

Polymerization and Thermal Characteristics of Acrylonitrile/Dicyclohexylammonium 2-Cyanoacrylate Copolymers for Carbon Fiber Precursors

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(Received January 16, 2011; Accepted February 24, 2011)

Abstract

This study experimentally investigated dicyclohexylammonium 2-cyanoacrylate (CA) as a potential comonomer for polyacrylonitrile (PAN) based carbon fiber precursors. The P(AN-CA) copolymers with different CA contents (0.19-0.78 mol% in the feed) were polymerized using solution polymerization with 2,2-azobis(isobutyronitrile) as an initiator. The chemical structure and composition of P(AN-CA) copolymers were determined by proton nuclear magnetic resonance and elemental analysis, and the copolymer composition was similar to the feeding ratio of the monomers. The effects of CA comonomer on the thermal properties of its copolymers were characterized differential scanning calorimetry (DSC) in nitrogen and air atmospheres. The DSC curves of P(AN-CA) under nitrogen atmosphere indicated that the initiation temperature for cyclization of nitrile groups was reduced to around 235°C. The heat release and the activation energy for cyclization reactions were decreased in comparison with those of PAN homopolymers. On the other hand, under air atmosphere, the P(AN-CA) with 0.78 mol% CA content showed that the initiation temperature of cyclization was significantly lowered to 160.1°C. The activation energy value showed 116 kJ/mol, that was smaller than that of the copolymers with 0.82 mol% of itaconic acids. The thermal stability of P(AN-CA), evidenced by thermogravimetric analyses in air atmosphere, was found higher than PAN homopolymer and similar to P(AN-IA) copolymers. Therefore, this study successfully demonstrated the great potential of P(AN-CA) copolymers as carbon fiber precursors, taking advantages of the temperature-lowering effects of CA comonomers and higher thermal stability of the CA copolymers for the stabilizing processes.

Keywords : *Dicyclohexylammonium 2-cyanoacrylate, Polyacrylonitrile copolymer, Carbon fiber precursor, Stabilization behavior*

1. Introduction

Carbon fibers were commercially introduced in the early 1970s, and they have been one of the most important reinforcing materials for advanced composites thanks to their high strength and stiffness [1]. The opening applications of carbon fibers were mainly driven by high performance industries such as aerospace and defense applications due to high cost of carbon fibers. However, in recent decades, carbon fibers have found extensive applications in civilian aircraft, land transportation, construction, sports, leisure, electric/electronics and industrial sectors owing to the increasing awareness of potential for high performance and lightweight materials since carbon fibers technologies became mature with cost reduction and fiber quality improvements [2,3].

Polyacrylonitrile (PAN) based precursors have proved to be the most popular for high strength carbon fibers because they are more easily converted to carbon fibers, give a higher carbon yield, and allow to be processed more economically

for commercial production than cellulosic and pitch precursors [1]. The nitrile (CN) groups are preferably positioned in PAN polymers for cyclization of nitrile groups to produce the ladder structures during thermal stabilization, which is the first stage to convert precursor fibers to carbon fibers followed by high temperature carbonization process. However, PAN homopolymers are not suitable for use as carbon fiber precursors because of a sudden uncontrollable exothermic reaction at a relatively high temperature, resulting in chain scission by thermal degradation and poor carbon fiber quality. Therefore, PAN copolymers are predominantly used as precursors by the incorporation of suitable comonomers such as itaconic acid (IA), acrylic acid (AA), methacrylic acid (MAA), and methyl acrylate (MA) to assist in the spinning and stabilization processes for better precursors and resulting carbon fibers. Such comonomers have stimulated significant interests in the effects of comonomers on spinning and stabilization processes of precursor fibers, which have been reported by a number of the previous studies [4-8].

This study experimentally investigated dicyclohexylammonium 2-cyanoacrylate (CA) as a potential comonomer for PAN based carbon fiber precursors. It is anticipated that the presence of one carbonyl group and one nitrile group in CA should facilitate stabilization processes with easy exothermicity and improve the productivity with high carbon yield for high strength carbon fibers. To the authors' knowledge, the study of P(AN-CA) copolymers has not been reported yet with regards to characteristics of carbon fiber precursors. This paper examines the effect of CA on thermal stabilization behavior of P(AN-CA) copolymers by comparing with PAN homopolymers and P(AN-IA) copolymers, particularly with an emphasis on the cyclization reaction of nitrile groups and thermal stability of PAN precursor polymers during heat treatment.

