# Indicators for Evaluation of Progress in Thermal Stabilization Reactions of Polyacrylonitrile Fibers

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**ABSTRACT:** Using different indices calculated from Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC) spectra, progress in stabilization reactions of three different commercial grade polyacrylonitrile (PAN) fibers is calculated. From each analysis technique quantitative indices are computed which could assess in some particular reactions. Combination of these indices gives further information about the progress of stabilization reactions which cannot be concluded from single indices. The results show that different indices are not fully consistent with each other, depending on the analysis technique and the changes they assess. The advantages and disadvantages of each index are investigated and practical indices are identified which can be used to design the optimum stabilization process. In addition, by combination of some indices it is possible to separate the temperature ranges in which reactions occur in amorphous or crystalline regions. This approach can be used to design appropriate stretching process during stabilization. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40343.

## INTRODUCTION

Thermal stabilization of polyacrylonitrile (PAN) fibers is an important step in the production of precursors for advanced fibers such as carbon fibers, smart PAN gel fibers, etc. The quality of substrate formed during stabilization process has great impact on properties of the final product.[1–10] During stabilization different chemical reactions including cyclization, dehydrogenation, and oxidation occur almost simultaneously. Kinetics and mechanism of these reactions depend strongly on the polymer composition (comonomer type and content) and temperature.[9–17] These reactions convert the C≡N groups in linear structure of PAN fibers to C=N groups in cyclized structure of the stabilized fibers. Therefore, the stability is attributed to the conversion of the linear polymer chains to a ladder semicyclized structure.[4,6,12]

Accordingly, degree of conversion plays an important role in the quality of the final products. For instance, a too high degree of cyclization may result in poor mechanical properties of carbon fibers[5,19] or poor pH-response of gel-fibers.[8] Therefore, quantitative evaluation of the stabilization reactions has raised great

interest among scientists. Padney and Kumar[20] realized that there is a linear correlation between infra-red (IR) absorbance ratios and density of stabilized fibers. Mathur et al.[21] used density to judge the extent of stabilization progress. Yu et al.[19] calculated a stabilization index (SI) based on intensity change of XRD peaks around $2\theta = 17°$. Tsai[22] calculated cyclization index (CI) using heat release during stabilization as measured by DSC. An index for evaluation of extent of reactions was proposed by Ouyang et al.[23] using FTIR bands related to C≡N groups in linear structure and C=C, C=N, and N—H groups in cyclized structure of fibers. Each method has advantages and disadvantages and may not be compatible with other methods in all terms.

Another important factor in optimizing the stabilization process is different responses of polymer chains to heat and stretch in amorphous and crystalline regions. As a result, the formed substrate in these regions is different.[23,24] The stabilization reactions take place more readily in the amorphous region due to presence of comonomers and higher diffusion rate of oxygen compared with dense pure crystalline regions.[23,24] As stabilization temperature increases, reactions penetrate to the boundary of

**Table I.** Characteristics of PAN Fibers

| Fibers | Linear density (dtex) | Density (g/cm³) | $[\eta]$ (dL/g) | $M_v$ (g/mol) | Sonic modulus (cN/tex) |
|---|---|---|---|---|---|
| P(AN/IA/MA) | 1.17 | 1.185 | 2.216 | 202,000 | 1592 |
| P(AN/IA) | 1.3 | 1.187 | 2.174 | 197,000 | 1706 |
| P(AN/VAc) | 1.15 | 1.182 | 1.56 | 125,000 | 1176 |

crystalline regions and at higher temperatures they occur in crystalline phase as well.[23–25] Precise separation of temperature range in which reactions occur in crystalline or amorphous phases is difficult. Response of amorphous and crystalline chains to stretch is also different.[23,26] It is essential to design the stretching process such that high chain orientation is obtained without hindering the cyclization reactions.[24,27–31] Thus determination of sequence and temperature range in which reactions occur in each region is a key parameter to obtain high performance fibers.

Although there have been individual studies on different stabilization indices, yet there has not been a comprehensive evaluation and comparison between them in terms of efficiency and accuracy. Accordingly, we used ideas and indices proposed by other researchers using FTIR, XRD, and DSC analyses. Studying together and coupling the results based on the logic of each method, we tried to determine the best parameter for evaluation and estimation of progress in stabilization reactions. Meanwhile, we realized that combination of indices can help to separate temperature range in which reactions occur in amorphous or crystalline phases of chains. Since stretching has different effects when reactions occur in crystalline or amorphous regions of polymer, this approach can be used to design the proper stretching process during industrial stabilization processes.

## EXPERIMENTAL

### Materials

Three different commercial grade PAN fibers were supplied by Courtaulds (P(AN/IA/MA)), Jilin Chemical Fiber Group (P(AN/IA)) and Mitsubishi Rayon (P(AN/VAc)). IA, MA, and VAc stand for itaconic acid, methyl acrylate, and vinyl acetate, respectively. Properties indices of these fibers are listed in Table I. $M_v$ and $[\eta]$ are viscosity average molecular weight and intrinsic viscosity of the copolymers, respectively.

### Methods

Thermal stabilization was conducted in a furnace at air atmosphere with controlled air flow. A load cell applied 0.02 cN/tex tension to fiber tow during stabilization process. Temperature was increased with a rate of 2°C/min. Stabilization temperature varied from 100 to 275°C. According to literature data stabilization reactions usually start above 180°C.[8,9,29] Since we investigate commercial materials, we decided to study stabilization reactions already at 100°C in order to check for any unknown effects. However, The FTIR, XRD, and DSC graphs of P(AN/VAc) fibers did not show any stabilization changes below 200°C. Therefore, their characterization data for temperatures below 200°C are not reported here.

