Effect of Methyl Acrylate Composition on the Microstructure Changes of High Molecular Weight Polyacrylonitrile for Heat Treatment

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ABSTRACT: The acrylate comonomer in polyacrylonitrile (PAN) precursor markedly influences the microstructure of PAN fiber and its resulting carbon fiber. In this study, the change occurring during the heat treatment of PAN copolymers (acrylonitrile-*co*-methyl acrylate) in the presence of air up to 260°C has been examined using both physical and chemical techniques. Considering the effect of the methyl acrylate content of PAN copolymers on the cyclization mechanism and fine structural changes in polymer chains under various heat treatment conditions, the composition of acrylonitrile and methyl acrylate = 98 : 2 to 97 : 3 mol % was suitable for the precursor preparation because the cyclization mechanism and fine structural changes in the boundary of this composition of copolymers were significantly different. With increasing MA content, the exothermic onset and peak in the thermogram was found to shift toward higher temperatures, and the aromaticity index decreased. This evidence indicates that MA was believed not to activate at all but to interfere with the cyclization. Additionally, by means of ^{13}C nuclear magnetic resonance (^{13}C-NMR) analysis, the tacticities of copolymers were nearly same, regardless of the copolymer composition, and the cyclization occurred nonstereospecifically during the initial heat treatment at 240°C for 1 h. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 2205–2213, 1998

Key words: high molecular weight polyacrylonitrile; heat treatment; precursor; cyclization; X-ray diffraction; ^{13}C-NMR

INTRODUCTION

Polyacrylonitrile (PAN)-based precursor of carbon fiber generally contains methyl acrylate (MA) as a second comonomer to improve the solubility, spinnability, and drawability.[1] It also contains small amount of itaconic acid (IA) as a third comonomer to reduce the cyclization temperature during heat treatment.

However, the addition of MA reduces the producibility of carbon fiber due to the low yield of cyclization[2,3] and also accompanies the decrease of crystallinity and the crystallite size, which affects tensile strength and initial modulus of final carbon fiber.[4-6] Many scientists have focused on the preparation of precursor fiber from PAN copolymers with a lesser amount of MA to improve the mechanical properties of final carbon fiber.

Since recently, the development of spinning technologies, such as dry-jet-wet spinning[7-9] and gel spinning,[10] as well as multistage drawing technology, can compensate for the disadvantages of eliminating MA as a comonomer, with the preparation of precursor fiber with excellent physical and mechanical properties from high molecular

Table I   True Composition and Molecular Weight of PAN Copolymers

Sample	Feed Ratio (mol%) [AN]/[MA]	Polymer Composition (mol%) [AN]/[MA]	M_w	MWD
M0	100/0	100/0	240,000	1.93
M0.5	99.5/0.5	99.51/0.49	260,000	1.97
M1	99/1	99.07/0.93	260,000	2.00
M2	98/2	98.06/1.94	270,000	1.85
M4	96/4	96.92/3.08	280,000	2.01
M6	94/6	95.44/4.56	280,000	1.85
M8	92/8	94.06/5.94	290,000	1.95

Polymerization conditions: 400 rpm; 70°C; 2 h.

weight PAN copolymers containing a small amount of MA was possible.[11] This can also eliminate the limitation to produce the various grade carbon fibers by changing the amount of components instead of adding different comonomers during precursor copolymer preparation. However, the research on the microstructural changes and the cyclization behavior upon heat treatment of PAN copolymers containing various amount of MA has not been published so far.

