The activated samples were then reacted with CA in a mixture of THF and dioxane (50:50 v/v) for 3 h at the temperature of 60 ± 1°C in order to produce G1 product. In the succeeding reaction, G1 was used to prepare the next product, as designated by G2. The successive compounds, i.e. G3 and G4, were then prepared. The procedures for the next generations were similar to those for G1. The reactions of copolymerization, preparation of the film and the dendrigraft have been explained in detail in previous published works [29,30]. The composition of P(AN/AA) copolymer film, and the percentage of conversion of dendrigrafted CA on the film, and the abbreviated names of the samples are summarized in Table I. Scheme 1 shows the expected form of the first generation number of CA dendrigrafted on P(AN/AA) films.

C. Characterization

Thermal changes of the samples were probed using a differential scanning calorimetry (DSC), (TA Instrument 2010 differential scanning calorimetry, USA). Samples of 1–2 mg were heated up in the aluminum pans from 30 to 400°C with the heating rate of 5, 10 and 20 °C/min under air atmosphere with the flow rate of 40 ml/min. The triple temperature procedures [32] were used to calculate the kinetics.

To be certain of accuracy [33], heating runs were performed on the samples with four different masses (0.5, 1.0, 5.0 and 10.0 mg). It was found that a sample mass of 1-2 mg makes an error of lower than 1°C in the temperature.
Moreover, to avoid any temperature errors regarding to the heating rate, the temperature was calibrated at every used heating rate.

Thermogravimetric analysis measurements of the samples (4–5 mg) were made using a TGA instrument, (PL-1500 instrument, UK) under air and nitrogen atmospheres from 30 to 600°C at a constant heating rate of 5 °C/min.

Fourier transform infrared (FTIR) spectra of films were recorded between 400 and 4000 cm⁻¹ using a Nicolet 670 FTIR spectrophotometer in transmission mode. Nominal resolution for all spectra was 4 cm⁻¹, and there were 32 scans for each spectrum. All film samples were heated at 150, 170, 200 and 220 °C in a vacuum oven before being characterized via FTIR instrument.

III. RESULTS and Discussion

A. FTIR Results

The changes of FTIR spectra after dendrigraft formation have been studied in detail in the previous published works [29-31]. It was found that the carboxylic acid groups on the films increased by the increase in the generation numbers, which were depicted by the increase in the intensity of the peaks at 1724 cm⁻¹, which was also confirmed by NMR spectroscopy. In the present work the difference between the inclusion of carboxylic acid in the bulk of P(AN/AA) copolymer produced during copolymerization and the presence of carboxylic acid on the P(AN/AA) surface produced by dendrigraft formation, during thermal degradation is considered.

Fig.1 reveals the changes in the FTIR spectra of a P(AN/AA) film containing 10% AA, 10G0, heated at different temperatures. The characteristic bands appear at 2241, 1724 and 2873 cm⁻¹ due to the stretching of –C≡N, -C=O, CH₂, respectively. Fig. 1(a) presents the spectrum of P(AN/AA) film before heating and Figs. 1 (b) to 1(e) presents the spectra of the film heated at 150, 170, 200 and 220 °C, respectively. The band at about 1645 cm⁻¹ which is assigned to the cyclization of P(AN/AA) in DMF solvent, which decreases with increase in the generation number in dendrigraft formation [31]. In addition to the decrease in the intramolecular hydrogen bonding, as the heat-treatment temperature increased, the hydrogen bonding intensity decreased.