2. Experimental

2.1. Materials

Cyanoacetic acid (99%, Aldrich, USA), paraformaldehyde (95%, Aldrich), dicyclohexylamine (99%, Acros), triethylamine (99%, Junsei, Japan), hexane (95%, Samchun, Korea), and benzene (99.5%, Daejung, Korea) were used without additional purification for the synthesis of dicyclohexylammonium 2-cyanoacrylate. Acrylonitrile (95%, Daejung) was dried by molecular sieve 4Å and distilled at atmospheric pressure for purification. Dimethyl sulfoxide (DMSO, 99%, Junsei) was distilled at 70°C under vacuum of 10-12 Torr, and 2, 2'-azobis(isobutyronitrile) (AIBN, 99%, Daejung) was used as a polymerization initiator after recrystallization two times from methanol. IA (99%, Junsei) was purified by recrystallization with distilled water.

2.2. Synthesis of dicyclohexylammonium 2-cyanoacrylate

A mixture of cyanoacetic acid, paraformaldehyde, dicyclohexylamine, and triethylamine in benzene was refluxed for 20 min using a Dean-Stark apparatus. The solution was filtered to remove polymerized species and solvent was evaporated by vacuum drying. The resulting solid was suspended in hexane and filtered, and then purified by recrystallization from benzene to give CA [9].

2.3. Copolymerization of PAN copolymers

Acrylonitrile homopolymers and copolymers with IA and CA were prepared by solution polymerization technique in DMSO under nitrogen atmosphere at 60°C, using a 1000 mL reactor fitted with an overhead stirrer. The molar fraction of IA was 0.82 mol%, and the molar CA content was varied from 0.19 to 0.78 mol% to investigate the effects of CA content on polymer properties. Polymerization was initiated by AIBN

(0.5 wt% of monomers) and the reaction was carried out at a stirring speed of 200 rpm for 16 h. After the polymerization was completed, the polymers were solidified in distilled water and pulverized to powder. They were washed several times with distilled water to remove residual monomers, and dried for 24 h by vacuum oven. The conversion of copolymers was calculated using the following equation (1):

$$\text{Conversion(wt \%)} = \frac{\text{Weight of dried sample after washing(g)}}{\text{Weight of sample(g)} \times \text{Weight fraction of monomer}} \times 100$$

2.4. Characterization

A nuclear magnetic resonance (NMR) spectrometer (Mercury 400 MHz; Varian, USA) was used to investigate the chemical structure of PAN copolymers by proton NMR (¹H NMR) spectra in DMSO-d₆ solutions at room temperature using the proton signals of CA monomers and copolymers. The viscometric measurement was carried out in 0.5 g/dL concentrated dimethylformamide solution at 30±0.1°C with an Ubbelohde viscometer. The viscosity average molecular weight, M_v, was calculated from the following relationship [10]:

$$[\eta] = 2.86 \times 10^{-4} M_v^{0.733} \quad (2)$$

The chemical composition of the copolymers was determined by elemental analysis with Thermofinnigan EA1108 in standard conditions. Thermal behavior was characterized by TA Instruments (USA) differential scanning calorimetry (DSC) Q20 at different heating rates of 2, 5, 10 and 20°C/min from room temperature to 450°C in nitrogen and air environment. Thermogravimetric analysis was performed to characterize thermal stability in nitrogen and air atmospheres at a heating rate of 10°C/min from room temperature to 600°C with TA Instruments TGA Q50.

3. Results and Discussion

3.1. Preparation of PAN copolymers

Poly(acrylonitrile-co-dicyclohexylammonium 2-cyanoacrylate), P(AN-CA) copolymers were prepared with different molar fractions of CA ranging from 0.19 to 0.78 mol%. The polymerization scheme is shown in Fig. 1. The polymerization characteristics are listed in Table 1 as a function of monomer feeding contents in the feed. The conversion of P(AN-CA) copolymers is similar to that of PAN homopolymer and P(AN-IA) copolymer, but decreases with increasing the amount of CA comonomer. Moreover, the molecular weight and intrinsic viscosity of P(AN-CA) show a significant reduction in the higher CA content. This is probably due to the lower reactivity between AN and CA

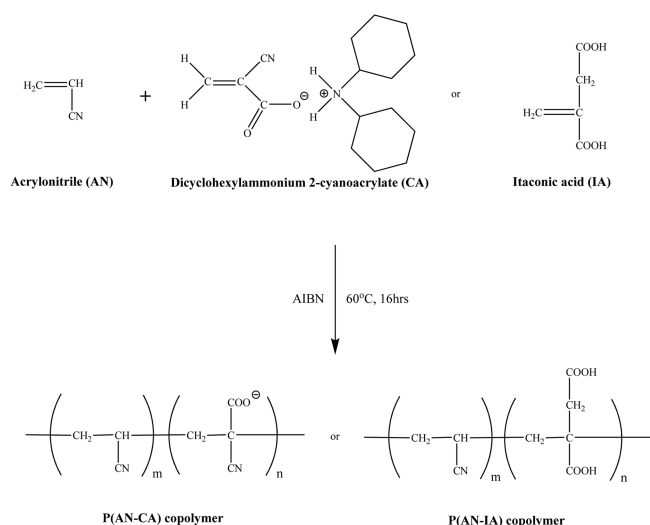


Fig. 1. Polymerization scheme for P(AN-CA) and P(AN-IA) copolymers.

monomers by stereo hindrance of the side chain in CA. In binary copolymerization, the presence of the second monomer increases the mutual termination reactions and the cross termination rate [11]. When CA concentration was increased, the rate of polymerization (R_p) and the degree of polymerization (D_p) of P(AN-CA) copolymers were decreased, leading to the decrease in conversion, molecular weight and intrinsic viscosity.