In this article, we prepared several high molecular weight PAN copolymers with various amounts and focused their microstructural changes and cyclization behaviors upon heat treatment.
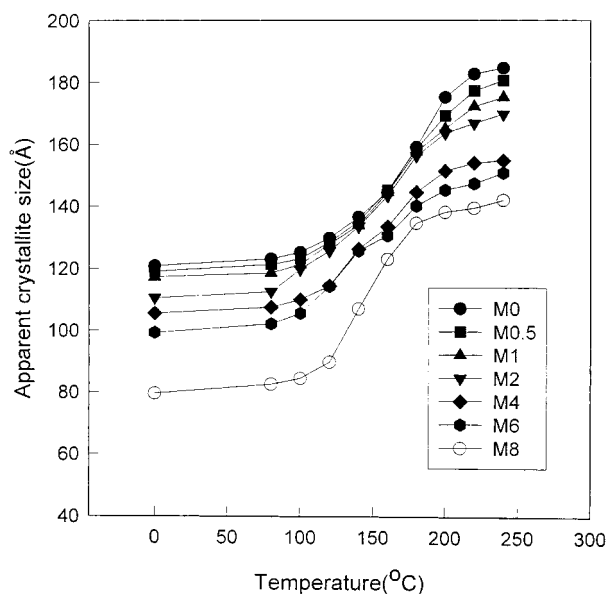

Figure 1 Variation of apparent crystallite size (100) with heat treatment and various MA composition for PAN copolymer.

EXPERIMENTAL

Copolymerization

High molecular weight PAN copolymers were prepared with AN and MA in water at 70°C for 2 h in the presence of potassium persulfate (KPS) and sodium bisulfite (SBS) redox initiator, then the crude copolymers were washed with hot water and acetone several times and dried under vacuum oven at 35°C for 60 h.

Heat Treatment

Heat treatment was carried out in the batch-type furnace for 60 or 120 min at 80 to 260°C with the increment of 20°C under air circumstance.

Measurement

The composition of copolymers was obtained from the calibration curve with optical density ratio (ODR) calculated by using the eq. (1) with the percentage of transmittances of nitrile (2240 cm^{-1}) and ester C=O (1745 cm^{-1}) in the infrared (IR) spectra obtained by Nicolet Impact 4000D IR spectroscopy with resolution of 4 cm^{-1} and scan number of 32.

$$ODR = \frac{\log(\text{baseline \% transmittance}/\text{MA \% transmittance})}{\log(\text{baseline \% transmittance}/\text{AN \% transmittance})} \quad (1)$$

The weight-average molecular weight (M_w) and molecular weight distribution (MWD) of copolymers were obtained by Waters Associates 440 gel permeation chromatography (GPC). Wide-
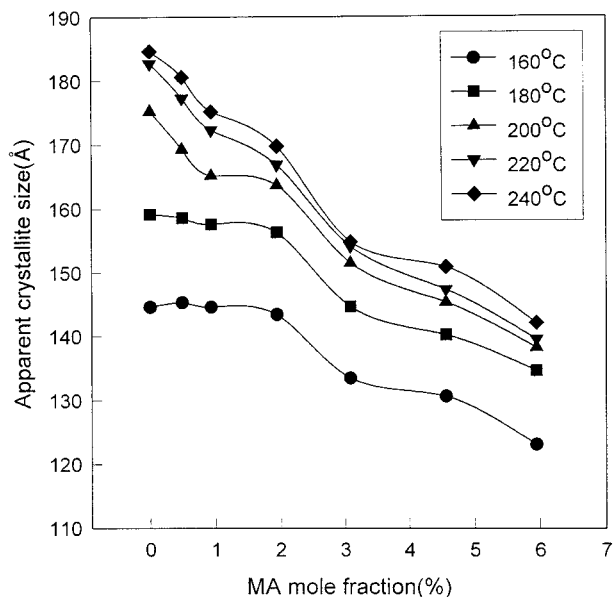
Figure 2 Variation of apparent crystallite size (100) with MA composition and various heat treatment temperature for PAN copolymers.

angle X-ray diffractograms were obtained by a Rigaku D/max-2400 X-ray diffractometer, and apparent crystallite size was calculated by the Scherrer eq. (2), as follows:

$$Lc \ (\text{Å}) = \frac{K\lambda}{\beta \cos \Theta} \qquad (2)$$

where λ is 1.54 (Å), β is the half-width (rad), and K is 0.91. And β was modified with the following Warren equation:

$$\beta^2 = \beta_m^2 - \beta_{si}^2$$

where β_m and β_{si} denote the half widths of the measured peak and the Si peak, respectively.