### Characterization

FTIR spectra of virgin and stabilized PAN fibers were recorded using a Nicolet Magna IR560F spectrometer in the range of 400–4000 cm$^{-1}$. Totally, 0.5 mg of finely ground samples was loaded on 200 mg potassium bromide (KBr) disks. To calibrate the FTIR, polystyrene calibration film was placed in the sample holder of the instrument and the spectrum of polystyrene was scanned. The peaks in the spectrum of the calibration film were compared with the peaks of polystyrene. To evaluate extent of reactions (EOR) during stabilization process, EOR$_1$ and EOR$_2$ were calculated using following equations[14,17,32–35] based on calculation of area under characteristic bands.[36–38]

$$EOR_1 = A_{1595}/A_{2243} \qquad (1)$$

$$EOR_2 = [A_{1595}/(A_{2243} + A_{1595})] \qquad (2)$$

Where, $A_{1595}$ and $A_{2243}$ are the area under 1595 cm$^{-1}$ and 2243 cm$^{-1}$ band, respectively.

X-Ray diffraction analysis was performed on a Philips, PW1840/01 diffractometer. Ni filtered CuK$\alpha$ radiation ($\lambda = 0.15$ nm) in 40 kV and 30 A was utilized. Step interval was 0.08° and scanning rate was 6°/min. XRD calibration was performed using silicon (Si) and the obtained pattern was compared with standard pattern of Si. Aromatization index (AI) was calculated from following equation to evaluate progress in cyclization reactions.[17,18,22,24,39–42]

$$AI = \frac{I_{25}}{(I_{17} + I_{25})} \times 100 \qquad (3)$$

Where $I_{25}$ and $I_{17}$ are intensity of peaks at diffraction angles of $2\theta = 25°$ and 17°, respectively.

Stabilization index (SI) was also used to evaluate quantitatively the structural changes related to the formation of cyclic structure using XRD patterns [eq. (4)].[19,34,43,44]

$$SI = \frac{I_0 - I_i}{I_0} \times 100 \qquad (4)$$

where $I_0$ is intensity of diffraction peak at $2\theta = 17°$ for virgin fibers and $I_i$ is intensity of this peak in stabilized fibers.

Thermal behavior of PAN fibers in different stabilization temperatures was analyzed by DSC 2010, TA Instrument in air atmosphere at a heating rate of 2°C/min. Thermograms were obtained in temperature range of 40–400°C. High purity (≥99.99%) Indium ($T_m = 156.59°C$, $\Delta H = 28.57$ J/g) and Zinc ($T_m = 419.527°C$, $\Delta H = 108$ J/g) metals were used for temperature and enthalpy calibration of DSC, as their transition temperatures span the sample transition interval. An empty aluminum pan was used as reference. The reproducibility of the DSC data was checked by measuring six specimens of P(AN/IA/MA).
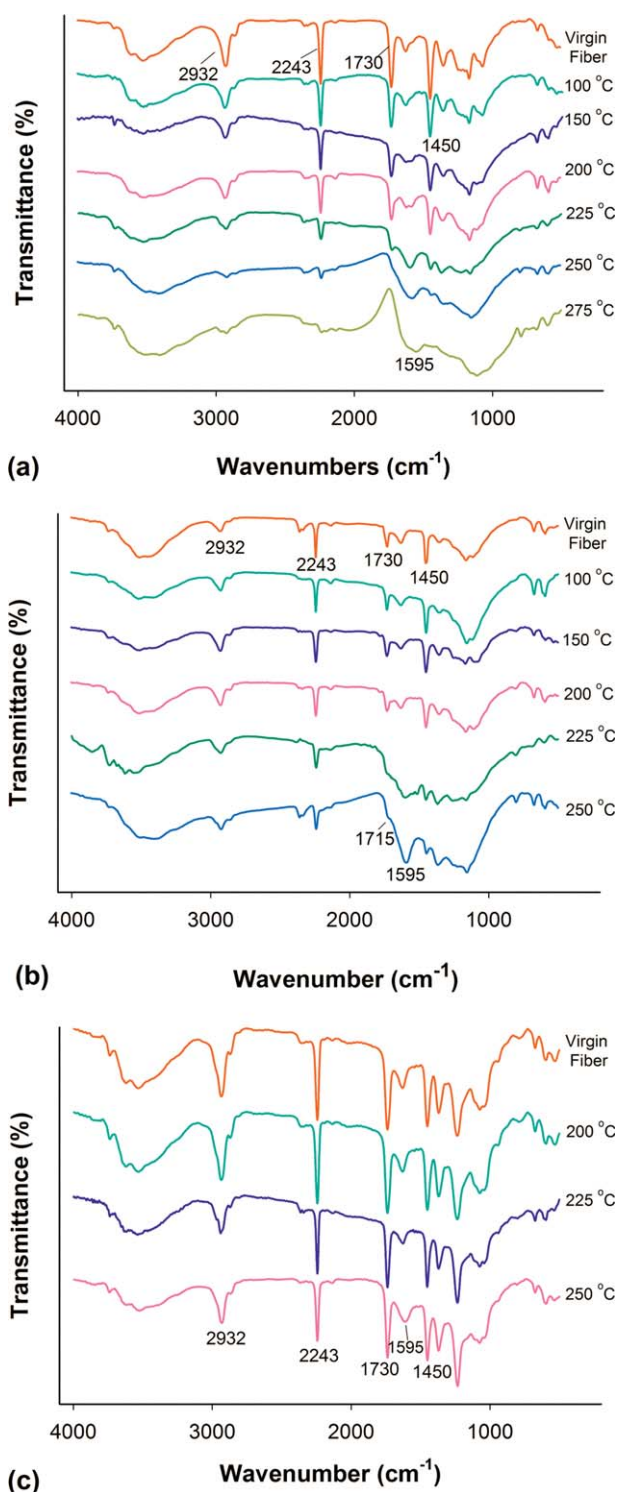
**Figure 1.** FTIR spectra of virgin and stabilized PAN fibers at different stabilization temperatures. (a) P(AN/IA/MA), (b) P(AN/IA), (c) P(AN/VAc). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