The $^1\text{H-NMR}$ and elemental analyses were performed to identify P(AN-CA) copolymers. Fig. 2 shows the $^1\text{H-NMR}$ spectra of AN and CA monomers, and P(AN-CA) and P(AN-IA) copolymers. In the spectrum of AN monomer, methine (-CH) proton signal of AN monomer appears between 5.96 and 6.03 ppm, and two doublet signals are observed at $\delta 6.21$ and $\delta 6.35$ due to the methylene (-CH₂) protons of AN. The signals at $\delta 6.27$ and $\delta 6.51$ in the CA spectrum are assigned to the methylene (-CH₂) protons of CA monomer. The methylene (-CH₂) proton peaks of

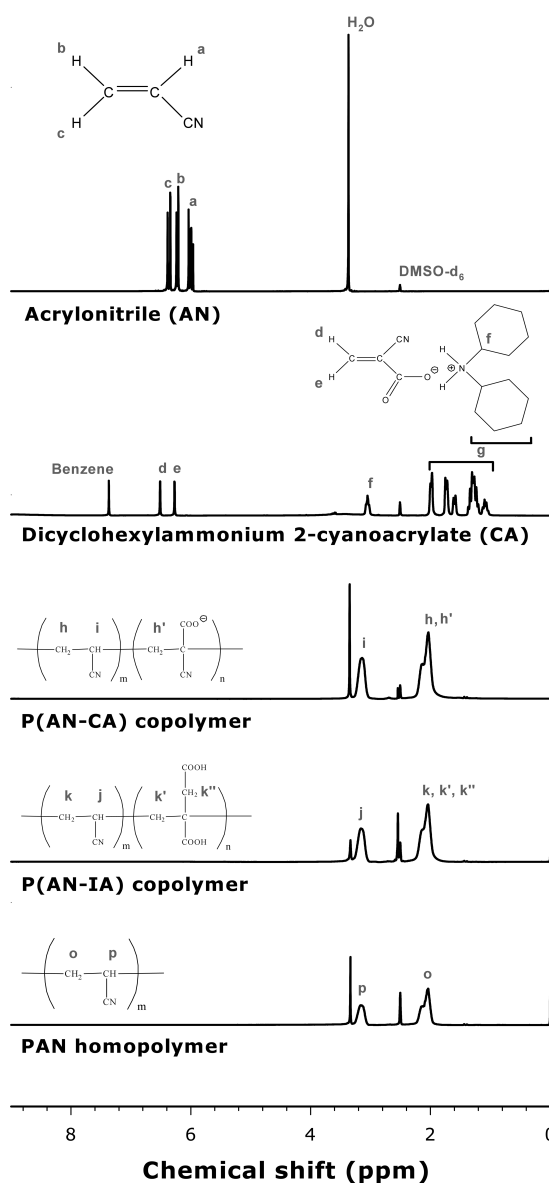


Fig. 2. Proton nuclear magnetic resonance spectra of monomers and polyacrylonitrile (PAN) precursors.

Table 1. Polymer Characteristics as a Function of Monomer Content in the Feed

Sample code	Monomer in feed (mol%)			Conversion (wt%)	M_w^a ($\times 10^4$)	PDI ^a (M_w/M_n)	M_v^b ($\times 10^4$)	$[\eta]^c$ (dL/g)
	AN	IA	CA					
PAN-homo	100	-	-	77.5	11.12	2.04	19.46	2.15
AI-0.82	99.18	0.82	-	77.6	13.76	1.81	24.23	2.53
AC-0.19	99.81	-	0.19	88.3	9.99	2.09	13.38	1.63
AC-0.38	99.62	-	0.38	78.4	9.11	2.26	8.98	1.22
AC-0.58	99.42	-	0.58	77.1	8.37	2.61	7.88	1.11
AC-0.78	99.22	-	0.78	74.1	6.26	3.19	4.87	0.78

AN: acrylonitrile, IA: itaconic acid, CA: dicyclohexylammonium 2-cyanoacrylate, PDI: Polydisperse Index, PAN: polyacrylonitrile.