The thermal behavior was detected through Seiko DSC : SSC-5200 differential scanning calorimeter with the 5°C/min of heating rate; the aromaticity index (AI), which is an index of cyclization, was calculated with the following equation:

$$\text{AI} \ (\%) = \frac{H_v - H_o}{H_v} \times 100 \qquad (3)$$

where H_v and H_o are heats for the untreated and thermally treated sample, respectively.

To identify the relationship between tacticity and cyclization Jeol FX-200, ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectroscopy was applied under DMSO-d_6 as solvent at 60°C with the condition of 16,000 data points, 64 × 120 accumulation, 1-s sampling time, 6.5-s pulse delay time, and 45° RF pulse.

RESULTS AND DISCUSSION

Preparation of Copolymers

As shown in Table I, the MA components of copolymers were decreased from those of feeds. Tsai and Lin[12] found that the PAN precursors appeared as a change of thermal behavior and A.I. as the differences of M_w; however, in this research, the differences of M_w were not so significant as to affect the change of the cyclization behaviors with heat treatment. MWD of all copolymers was less than 2.
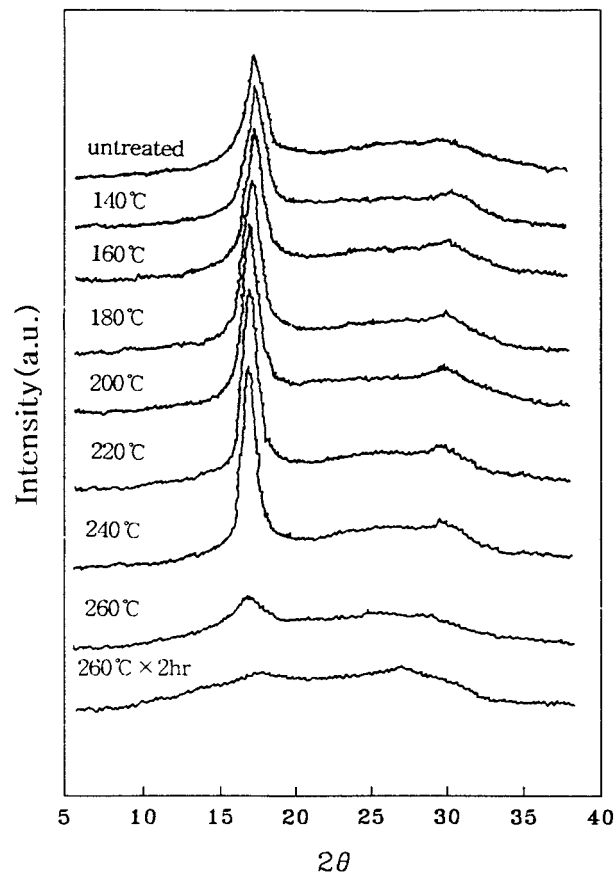

Figure 3 X-ray diffraction curves of M0 PAN copolymers heat-treated at various heat treatment temperatures for 1 h.
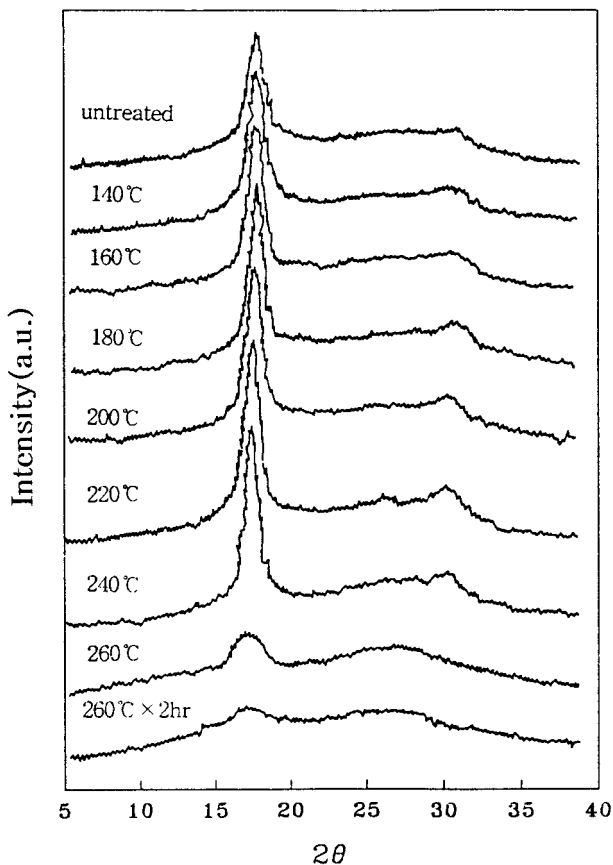
Figure 4 X-ray diffraction curves of M2 PAN copolymers heat-treated at various heat treatment temperatures for 1 h.