No shift in the peak position was observed and the error of the enthalpy was about 0.2%. Cyclization index (CI) was calculated using heat released related to exothermic DSC peaks [eq. (5)].[11,41,45,46]

$$CI = \frac{H_r - H_o}{H_r} \times 100 \qquad (5)$$

Where $H_r$ and $H_o$ are heat released in DSC thermograms of virgin and stabilized fibers, respectively. The amount of $H_r$ and $H_o$ was calculated by integrating the total area under exothermic peaks related to stabilization reactions.

Density of fibers was determined at 25°C using density-gradient-column method. A mixture of $n$-heptane and carbon tetrachloride was used.

Linear density of fibers was determined using Vibroskop 400, Lenzing Instruments according to ASTM D 1577. Thirty different fibers were tested and the average value is reported here.

Viscosity average molecular weight, $M_v$, of virgin fibers was measured by dilute solution viscometery of PAN/DMF solutions at 30°C using Mark-Houwink equation.[20–22]

Sonic modulus of fibers was measured in a Dynamic Modulus Tester PPM-5R, Lawson-Hemphill Inc.

## RESULTS AND DISCUSSION

### Analysis of FTIR Spectra

FTIR spectra of PAN fibers are shown in Figure 1. Assignments of IR bands are tabulated in Table II. Generally, stabilization leads to a reduction in intensity of C≡N band at 2243 cm$^{-1}$, related to linear structure of PAN. In addition, a new band at 1595 cm$^{-1}$ appears which is attributed to combination effects of C=C, C=N, and N—H links in the aromatic structure of stabilized PAN fibers.[14,18,32,47]

FTIR spectra of P(AN/IA/MA) shows that above 200°C intensity of 1730 cm$^{-1}$ band, attributed to stretching vibrations of C=O groups in acidic (IA) and ester (MA) comonomers, has decreased. At 250°C this peak has completely disappeared. It seems that in this fiber the main changes occur mostly above 200°C, Figure 1(a). At the same time a shoulder-like peak, attributed to C=O groups in the structure of cyclized PAN, has appeared at 1715 cm$^{-1}$. According to theoretical prediction, C=O groups in comonomer initiate the cyclization reactions and crosslink the structure with ionic mechanism [14]. Therefore, cyclization reactions, decrease the number of C=O groups in linear structure and the number of these groups in cyclized structure increases, due to oxidation reactions.

Similar to P(AN/IA/MA), C≡N band of P(AN/IA) fibers weakens above 200°C and new band at 1595 cm$^{-1}$ grows due to formation of the cyclic structure, Figure 1(b). In the FTIR spectra of P(AN/VAc) fibers very limited changes occur until 250°C, compared with P(AN/IA/MA) and P(AN/IA) fibers, Figure 1(c). Intensity of the 2243 cm$^{-1}$ peak decreases only to a limited amount and the 1595 cm$^{-1}$ peak does not grow significantly. Comparing qualitative results of FTIR, it seems that formation of cyclic structure in P(AN/IA/MA) and P(AN/IA) is intensified above 200°C, while in P(AN/VAc) the formation of cyclic structure is not prominent even at 250°C.

Decrease in the number of C≡N groups and increase in the number of C=C, C=N, and N—H groups is due to cyclization reactions in fibers. Dehydrogenation reactions also contribute to

**Table II.** Assignment of IR Bands for PAN Fibers

| Wavenumber (cm$^{-1}$) | Functional groups and mode of vibration | Wavenumber (cm$^{-1}$) | Functional groups and mode of vibration |
|---|---|---|---|
| 2243 | C≡N (stretching) | 1224 | CH$_2$ (twisting) |
| 1595 | Combination of C=N, C=C (stretching), N—H (in-plane bending) | 1250 | CH$_2$ (bending) |
| 1731 | C=O (stretching) | 1073 | CH (bending) |
| 1450 | CH$_2$ (in plane bending) | 3450 | OH (stretching) |
| 2932 | CH$_2$ (stretching) | 1100-1300 | C-O (Stretching) |