^a Measured by Gel permeation chromatography.

^b Measured by Ubbelohde viscometer.

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

Table 2. Elemental Analysis and Chemical Composition of Copolymers

Sample code	Feed ratio (mol%)	Component (wt%)				Copolymer composition (mol%)
		C	H	N	O	
PAN-homo	100:0	-	-	-	-	-
AI-0.82	99.18:0.82	65.59	5.63	24.40	1.75	98.52:1.48
AC-0.19	99.81:0.19	67.80	5.76	26.01	0.07	99.88:0.12
AC-0.38	99.62:0.38	67.60	5.72	25.94	0.13	99.78:0.22
AC-0.58	99.42:0.58	67.84	5.82	25.99	0.22	99.63:0.37
AC-0.78	99.22:0.78	67.06	5.86	26.18	0.44	99.25:0.75

PAN: polyacrylonitrile.

cyclohexyl groups strongly appear between $\delta 1.09$ and $\delta 1.97$. In the $^1\text{H-NMR}$ spectrum of P(AN-CA), two broad signal peaks at $\delta 2.07$ and $\delta 3.13$ are presented due to methylene ($-\text{CH}_2$) protons in AN and CA and methine ($-\text{CH}$) protons in AN, respectively. However, the $^1\text{H-NMR}$ spectrum shows no characteristic peak of P(AN-CA) because the spectrum is almost identical to that of PAN homopolymer, as shown in Fig. 2. Since it is hard to determine the chemical composition of the copolymers by $^1\text{H-NMR}$ due to the overlapped signals of methylene ($-\text{CH}_2$) protons in AN and CA, elemental analysis was carried out to measure the content of carbon, hydrogen, nitrogen, and oxygen in the copolymers. The results are summarized in Table 2, indicating that the oxygen content in P(AN-CA) increases with increasing the feeding mol fraction of CA. It is evident that the increase in CA mol fraction in the copolymers confirms the successful incorporation of CA and copolymerization of P(AN-CA) copolymers.

3.2. Thermal and cyclization behavior of copolymers

3.2.1 Differential scanning calorimetric analysis in nitrogen and air atmospheres

Fig. 3 presents the DSC thermograms of P(AN-CA) copolymers containing various molar mass of CA for the comparison with those of PAN homopolymers and P(AN-IA) in nitrogen atmosphere. They all have only single sharp exothermic peak, which is attributed to cyclization without oxidation reaction during heat treatment. As the DSC characteristics are tabulated in Table 3, the PAN homopolymer shows the initiation temperature of exothermic transition (T_i) at 252°C and final temperature (T_f) at 296°C with the peak temperature of 275°C and evolved heat (ΔH) of 490.1 J/g while P(AN-IA) has the lower DSC characteristic temperatures with ΔH of 383.4 J/g . This result is not consistent with the previous report [4] that IA comonomer plays neither evident facilitating nor inhibiting role on cyclization reaction in nonoxidative atmosphere, in other words, efficiency of IA in initiating nitrile group cyclization can be found only in the oxidative condition during thermal stabilization of PAN. However, for P(AN-IA) and P(AN-CA) copolymers in this study, the lower T_i and broader exotherm

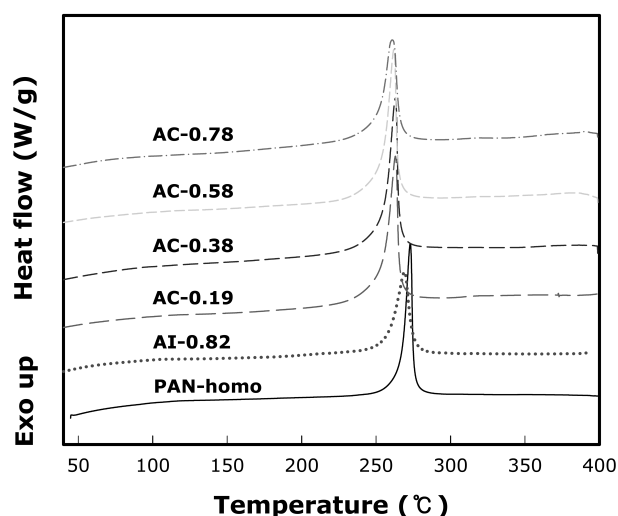


Fig. 3. Differential scanning calorimetry thermograms of polyacrylonitrile (PAN) precursor in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

trace implies that the incorporation of IA and CA can affect the cyclization reaction temperature and rate for stabilization process. As shown in Table 3, the shift of exothermic onset temperature to lower temperature during heat treatment suggests that the cyclization should be easily initiated through an ionic mechanism rather than radical mechanism.