X-ray Diffraction of Copolymers

Apparent crystallite sizes (100) of samples thermally treated at 80 to 240°C for 1 h with a 20°C interval were shown in Figure 1. The apparent crystallite size of all samples increased with thermal treatment but decreased with the content of MA in copolymers. This phenomenon was very significant for the samples thermally treated at 100 to 180°C. This behavior was due to the increase of the flexibility of molecular chain and consequent regular orientation of polymer chains through the higher dipole–dipole interaction. However, the color of copolymers was changed to dark yellow due to the cyclization of nitrile groups over 200°C, not shown here, and, consequently, the increase of apparent crystallite size was smooth. From these results, the maximum temperature to increase the microstructural perfection of copolymers without any chemical reaction was found to be around 180°C.

Introduction of MA into PAN chain generally reduces the parallel between chains in the ordered regions due to the bulkiness and flexibility of MA. However, Gupta and Singhal[13] reported that the half-width at $2\theta \approx 16.9°$ in the X-ray diffractogram of PAN copolymers became broader if a much higher content of comonomer like MA was introduced into PAN. This means there is a critical concentration of comonomer introduced into PAN, which acts as a defect to destroy the crystal structure. Grobelny et al.[14] also reported that the crystallite size of the thermally treated PAN copolymers containing comonomer than with below the critical concentration was increased from that of PAN homopolymer due to the enhance of parallization between chains through the better chain flexibility.

Our results showed the changes of apparent crystallite size of thermally treated for all copolymers divided into two groups, that, is M0–M2
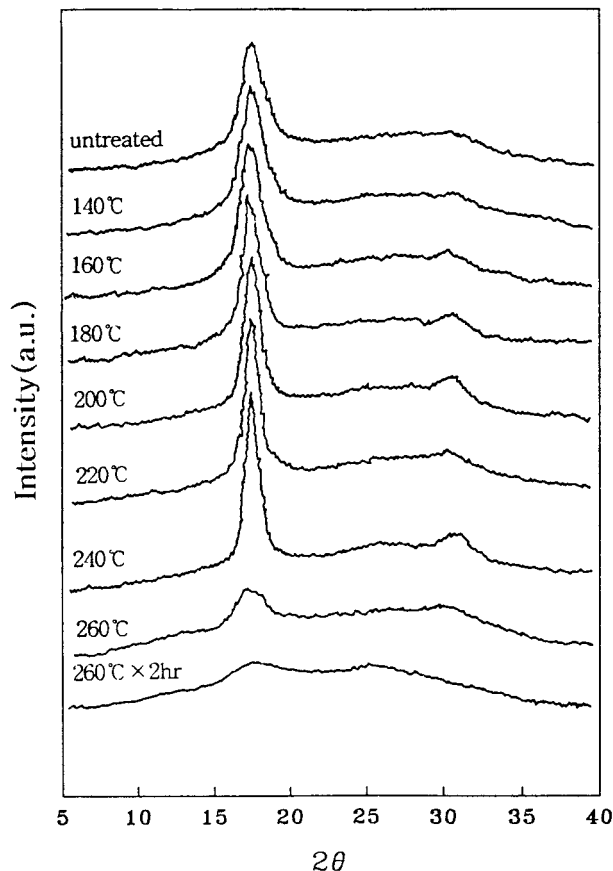