![FTIR spectra of the P(AN/AA) copolymer films containing 10%AA (G0) heated at different temperatures for 10 min: (a)original (not heated), (b) 150 °C, (c) 170 °C, (d) 200 °C, and (e) 220 °C.](image)

**G0**

![Scheme 2. Proposed structure of P(AN/AA) copolymer during thermal stabilization](image)

Similar to G0, the ladder-frame structure of the stabilized dendrigrafted sample take place above 170°C. The proof of this event is that no new bands at 1613 cm⁻¹ can be found in the P(AN/AA) copolymer films dendrigrafted with CA first generation (10G1) and those heated at different temperatures, Fig. 2(a–c), and also for the fourth generation number (10G4) heated at different
temperatures, Fig. 3(a-c). In the meantime, the weak shoulder at 1801 cm\(^{-1}\) above 170ºC possibly indicates the formation of anhydride rings; it is shown in Scheme 3. By increasing generation numbers, the 1613 cm\(^{-1}\) band continues to grow which means cyclization and oxidation have been promoted by the inclusion of carboxylic acid groups on the surface. However, it is hard to establish the exact mechanism of stabilization only with the present FTIR spectra.

**Fig. 2.** FTIR spectra of the P(AN/AA) copolymer films containing 10% AA dendrigrafted with CA at first generation number (G1) heated at different temperatures for 10 min: (a) original (not heated), (b) 150 ºC, (c) 170 ºC, (d) 200 ºC, and (e) 220 ºC.

**Fig. 3.** FTIR spectra of the P(AN/AA) copolymer films containing 10% AA dendrigrafted with CA at forth generation number (G4) heated at different temperatures for 10 min: (a) original (not heated), (b) 150 ºC, (c) 170 ºC, (d) 200 ºC, and (e) 220 ºC.

**B. Differential Scanning Calorimetry (DSC)**

Fig. 4 shows the DSC curves of the P(AN/AA) copolymer films containing 10% AA (10G0) heated at different temperatures for 10 min: (a) original (not heated), (b) 100 ºC, (c) 170 ºC, (d) 200 ºC, and (e) 220 ºC. Samples were similar to the sample with 10% AA content (10G0), which are not shown here. DSC measurements during the stabilization of P(AN/AA) show a distinct doublet exotherm; the one at lower temperature mainly attributed to the exothermic cyclization and the other attributed to the oxidative reactions [5,7].

As shown in Fig. 4, with increase in heating rate, the exotherms shift to a higher temperature, and the exothermic peaks become more and more strong, which is similar to the previous results [5]. By increasing the heating rate, the doublet character of the DSC exotherms corresponding to the sequence of cyclization and oxidation, turns into one peak. It seems that cyclization and oxidation reactions are now occurring simultaneously.

**Scheme 3.** Proposed structure of P(AN/AA) copolymer dendrigrafted with CA during thermal stabilization.

**Fig. 4.** DSC curves of P(AN/AA) copolymer films containing 10% AA (G0) and dendrigrafted with CA at first generation (G1), heated at different heating rates: (a) 5 ºC/min (R5), (b) 10 ºC/min (R10), (c) 20 ºC/min (R20).
are designated by initiation temperature ($T_i$), maximum peak temperature ($T_{max}$), final temperature ($T_f$), and the total heat liberated ($\Delta H$). Tables II and III show the characteristic parameters extracted from DSC curves at different heating rates for P(AN/AA) copolymers containing different amount of AA and dendrigrafted film. Accordingly, as the acid content of the copolymer increases the released heat decreases. Moreover, the related curves become broader with lower initiation temperature ($T_i$), and final peak temperature ($T_f$) as well as smaller $\Delta H$, due to the different initiation mechanism and relatively much slower propagation rate of the cyclization reaction, which are in agreement with the literature [5,7,22]. For acrylonitrile-carboxylic acid copolymer, the initiation of cyclization reaction follows an ionic mechanism in comparison with radical mechanism suggested for acrylonitrile homopolymer [5].

![Fig. 5. DSC curves of P(AN/AA) copolymer films containing 5, 10, 20% AA, heated at the rate of 10°C/min.](image)

In the previous publication [33] for the same polymer using NMR techniques, we have shown that by increasing the acidic comonomer, the isotactity and the blocky character of the copolymers increase. It is also suggested that the rate of cyclization depends on the sequence distribution of the comonomer in the acrylonitrile copolymers [22]. The lower $T_i$ and $\Delta H$ values for higher AA content that we observed in the present work may be related to the increase in isotacticy, which tends to shorten the induction period in the thermal treatment of P(AN/AA).