an increase in the number of C=C groups in the structure. Therefore, EOR$_1$ is a quantitative measure of progress in cyclization and dehydrogenation reactions. Oxidation reactions do not have significant influence on EOR$_1$. Below stabilization temperature of 100°C, EOR$_1$ is almost constant in three fibers [Figure 2(a)]. In P(AN/IA/MA) and P(AN/IA) fibers, only a limited increase can be observed in the range of 100–200°C. As temperature increases to 225°C, EOR$_1$ rises sharply. However, in the case of P(AN/VAc) there are insignificant changes below 225°C. Only a limited increase can be observed at 250°C. EOR$_1$ variations indicate that stabilization reactions of P(AN/IA/MA) and P(AN/IA), in particular cyclization and dehydrogenation reactions, intensify in the range of 200–225°C. Progress of reactions in P(AN/IA/MA) and P(AN/IA) is much greater than in P(AN/VAc). Increasing stabilization temperature of P(AN/IA/MA) to 275°C leads to further increase in EOR$_1$, showing that more reactions occur in this range. P(AN/IA) and P(AN/VAc) decomposed at 275°C. This can be attributed to the simultaneous and uncontrollable exothermic reactions in the range of 250–275°C. Combining the results of different analysis techniques, Arbab et al.[8,9] proposed that onset of exothermic reactions in P(AN/IA/MA), P(AN/IA), and P(AN/VAc) is 175, 210, and 240°C, respectively. In P(AN/IA) and P(AN/VAc) the starting reactions are cyclization. However, in P(AN/IA/MA) oxidation reactions preceded the cyclization reactions, which started above 210°C. Therefore, it seems that abrupt increase of EOR$_1$ in P(AN/IA/MA) and P(AN/IA) in the range of 200–225°C and in P(AN/VAc) in the range of 225–250°C is consistent with analysis results suggesting that onset of cyclization reactions is within these ranges. Main changes in FTIR spectra of P(AN/IA/MA) and P(AN/IA) were above 200°C as well.

EOR$_2$ is another proposed index for prediction of progress in stabilization reactions. In P(AN/IA/MA) and P(AN/IA) fibers, EOR$_2$ increases with a considerable slope above 100°C [Figure 2(b)]. As it was mentioned earlier onset of stabilization reactions in P(AN/IA/MA) and P(AN/IA) is at 175 and 210°C, respectively.[8,9] Therefore, it seems that the basis for computing EOR$_2$ is not proper and the increasing trend of EOR$_2$ does not show the temperature range in which stabilization reactions initiate and propagate in fibers.

### Analysis of XRD Patterns
Generally, increasing the stabilization temperature leads to a reduction in peak intensity related to (100) and (110) crystalline planes at $2\theta = 17°$ and $2\theta = 29°$ of the XRD spectra. In addi-

tion, a broad and scattered peak at $2\theta = 25°$ appears at higher stabilization temperatures. These changes are related to the formation of cyclic structure and changes in crystalline structure of PAN fibers including changes in crystallinity and crystallite size.[1,18,24,47–49] Therefore, as stabilization temperature increases, aromatization index (AI), which is a measure of conversion of linear structure to cyclic structure, increases.
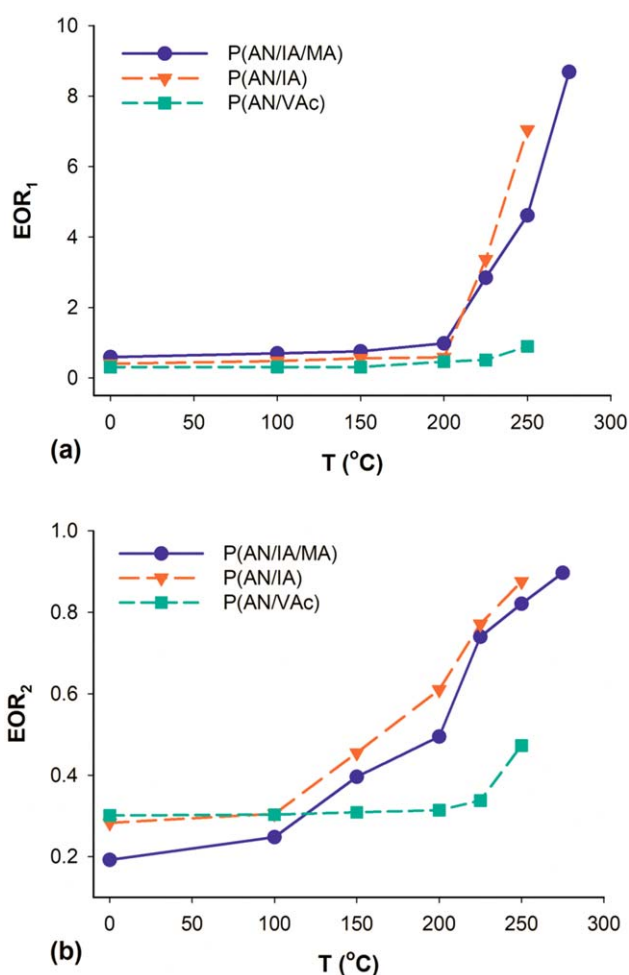