For carbon fiber production, PAN based precursors normally are subjected to thermal treatment, so called "stabilization process" in air or oxygen-containing atmosphere at a temperature range of $200\text{--}400^\circ\text{C}$ for a long period time. The oxidative stabilization produces a stable ladder structure for the transformation of thermoplastic polymers into stable and infusible intermediate to sustain high temperature carbonization treatment for carbon fiber production [5]. The DSC thermograms in air atmosphere are shown in Fig. 4, indicating that two or three maximum peaks are responsible for complicated reactions such as cyclization, primary and secondary oxidation [6]. The DSC curve of PAN homopolymer exhibits the visible shoulder/peak/shoulder in air at about 270°C , 319°C and 390°C , respectively, but it has only one sharp peak in nitrogen. The air atmosphere

Table 3. DSC Characteristics of PAN Precursors in Nitrogen Atmosphere at a Heating Rate of 10°C/min

Sample code	T_i^a (°C)	T_f^b (°C)	ΔT^c (°C)	T_{pk}^d (°C)	ΔH^e (J/g)	$\Delta H/\Delta T$ (J/g·min)
PAN-homo	251.8	295.5	43.7	274.8	490.1	112.2
AI-0.82	242.9	294.6	51.7	271.0	383.4	74.2
AC-0.19	236.8	288.2	51.4	265.1	404.5	78.7
AC-0.38	236.1	287.4	51.3	265.6	410.9	80.1
AC-0.58	236.0	286.8	50.8	263.9	404.5	79.6
AC-0.78	235.6	285.9	50.3	263.2	401.2	79.8

DSC: differential scanning calorimetry, PAN: polyacrylonitrile.

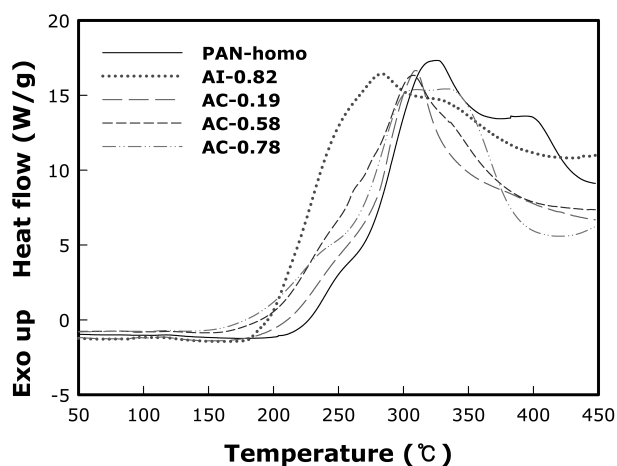
^a T_i = initiation temperature.

^b T_f = finish temperature.

^c $\Delta T = T_f - T_i$.

^d T_{pk} = maximum peak temperature.

^e ΔH = the amount of heat released by cyclization reaction.


Fig. 4. Differential scanning calorimetry thermograms of polyacrylonitrile (PAN) precursor in air atmosphere at a heating rate of 10°C/min.

decreases the onset temperature (T_i) and increases the final temperature (T_f) with a broader exothermic peak and higher overall enthalpy of exothermic reaction, compared with the

DSC trace in nitrogen atmosphere [4]. In P(AN-IA), T_i is further reduced to 181°C because the cyclization reaction can be more easily initiated in the oxidative condition through an ionic mechanism by carboxylic acid. It is well known that IA is the most effective comonomer in the ease of oxidation and exothermicity, and high carbon yield [12,13].

P(AN-CA) copolymer is most effective to reduce the initiation temperature, T_i , among the PAN copolymer precursors, as shown in Table 4. T_i decreases with an increase in CA content. For all the P(AN-CA) copolymers except AC-0.19, T_i is lower than PAN homopolymer and P(AN-IA) copolymer. Similarly to the DSC curves for P(AN-IA) in air, the exothermic multiple peaks in the form of shoulder are observed with broader exotherms. It is generally believed that the first peak at the lower temperature is attributed to both cyclization and dehydrogenation reactions, and the other peak and shoulder at the higher temperature are due to the oxidation reaction [6]. The total heat of exothermic reaction (ΔH) for all the P(AN-CA) is lower than that of PAN homopolymers and AC-0.78 is comparable to that of P(AN-IA). The rate of heat evolution ($\Delta H/\Delta t$) indicates heat liberation per unit time. The lower

Table 4. DSC Characteristics of PAN Precursors in Air Atmosphere at a Heating Rate of 10°C/min

Sample code	T_i^a (°C)	T_f^b (°C)	ΔT^c (°C)	T_{pk}^d (°C)	ΔH^e (J/g)	$\Delta H/\Delta T$ (J/g·min)
PAN-homo	209.1	445.3	236.2	318.8	3960	167.7
AI-0.82	180.6	411.0	230.4	279.7	2993	129.9
AC-0.19	184.4	430.2	245.8	308.5	4094	166.6
AC-0.38	168.3	415.9	247.6	307.2	3903	157.6
AC-0.58	160.5	409.7	249.2	305.6	3464	139.0
AC-0.78	160.1	410.1	250.0	304.3	2914	116.6

DSC: differential scanning calorimetry, PAN: polyacrylonitrile.