The DSC curves of P(AN/AA) copolymer films containing 10%AA dendrigrafted with CA (10G1, 10G4), at a heating rate of 10 °C/min are illustrated in Fig. 6. The characteristic parameters obtained from DSC curves at different heating rates are listed in Table III. The results revealed that by increasing the generation number, the exotherm curves of samples become a little broader with lower initiation ($T_i$) and final peak ($T_f$) temperatures, while $\Delta H$ values increase considerably.

![Fig. 6. DSC curves of the P(AN/AA) copolymer films containing 10% AA content (G0) dendrigrafted with CA at first (G1) and forth (G4) generation number at a 10 °C/min heating rate.](image)

According to the literature [5,17], acidic co-monomers promotes the thermo-oxidative stabilization. It seems that the role of carboxylic acid produced from acrylic acid in the bulk during copolymerization process differs from the

### Table II

**PARAMETERS FROM DSC EXOTHERMS OF P(AN/AA) COPOLYMER CONTAINING 5, 10 AND 20 % AA AT DIFFERENT HEATING RATES**

<table>
<thead>
<tr>
<th>AA%</th>
<th>Rate 5 (°C/min)</th>
<th>Rate 10 (°C/min)</th>
<th>Rate 20 (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$ (°C) $T_f$ (°C) $\Delta H$ (J/g)</td>
<td>$T_i$ (°C) $T_f$ (°C) $\Delta H$ (J/g)</td>
<td>$T_i$ (°C) $T_f$ (°C) $\Delta H$ (J/g)</td>
</tr>
<tr>
<td>5</td>
<td>200 300</td>
<td>270 284</td>
<td>211 209</td>
</tr>
<tr>
<td>10</td>
<td>191 302</td>
<td>267 307</td>
<td>202 213</td>
</tr>
<tr>
<td>20</td>
<td>183 306</td>
<td>260 295</td>
<td>194 211</td>
</tr>
</tbody>
</table>

### Table III

**PARAMETERS FROM DSC CURVES OF P(AN/AA) COPOLYMER DENDRIGRAFTED FILM CONTAINING 10% AA AT DIFFERENT HEATING RATES**

<table>
<thead>
<tr>
<th>#Generation</th>
<th>Rate 5 (°C/min)</th>
<th>Rate 10 (°C/min)</th>
<th>Rate 20 (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_i$ (°C) $T_f$ (°C) $\Delta H$ (J/g)</td>
<td>$T_i$ (°C) $T_f$ (°C) $\Delta H$ (J/g)</td>
<td>$T_i$ (°C) $T_f$ (°C) $\Delta H$ (J/g)</td>
</tr>
<tr>
<td>G1</td>
<td>191 302</td>
<td>267 307</td>
<td>202 213</td>
</tr>
<tr>
<td>G4</td>
<td>182 305</td>
<td>259 506</td>
<td>191 319</td>
</tr>
</tbody>
</table>

**Fig. 5. DSC curves of P(AN/AA) copolymer films containing 5, 10, 20% AA, heated at the rate of 10°C/min.**

**Fig. 6. DSC curves of the P(AN/AA) copolymer films containing 10% AA content (G0) dendrigrafted with CA at first (G1) and forth (G4) generation number at a 10 °C/min heating rate.**
role of carboxylic acid generated in the dendrigraft formation. Having carboxylic acid in the bulk reduces the \( \Delta H \) value due to the change in the mechanism of cyclization from radical mechanism to ionic catalyzed one [22]. However, the presence of carboxylic acid caused by the dendrigraft formation increases the \( \Delta H \) value because of providing more opportunities for the interaction between carboxylic groups and nitrile groups.