Figure 5 X-ray diffraction curves of M4 PAN copolymers heat-treated at various heat treatment temperatures for 1 h.
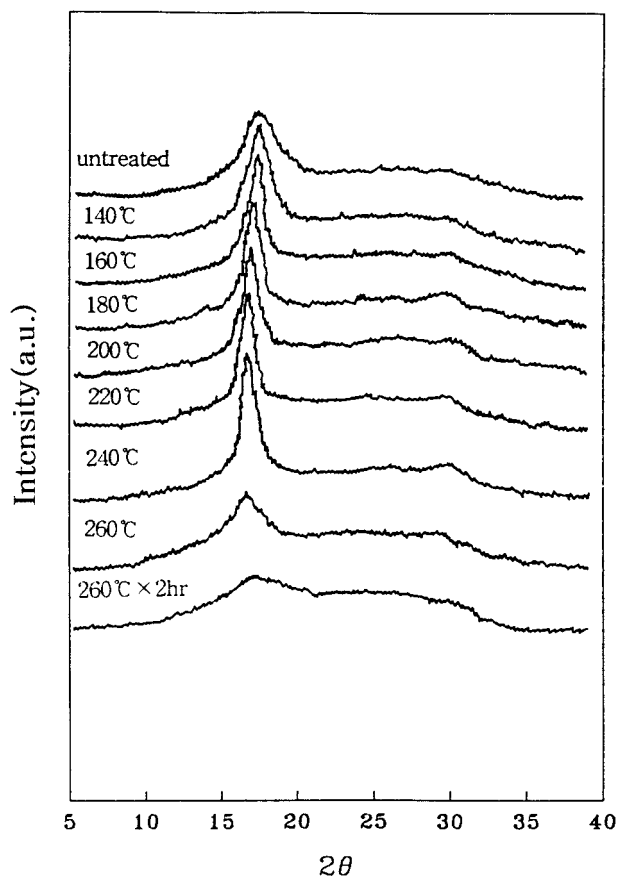
Figure 6 X-ray diffraction curves of M8 PAN copolymers heat-treated at various heat treatment temperatures for 1 h.

Figure 7 DSC thermograms with various MA compositions for PAN copolymers.

are shown in Figures 3 to 6. The main diffraction by (100) lattices at $2\theta \approx 16.9°$ was increased, but the spread of the peak decreased with the heat treatment temperature below 240°C. This phenomenon was more clear in the case of copolymers containing a small amount of MA. From these re-

and M4–M8. The former group containing a small amount of MA showed nearly similar changes of apparent crystallite size regardless of the amount of MA at a range of 100–180°C. This denotes the introduction of bulky MA reduces the chain orientation as well as improves the consequent chain flexibility.

The changes of apparent crystallite size with the content of MA and thermal treatment condition (160–240°C) is shown in Figure 2. Regardless of the treatment temperature, the apparent crystallite size of copolymers containing 2–3 mol % of MA was significantly changed. From this result, we found that the critical concentration of MA to improve the drawability of PAN fiber without destruction of the crystal structure was around 2.0 mol %.