**Figure 2.** Changes in (a) EOR$_1$ and (b) EOR$_2$ for P(AN/IA/MA), P(AN/IA), and P(AN/VAc) fibers at different stabilization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
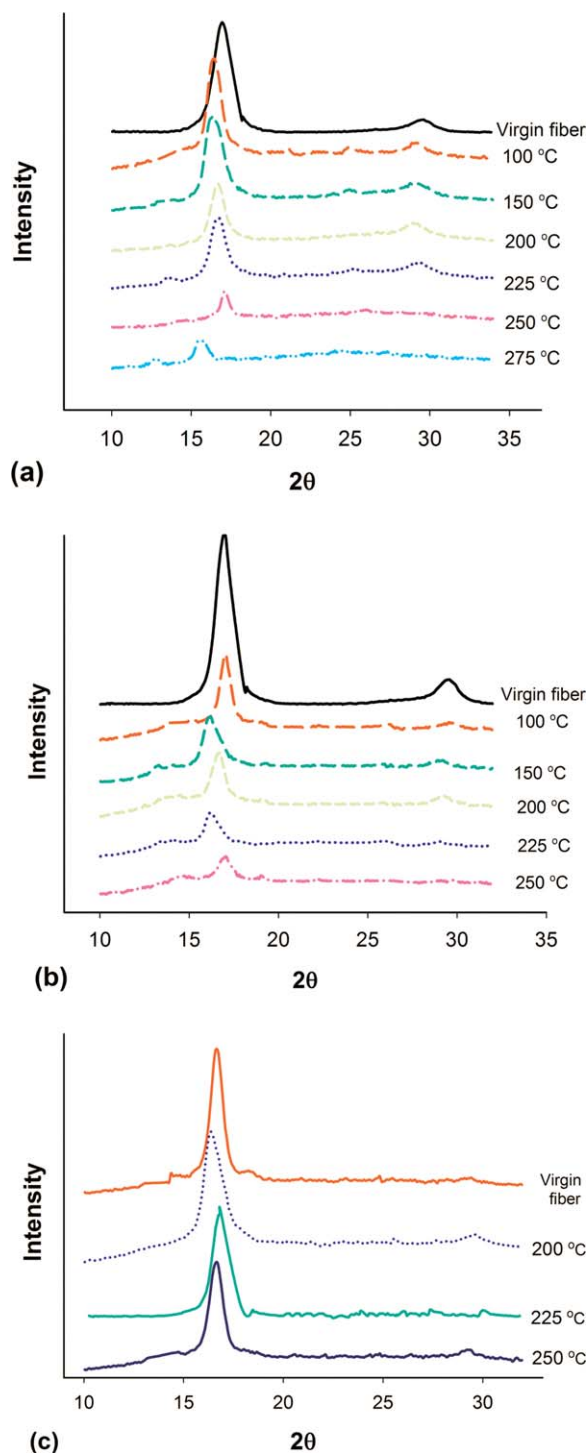
**Figure 3.** XRD patterns virgin and Stabilized PAN fibers at different stabilization temperatures. (a) P(AN/IA/MA), (b) P(AN/IA), (c) P(AN/VAc). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In P(AN/IA/MA), intensity of peaks related to (100) and (110) planes reduces, especially in the range of 225–250°C [Figure 3(a)]. Abrupt increase of AI in this temperature range, confirms the higher rate of progress in stabilization reactions and formation of cyclized structure in crystalline phases [Figure 4(a)].

$EOR_1$ and AI are both measures of conversion of linear structure of virgin PAN fibers to intermediate cyclic structure of stabilized fibers. $EOR_1$ displays chemical changes in entire fiber, including crystalline and amorphous phases, whereas AI represents changes in the crystalline phases of fibers. According to $EOR_1$ and AI results, it seems that in the range of 200–225°C, cyclization reactions of P(AN/IA/MA) mostly occur in amorphous phase of the fibers. As stabilization temperature increases, reactions spread to crystalline regions, especially in the range of 225–250°C. Therefore, comparison of AI and $EOR_1$ in different stabilization temperatures can be used to separate the progress of cyclization reactions in amorphous and crystalline phases.

SI, calculated from XRD patterns, is another measure of changes in crystalline structure of PAN fibers as a result of stabilization reactions. In P(AN/IA/MA), the most increase in SI is observed in the range of 225–250°C [Figure 4(b)], indicating that main changes in crystalline regions occur in this temperature range. According to onset of cyclization reactions of P(AN/IA/MA) at 210°C, considerable increase of SI in the range of 150–200°C, and decrease in the range of 200–225°C suggests
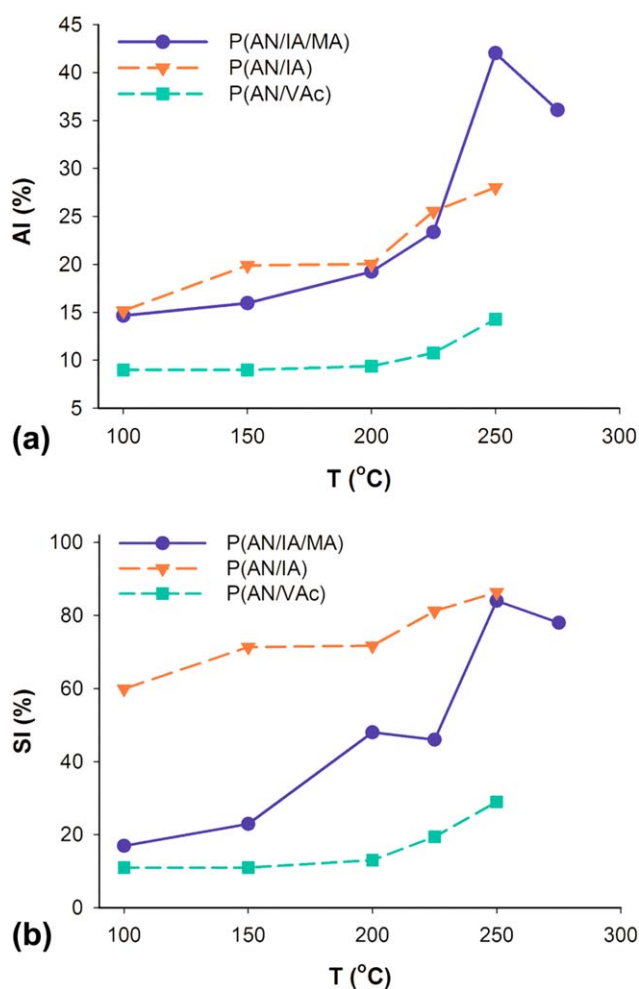