It was demonstrated that the increase in \( \Delta H \) is associated with the increase in the number of opportunities for the reactions [35]. Accordingly, the presence of more carboxylic acid groups on the surface of the present samples by dendrigraft formation increases the \( \Delta H \) values.

C. Activation Energy

Differential isoconversional method was used to determine the activation energy of the reactions. Isoconversional principle states that the reaction at constant extent of conversion (\( \alpha \)) is only a function of temperature, \( T \). For linear non-isothermal procedures, the differential isoconversional method based on (1), [32] is used.

\[
\ln \beta \left[ \frac{d\alpha}{dT} \right]_{E_a} = \ln f(\alpha) A_\alpha - \frac{E_a}{RT_{i} \alpha},
\]

where \( E_a \) is the activation energy at each \( \alpha \), \( R \) is the universal gas constant, \( \ln f(\alpha) A_\alpha \) is the intercept, \( \beta \) is the heating rate and the subscript \( i \) denote the individual heating rate. To calculate the activation energy (\( E_a \)) of the samples, first the values of \( \alpha \) are calculated from (2).

\[
\alpha = \frac{\Delta H_f}{\Delta H}
\]

where \( \Delta H_f \) and \( \Delta H \) are the enthalpy from zero to \( T \) and the total enthalpy extracted from DSC exotherms, respectively. Fig. 7 shows the values of \( \alpha \) against the temperature for the sample 10G0 heated with different rates of 5, 10, and 20\(^\circ\)C /min. The trends of the extent of conversion (\( \alpha \)) against the temperature for other samples are found to be similar to that for the 10G0, that are not shown here.

The value of \( E_a \) is obtained from (1). At each value of \( \alpha \), the value of \( E_a \), is determined from the slope of the plot of \( \ln (d\alpha/dT)_{E_a} \) against \( 1/T_{\alpha} \).

Fig. 8 reveals the activation energy against the extent of conversion for P(AN/AA) copolymer films containing 5, 10 and 20 % AA. Of particular interest is the high extent of conversion for \( \alpha > 0.4 \), which is assigned to the cyclization and oxidation reactions. The value of \( E_a \) increases sharply for the samples with higher AA content presumably due to the ionic mechanism in thermal stabilization in the presence of acidic co-monomer, which is in agreement with the results of the previous published work [34].

By increasing acidic comonomer, the isotacticity of the copolymers increase with a more randomness in the distribution of the co-monomers. More isotactic unit as well as blocky character may facilitate cyclization and oxidation reaction [34]. As a result, more AA content reduces \( E_a \) value of cyclization and oxidation reactions in the thermal treatment. Also, it is evident that the activation energy has been reduced by incorporation of itaconic acid as commoner into PAN [5] which consists of two carboxylic acid groups comparing to one carboxylic acid group in acrylic and methacrylic acid.

The \( E_a \) value against \( \alpha \) for P(AN/AA) copolymer films containing 10% AA dendrigrafted with CA at first (10G1) and fourth (10G4) generation numbers are illustrated in Fig. 9. Since the percentage conversion of the reaction of dendrigrafted formation was low (according to Table 1), the activation energies are close to each other. The \( E_a \) value of 10G1 is lower than the other samples (10G0, 10G4) at the high extent of conversion for \( \alpha > 0.4 \). The lower \( E_a \) value of 10G1 may be related to its "dense shell" dendritic
structure. Dense shell is formed in the first generation which has the lowest density. These are according to the de Gennse dense packed theory completely explained in the previous work [31].

Fig. 9. Activation energy vs. extent of conversion for P(AN/AA) copolymer films containing 10% AA (10G0) dendrigrafted with CA at first (10G1) and forth (10G4) generation numbers.

The activation energies of PAN copolymers for degradation reactions from various literatures are summarized in Table IV. Comparison of the activation energies ($E_a$) indicate that different methods and various temperatures lead to different values. The values of $E_a$ obtained from the experiments in this work using the differential isoconversional method is in the range of the other calculated activation energies.