^a T_i = initiation temperature.

^b T_f = finish temperature.

^c $\Delta T = T_f - T_i$.

^d T_{pk} = maximum peak temperature.

^e ΔH = the amount of heat released.

heat rate of P(AN-CA) is beneficial in the production of carbon fibers because a higher rate of heat evolution during thermo-oxidative stabilization process would lead to burning out the core, resulting in a poor quality of carbon fibers [7].

It is concluded that the presence of carbonyl groups and nitrile groups in P(AN-CA) can facilitate the exothermic reaction at a lower temperature and reduce heat evolution. Since CA has one carbonyl and one nitrile groups in its molecular, cyclization reactions can be initiated at a lower temperature by carbonyl groups through an ionic mechanism. The decreased rate of exothermic reaction, as evidenced from the lower $\Delta H/\Delta t$ and broader exothermicity

in Fig. 4, may be due to steric hindrance or interruption in AN sequence imposed by bulky side groups in P(AN-CA), thereby adversely affecting the cyclization process [6,8]. In addition, the more extent of oxidation reaction implies the enhanced oxidation reaction in P(AN-CA). This is probably due to the increase of amorphous region in the polymers by the incorporation of CA [6,8]. The higher amorphous region due to bulkier side groups can lead to the higher diffusion rate of oxygen and greater possibility of contact between oxygen and molecules. Such oxygen uptake to make oxygen containing groups (C=O, -OH) in polymer backbones facilitate the formation of thermally stable carbon networks and insures high carbon yield during carbonization [4].

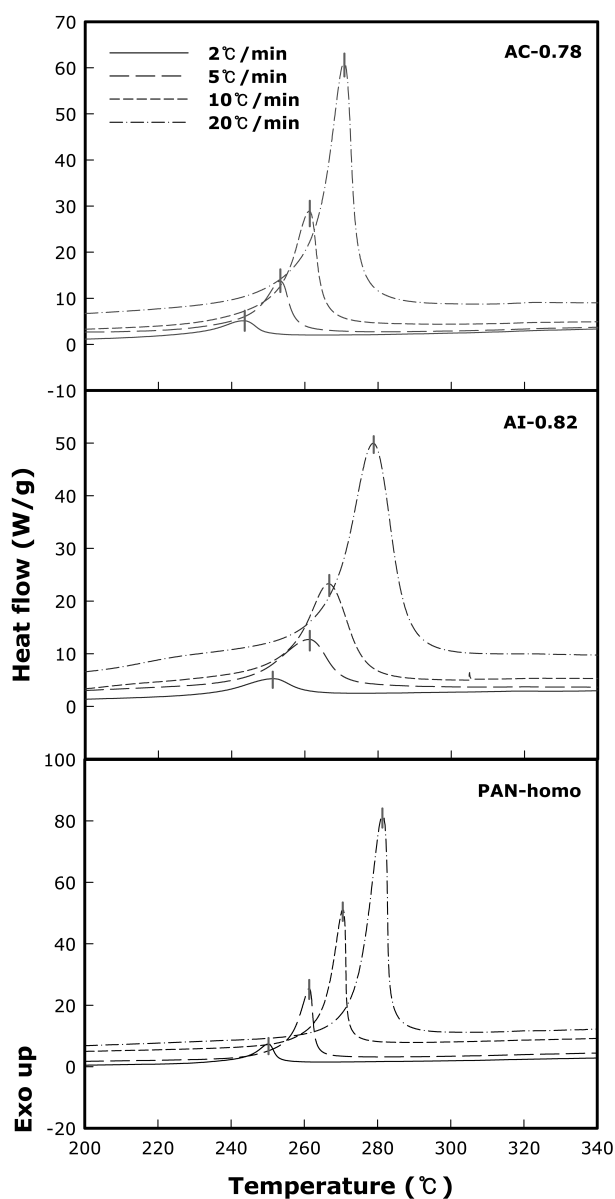


Fig. 5. Differential scanning calorimetry thermograms in nitrogen atmosphere at different heating rate of 2, 5, 10, and 20 °C/min.

3.2.2. Activation energy for cyclization reaction

The Kissinger method [14] was used to determine the activation energy (E_a) of cyclization reaction using the DSC data [5,7,15]. The general equation of the Kissinger method is expressed as the following equation:

where R , β and T_{pk} are the gas constant, the heating rate and the maximum peak temperatures, respectively.