**Figure 4.** Changes in (a) stabilization index (SI) and (b) aromatization index (AI) with increasing stabilization temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
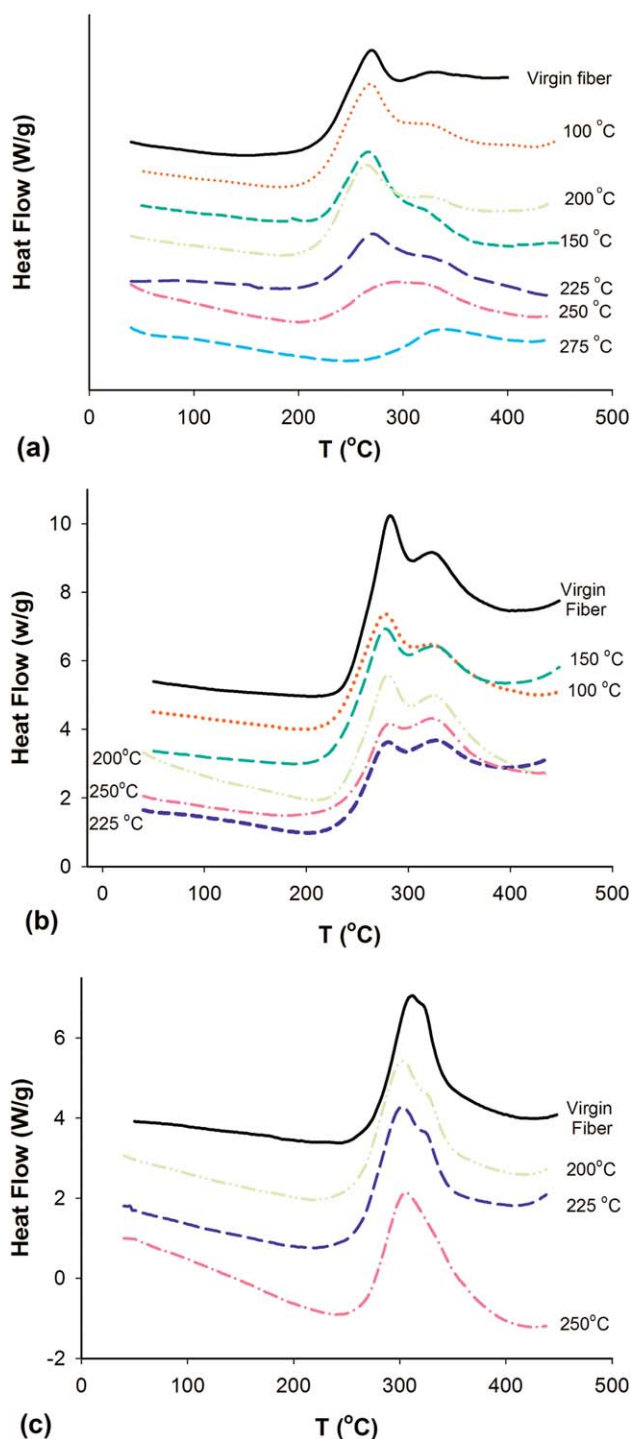
**Figure 5.** DSC thermograms of PAN fibers at different stabilization temperatures. (a) P(AN/IA/MA), (b) P(AN/IA), (c) P(AN/VAc). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, stabilization reactions have the most impact on crystallites in this range. $EOR_1$ also showed the main progress of cyclization and dehydrogenation reactions in the range of 200–225°C. Since onset of cyclization of P(AN/IA) is at 210°C,[8,9] it seems that cyclization reactions in both crystalline and amorphous phases occur in the range of 200–225°C. In these sets of experiments, wide temperature steps are chosen for production of stabilized fibers. Hence, precise separation of reactions in crystalline and amorphous regions of P(AN/IA) is not possible.

Changes in XRD patterns of P(AN/VAc) are very limited, compared with other fibers. AI shows only a limited increase in the range of 225–250°C [Figures 3(c) and 4(a)]. Therefore, it seems that crystalline structure of P(AN/VAc) does not change significantly below 250°C and limited changes occur mainly in amorphous phase. This confirms the FTIR results regarding fewer changes in P(AN/VAc) below 250°C. Arbab et al.[8,9] also analyzed that stabilization reactions of P(AN/VAc) starts at 240°C. In P(AN/VAc), SI increases abruptly after 200°C, which shows that it is not a proper index for evaluating stabilization process.