The calculated activation energies indicate that the energy barrier of stabilization reactions of the first generation (10G1) dendrigrafted P(AN/AA) copolymer decreases while that of the 4th generation (10G4) increases in comparison with the copolymer before dendrigraft formation (10G0).

Often Kissinger method [36,32,17] has been applied to determine the activation energies. In this method it is assumed that the reaction rate is maximum. However, it can be used to quantify $E_a$ without any prior knowledge of reaction mechanism, by just having a series of DSC curves at different heating rates [5,22,32]. Kissinger method produces a single value of the activation energy for any process regardless of its actual kinetic complexity, while the differential isoconversional method produces a range of $E_a$ and $A$ values [32].

Equation (3) is used to calculate the activation energies from Kissinger method, from the slope of the plot of

$$\ln \left( \frac{\beta}{T_{m,j}^2} \right) \text{ against } \frac{1}{T_{m,j}}$$

where subscript $m$ denote the values related to the maximum rate and $f'(\alpha_m) = \frac{d\alpha}{dt}$. Other symbols have the same meaning as in (1).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Method</th>
<th>reaction</th>
<th>$E_a$ (KJ/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>DSC b</td>
<td>Stabilization</td>
<td>123.7</td>
<td>5</td>
</tr>
<tr>
<td>AN/IA (98.5/1.5)</td>
<td>DSC b</td>
<td>Cyclization</td>
<td>103.7</td>
<td>5</td>
</tr>
<tr>
<td>AN/IA (98.5/1.5)</td>
<td>Oxidation</td>
<td>117.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN/MA (95/5)</td>
<td>Shrinkage</td>
<td>oxidation and dehydrogenation</td>
<td>265.9</td>
<td>14</td>
</tr>
<tr>
<td>PAN/MA/IA (93/6/1)</td>
<td>DSC (Kissinger method)</td>
<td>Cyclization</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>dehydrogenation</td>
<td>108</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxidation</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>PAN/AA (96.9/3.1)</td>
<td>DSC (Kissinger method)</td>
<td>Cyclization</td>
<td>184.8</td>
<td>22</td>
</tr>
<tr>
<td>PAN/MAA (97.4/2.6)</td>
<td>Cyclization</td>
<td>123.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAN/IA (97.8/2.2)</td>
<td>109.1</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Commercial PAN with Small amount of MA/IA</td>
<td>DSC b</td>
<td>Cyclization</td>
<td>188.2</td>
<td>17</td>
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<tr>
<td></td>
<td>TMA b</td>
<td>182.7</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>TG b</td>
<td>309.3</td>
<td></td>
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<tr>
<td>PAN</td>
<td>DTA</td>
<td>Cyclization under $N_2$</td>
<td>126.42</td>
<td>19</td>
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<tr>
<td>PAN/MA (95/5)</td>
<td>Cyclization under air</td>
<td>141.96</td>
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<tr>
<td></td>
<td>Cyclization under $N_2$</td>
<td>107.1</td>
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<td>Cyclization under air</td>
<td>111.72</td>
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<tr>
<td>PAN</td>
<td>DSC</td>
<td>Cyclization at 175-200° C</td>
<td>153.2</td>
<td>23</td>
</tr>
<tr>
<td>PAN/IA (98.5/1.5)</td>
<td>110.3</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*All $E_a$ value have changed to KJ/mol

b Kissinger and Ozawa method gives nearly identical values for each $E_a$ and $A$. As a result, in this Table only the result of Kissinger method is shown.
Activation energies were calculated by Kissinger method. Table V indicates that the energy barrier for the reactions of 10G1 is less than that of 10G4 and that of the copolymer before dendrigraft formation (10G0), which is similar to that calculated by isoconversional method.