Fig. 5 demonstrates the effect of the heating rate on thermal behavior of PAN polymers in nitrogen atmosphere. As the heating rate increases, the exotherms shift to a higher temperature with a higher intensity. The activation energy can be determined from the slope by plotting $\ln(1/T_{pk}^2)$ against $1/T_{pk}$, as shown in Fig. 6. As mentioned earlier, PAN homopolymer and copolymers have only one peak in the DSC thermograms under nitrogen atmosphere. However, the broad DSC curves are observed with two or three maxima peaks under air atmosphere due to cyclization, dehydrogenation and oxidation reaction during heat treatment. Grams-32 software was used for Gaussian curve fitting of whole exotherm to resolve into three peaks. The typical revolved DSC curves are shown in Fig. 7, where the first peak temperature corresponding to cyclization reaction is used to

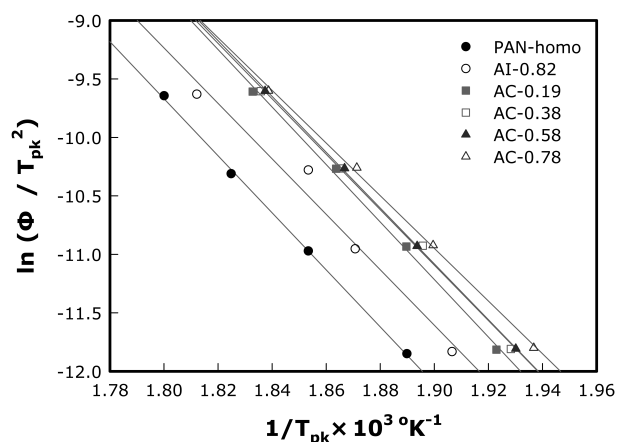


Fig. 6. Plot of $\ln(1/T_{pk}^2)$ against $1/T_{pk}$ for the activation energy of cyclization. PAN: polyacrylonitrile.

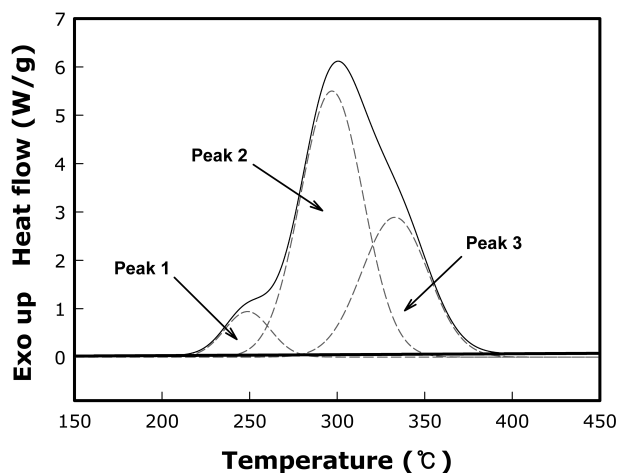


Fig. 7. Typical resolved differential scanning calorimetry curves of polyacrylonitrile homopolymer in air atmosphere.

Table 5. Activation Energy for Cyclization in Nitrogen and Air Atmosphere

Sample code	Activation energy (kJ/mol)	
	Nitrogen	Air
PAN-homo	202.7	135.0
AI-0.82	197.2	127.8
AC-0.19	204.4	137.3
AC-0.38	197.1	121.7
AC-0.58	198.4	120.7
AC-0.78	187.2	116.0

PAN: polyacrylonitrile.

calculate the activation energy of cyclization.

The calculated activation energy under nitrogen and air atmospheres is compiled in Table 5. Under nitrogen atmosphere, the values of E_a for PAN homopolymer and P(AN-IA) are about 202.7 kJ/mol and 197.2 kJ/mol, respectively. The activation energy of P(AN-CA) decreases to 187.2 kJ/mol with increasing the CA content to 0.78 mol%. It is reconfirmed that the incorporation of CA in PAN copolymers is effective to facilitate the initiation of cyclization reaction due to the lower E_a for cyclization reaction. The activation energy of all the precursor polymers under air is lower than that of nitrogen condition due to easier cyclization under the oxidative atmosphere. Especially, the value of activation energy of AC-0.78 (116.0 kJ/mol) is lower than that of AI-0.82 (127.8 kJ/mol) despite the similar content of comonomer. This indicates that CA comonomer seems to be more effective than IA in lowering the initiation temperature of cyclization reaction.