### Analysis of DSC Thermograms

Due to progress in exothermic stabilization reactions including cyclization, dehydrogenation, and oxidation, the heat released in DSC thermograms of PAN fibers decreases with increasing stabilization temperature (Figure 5). Chain scission at higher temperatures also contributes to heat release during stabilization.[12]

In P(AN/IA/MA), cyclization index (CI) increases slightly from 100 to 200°C and abruptly from 200 to 225°C. These changes suggest that a great amount of exothermic reactions occur in the range of 200–225°C, leading to sudden heat release and increase in CI (Figure 6). According to our other work,[8,9] the initiation temperature of oxidation reactions in P(AN/IA/MA) is 175°C. Therefore, the increase of CI in the range of 150–200°C is attributed to oxidation reactions. The abrupt increase in CI in the range of 200–225°C is attributed to cyclization and dehydrogenation that also led to rapid increase in $EOR_1$. Sudden heat release during stabilization at higher temperatures makes the control of process difficult, which may lead to chain
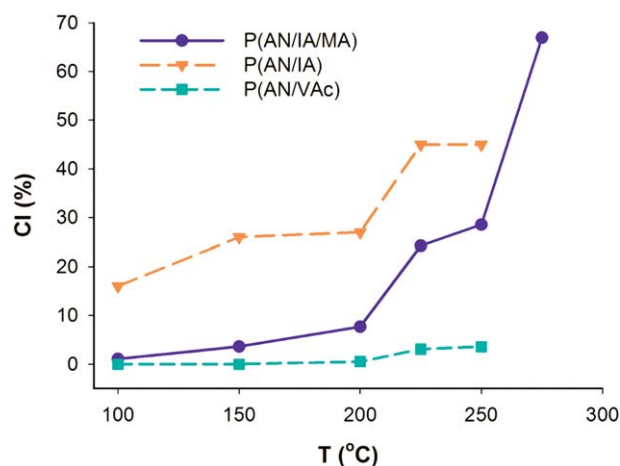


**Figure 6.** CI changes as a function of stabilization temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that SI is not a proper index for evaluating stabilization reactions.

In P(AN/IA) fibers most changes in crystalline phase of fibers occur in the range of 200–225°C, leading to a decrease in peak intensity and an increase in AI, [Figures 3(b) and 4(a)].

scission.[14,50] Hence, CI shows the maximum slope in the range of 250–275°C.

In P(AN/IA) fibers, the maximum slope of CI was observed between 200 and 225°C. According to $EOR_1$ and analysis results of Arbab et al.[8,9] onset of cyclization reactions is in this range. In P(AN/VAc) fibers, CI is constant until 200°C, and increases slightly from 200 to 250°C. FTIR results also indicated that limited amount of cyclization reactions occur below 250°C. These results suggest that CI is an appropriate index for quantitative study of stabilization changes in PAN fibers.

## CONCLUSIONS

By means of different indices proposed by other researchers using FTIR, XRD, and DSC analysis, the more practical indices for estimation of progress in stabilization reactions were determined. The results revealed that different indices were not completely compatible with each other. We studied benefits and drawbacks of each index and identified the most useful indices for assessment of stabilization process. It was shown that $EOR_1$ (calculated from FTIR spectra) and CI (calculated from DSC thermograms), increased abruptly in the temperature range that stabilization reactions initiate. Thus they were considered as a proper index for quantitative study of stabilization process. However, $EOR_2$, another index calculated from FTIR spectra, was not compatible with analysis results regarding onset of stabilization reactions. In addition to mentioned indices, AI and SI were both calculated from XRD patterns to evaluate stabilization reactions in crystalline regions of fibers. Results showed that AI was a proper index compatible with findings regarding the onset of reactions. Furthermore, according to various effects of stretching at different stages of stabilization on the properties of carbon fibers, a new approach for separation of progress of reactions in crystalline and amorphous regions was proposed. It was observed that by combination of AI and $EOR_1$ indices, it is possible to identify the temperature range in which reactions occur in each crystalline or amorphous phases. This approach can be utilized to design the annealing stage as well as stretching and shrinkage applied on fibers. It can help to obtain a high quality substrate for production of highly responsive PAN gel fibers and high strength carbon fibers.