TABLE V

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$(KJ/mol)</th>
<th>$A$(S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5G0</td>
<td>146.97</td>
<td>4.02×10$^{16}$</td>
</tr>
</tbody>
</table>
| 10G0     | 110.60        | 1.29×10$^{7}$
| 20G0     | 110.72        | 1.72×10$^{7}$
| 10G1     | 90.43         | 1.42×10$^{7}$
| 10G4     | 100.55        | 1.50×10$^{6}$

D. Thermogravimetric (TGA) and Derivative Thermogravimetric (DTG) Analysis

The TGA and DTG curves of the P(AN/AA) films containing 10%AA, 10G0, under nitrogen as a purge gas are shown in Fig. 10 and the relevant parameters are summarized in Table VI. The TGA curves show the change of weight, while the DTA curves show the rate of different reactions taking place. The nature of these reactions has been documented in the literature [17-22]. The first step, up to 250°C, in which losing weight is not substantial, is followed by a second step (from 250 to 300°C) in which losing weight occurs rapidly. In the last step, above 350°C, the weight loss is quite steady [17]. The starting and ending temperature of different steps, depicted from TGA curves depends on the samples, the testing environment, the purity of purging nitrogen, and the heating rate.

The TGA curves of these dendrigrafted copolymers under nitrogen purge show slightly different behavior from that of 10G0. Furthermore, at 600°C the total weight loss of the samples in air is less than that in the nitrogen purge (Table VI), this is because in the air atmosphere oxidation reactions take place, which improves the weight retention. This is in agreement with the explanation [17] that the pyrolysis in the air results in a lesser weight loss than that in the nitrogen atmosphere. By other researchers [19], however, it has been shown that the activation energy for the cyclization reaction under N2 is lower than that in the air atmosphere. Such controversial contradictions in results reconfirm the complexity of the nature of these reactions.

The TGA curves of the 10G0 and 10G4 show a steady region up to the second step in which the weight loss of both samples indicates a slightly different behavior. In the third step, the weight loss is fast, particularly for 10G4. The total weight loss at 600°C is 39.65% for 10G0 and 81.08% for 10G4, respectively. The greater and the faster rate of weight lose is due to rapid cyclization and decomposition of carboxylic groups on the surface. Furthermore, in previous sections it was shown that the presence of carboxylic acid in dendrigrafted structure leads to a higher $\Delta H$ value.
IV. CONCLUSION

Thermal behavior of (PAN/AA) copolymer films containing 5, 10, and 20 % AA and also CA dendrigrafted films containing 10 % AA at first and fourth generation numbers were studied using FTIR, DSC, TGA and DTG analyses. Analyses of the FTIR spectra of the films heated up to 220°C reveals that the stabilization reactions occur above 170°C, where the dendrigrafted samples are stabilized in a ladder frame structure. During the degradation of the copolymer films in DSC, the oxidation reactions become less intense by increasing of AA content in the copolymer. The carboxylic acid groups in the bulk resulting from copolymerization process behave differently from the carboxylic acid groups generated during dendrigraft formation. The carboxylic acid in the bulk reduces the ΔH value, while the presence of carboxylic acid in the dendrigraft formation increases the value of ΔH. The apparent activation energies were determined with the help of differential isosconvensional and Kissinger method. Since cyclization and oxidation process is a requisite process to produce stable ladder like molecular structure in the production of carbon fibers from PAN, the presence of carboxylic acid groups on the film can improve the cyclization and oxidation and even it modifies the thermal properties of the manufactured fibers. Modification to the first generation dendrigraft reduces thermal degradation reaction energy barriers.

Acknowledgements

We would like to thank Prof. S.H. Bahrami for many valuable discussions and collaborations. The authors are also grateful to Mrs. Mahmoodi, Dr. M. Radjabian and Mr. N. Rabiei from Analytical Laboratory, Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran. We acknowledge the partial financial support of the Center of Excellence for Modern Textile (CENMIT).

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