3.2.3. Thermogravimetric analysis in nitrogen and air atmospheres

Figs. 8 and 9 show the thermogravimetric analysis (TGA)

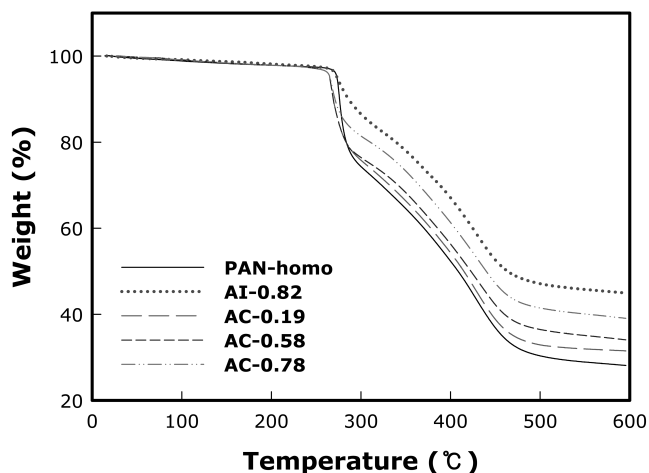


Fig. 8. Thermogravimetric analysis curves of polyacrylonitrile (PAN) precursors in nitrogen atmosphere at a heating rate of 10°C/min.

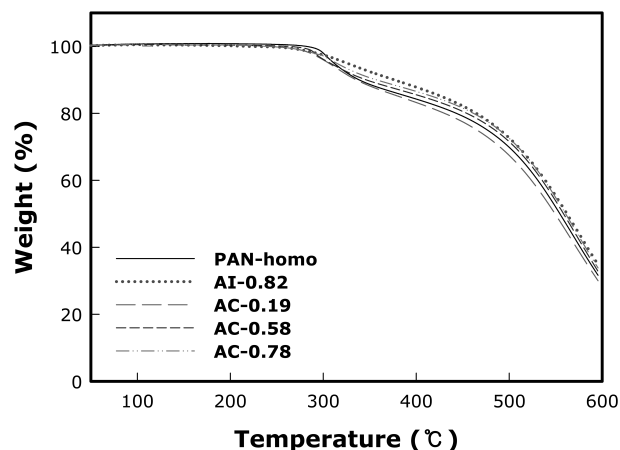


Fig. 9. Thermogravimetric analysis curves of polyacrylonitrile (PAN) precursors in air atmosphere at a heating rate of 10°C/min.

curves of AN homopolymer and copolymers in nitrogen and air atmospheres, respectively. The TGA curves in nitrogen for the given polymers can be divided into 3 steps according to the extent of weight loss. The curves show very small weight loss in the first zone up to around 250°C for PAN and P(AN-IA). In conjunction with the mentioned-above DSC results, only cyclization reaction takes place in this step because nitrile cyclization theoretically does not accompany the substantial weight loss. In the following second step, up to the approximately peak temperatures of the DSC curve (around 270°C), the TGA curves indicate the rapid and fast reactions with the greatest rate in the weight loss due to dehydrogenation and molecular fragmentation. The last step above the DSC exotherms shows the steady rate of weight loss, where polymer chain scission occurs producing volatile particles with weight loss.

The TGA curves in air show a slightly different thermal behavior from those in nitrogen. The first step shows no substantial weight loss up to around 270°C and 250°C for AN homopolymers and copolymers, respectively. This step is accompanied only by cyclization reaction for all the polymers. Above the temperatures, the second step shows the gradual weight loss with all types of reactions such as cyclization, dehydrogenation, and chain scission. However, the total weight loss in air is significantly less than that in nitrogen due to additional oxidation reactions. The oxygen uptake reactions undoubtedly compensate for weight loss due to chain fragmentation and dehydrogenation. The importance of oxygen uptake into the molecular chain was reported by the previous reports [4,5] for the stability of the polymer chains. The higher thermal stability of P(AN-CA) and P(AN-IA) during stabilization processes leads to the stable carbon structures with high carbon yield and less damages in carbon structures, consequently providing better precursor polymers for high performance carbon fibers.

4. Conclusions

P(AN-CA) copolymers were successfully synthesized via solution polymerization to develop new precursor polymers for high performance carbon fibers. Their chemical structures and composition were confirmed by ¹H-NMR and elemental analyses. Thermal analyses such as DSC and TGA in nitrogen and air atmospheres were carried out to infer the stabilization behavior of P(AN-CA), which was compared with PAN homopolymer and P(AN-IA) copolymers. It is discovered that P(AN-CA) copolymer was most effective to reduce the initiation temperature, T_i , among the PAN copolymer precursors. Their ability to alleviate heat release was comparable to that of P(AN-IA) copolymers in air or nitrogen. The TGA analysis indicated the higher thermal stability of P(AN-CA), which could lead to high carbon yield and less damage in carbon structures. These findings in this study suggest that the incorporation of CA should make clear contributions to facilitate thermal stabilization reactions by reducing onset temperature and exothermicity, and

improving thermal stability which are the indispensable processing parameters in the manufacture of high performance carbon fibers.

Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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