## REFERENCES

1. He, D.; Wang, C.; Bai, Y.; Zhu, B. *J. Mater. Sci. Technol.* **2005**, *21*, 376.
2. Bajaj, P.; Roopanwal, A. K. *Polym. Rev.* **1997**, *37*, 97.
3. Bashir, Z. *Carbon.* **1991**, *29*, 1081.
4. Yusof, N.; Ismail, A. F. *J. Anal. Appl. Pyrol.* **2012**, *93*, 1.
5. Morgan, P. In Carbon Fibers and Their Composites; CRC Press: Boca Raton, FL, **2005**.
6. Rahaman, M. S. A.; Ismail, A. F.; Mustafa, A. *Polym. Degrad. Stab.* **2007**, *92*, 1421.
7. Shen, X.; Ji, Y.; Wang, J. *J. Appl. Polym. Sci.* **2008**, *110*, 313.
8. Mirbaha, H.; Arbab, S.; Zeinolebadi, A.; Nourpanah, P. *Smart. Mater. Struct.* **2013**, *22*, 045019.
9. Arbab, S.; Zeinolebadi, A. *Polym. Degrad. Stabil.* **2013**, *98*, 2537.
10. Xue, Y.; Liu, J.; Liang, J. *Polym. Degrad. Stabil.* **2013**, *98*, 219.
11. Qin, X. *J. Therm. Anal. Calorim.* **2010**, *99*, 571.
12. Sanchez-Soto, P. J.; Aviles, M. A.; del Rio, J. C.; Gines, J. M.; Pascual, J.; Perez-Rodriguez, J. L. *J. Anal. Appl. Pyrol.* **2001**, *58-59*, 155.
13. Rangarajan, P.; Yang, J.; Bhanu, V.; Godshall, D.; Mcgrath, J.; Wilkes, G.; Braid, D. *J. Appl. Polym. Sci.* **2002**, *85*, 69.
14. Ouyang, Q.; Cheng, L.; Wang, H.; Li, K. *Polym. Degrad. Stabil.* **2008**, *93*, 1415.
15. Crook, V.; Ebdon, J.; Hunt, B.; Joseph, P.; Wyman, P. *Polym. Degrad. Stabil.* **2010**, *95*, 2260.
16. Zhao, Y.; Wang, C.; Bai, Y.; Chen, G.; Jing, M.; Zhu, B. *J. Colloid. Interface. Sci.* **2009**, *329*, 48.
17. Liu, J.; Zhou, P.; Zhang, L.; Ma, Z.; Liang, J.; Fong, H. *Carbon* **2009**, *47*, 1087.
18. Devasia, R.; Reghunadhan Nair, C. P.; Sadhana, R.; Babu, N. S.; Ninan, K. N. *J. Appl. Polym. Sci.* **2006**, *100*, 3055.
19. Yu, M.; Bai, Y.; Wang, C.; Xu, Y.; Guo, P. *Mater. Lett.* **2007**, *61*, 2292.
20. Padney, G. C.; Kumar, A. *Polym. Test.* **2002**, *21*, 397.
21. Mathur, R. B.; Bahl, O. P.; Sivaram, P. *Curr. Sci. India.* **1992**, *62*, 662.
22. Tsai, J. *J. Mater. Sci. Lett.* **1993**, *12*, 1911.
23. Lian, F.; Liu, J.; Ma, Z.; Liang, J. *Carbon.* **2012**, *50*, 488.
24. Wu, G.; Lu, C.; Ling, L.; Hao, A.; He, F. *J. Appl. Polym. Sci.* **2005**, *96*, 1029.
25. Gupta, A.; Harrison, I. R. *Carbon.* **1996**, *34*, 1427.
26. Wang, L.; Lu, W.; Zhang, L.; Xue, L.; Ryu, S. K.; Jin, R. G. *Carbon. Lett.* **2011**, *12*, 107.
27. Bajaj, P.; Sreekumar, T. V.; Sen, K. *J. Appl. Polym. Sci.* **2002**, *86*, 773.
28. Wang, P. H. *J. Appl. Polym. Sci.* **1998**, *67*, 1185.
29. Sen, K.; Bajaj, P.; Sreekumar, T. V. *J. Polym. Sci. Part B. Polym. Phys.* **2003**, *41*, 2949.
30. Qin, X.; Lu, Y.; Xiao, H.; Hao, Y.; Pan, D. *Carbon* **2011**, *49*, 4598.
31. Qin, X.; Lu, Y.; Xiao, H.; Zhao, W. *Polym. Eng. Sci.* **2013**, *53*, 827.
32. Ouyang, Q.; Cheng, L.; Wang, H.; Li, K. *e-polymers.* **2009**, *15*, 1.
33. Dalton, S.; Heatley, F.; Budd, P. M. *Polymer* **1999**, *40*, 5531.
34. Hou, Y.; Sun, T.; Wang, H.; Wu, D. *J. Appl. Polym. Sci.* **2009**, *114*, 3668.
35. Lee, S.; Kim, J.; Ku, B. C.; Kim, J.; Joh, H. I. *Adv. Chem. Eng. Sci.* **2012**, *2*, 275.
36. Mijovic, J.; Andjeli, S. *Macromolecules* **1995**, *28*, 2787.
37. Mijovic, J.; Andjelic, S.; Yee, C. F. W. *Macromolecules.* **1995**, *28*, 2797.
38. Nikolic, G.; Zlatkovic, S.; Cakic, M.; Cakic, S.; Lacnjevac, C.; Rajic, Z. *Sensors.* **2010**, *10*, 684.

39. Yu, M. J.; Wang, C. G.; Bai, Y. J.; Xu, Y.; Zhu, B. *J. Appl. Polym. Sci.* **2008**, *107*, 1939.

40. Ge, H.; Liu, H.; Chen, J.; Wang, C. *J. Appl. Polym. Sci.* **2009**, *113*, 2413.

41. Tsai, J. S.; Hsu, H. N. *J. Mater. Sci. Lett.* **1992**, *11*, 1403.

42. Yu, M.; Wang, C.; Bai, Y.; Wang, Y.; Xu, Y. *Polym. Bull.* **2006**, *57*, 757.

43. Shin, H.; Jeun, J.; Kang, P. *Fibers. Polym.* **2012**, *13*, 724.

44. Liu, Y.; Chae, H.; Choi, Y.; Kumar, S. *Carbon* **2011**, *49*, 4487.

45. Tsai, J. S.; Lin, C. H. *J. Appl. Polym. Sci.* **1991**, *42*, 3045.

46. Bang, Y. H.; Lee, S.; Cho, H. H. *J. Appl. Polym. Sci.* **1998**, *68*, 2205.

47. He, D.; Wang, C.; Bai, Y.; Lun, N.; Zhu, B.; Wang, Y. *J. Mater. Sci.* **2007**, *42*, 7402.

48. Suresh, K. I.; Saji Thomas, K.; Rao, B. S.; Nair, C. P. R. *Polym. Adv. Technol.* **2008**, *19*, 831.

49. Ji, M.; Wang, C.; Bai, Y.; Yu, M.; Wang, Y. *Polym. Bull.* **2007**, *59*, 527.

50. Huang, X. *Materials* **2009**, *2*, 2369.