The changes of X-ray diffraction curves of heat-treated PAN copolymers containing different amounts of MA at various temperatures for 1 h
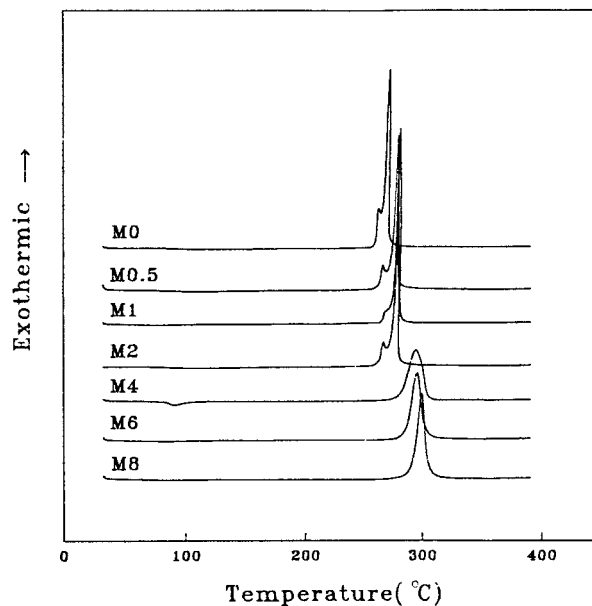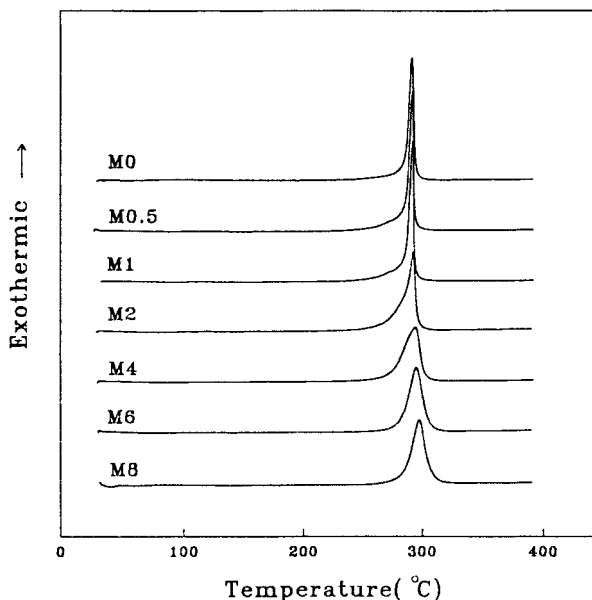

Figure 8 DSC thermograms with various MA compositions for PAN copolymers heat-treated at 240°C for 1 h.

Table II   Exothermic Onset and Peak Temperatures of PAN Copolymers

Sample	Onset Temperature (°C)			Peak Temperature (°C)		
M0	257.63[a]	232.24[b]	215.41[c]	273.96[a]	292.65[b]	307.15[c]
M0.5	262.46	237.19	210.43	280.79	293.15	303.01
M1	263.96	237.19	143.11	282.92	293.15	305.18
M2	263.31	236.30	99.22	281.79	292.60	297.85
M4	272.54	243.90	—	294.83	294.60	296.32
M6	279.09	246.61	—	296.16	295.37	291.67
M8	283.10	267.52	—	299.81	297.85	289.60

[a] Untreated sample.
[b] Sample heat-treated at 240°C for 1 h.
[c] Sample heat-treated at 240°C for 2 h.

sults, we can conclude that the heat treatment of PAN copolymers at 180 to 240°C for 1 h enhances the apparent improvement in morphology order. However, the color change of PAN copolymers from yellow to dark brown, depending on the heat treatment temperature, denoted that the cyclization took place at a not ordered region but in some other region. In addition, the yellowing of heat-treated PAN copolymers containing a small amount of MA was more serious, which means there is no relationship between the degree of cyclization at initial stage of heat treatment and the crystal structure of copolymers.

The main diffraction of copolymers treated at 260°C for 1 h was sharply decreased, and the spread of peak was increased, indicating a decrease in ordered regions. A new diffraction at $2\theta \approx 25.5°$ appeared and corresponds the (002) spacing in the consequent carbon fibers during the carbonization treatment. This tells us the PAN copolymers was transformed to a ladder-shaped polymer at the ordered region.

Table III   Aromaticity Index (AI) of PAN Copolymers

Sample	AI (%)	
M0	4.21[a]	80.90[b]
M0.5	3.45	79.07
M1	2.89	79.49
M2	1.76	78.14
M4	0.54	73.36
M6	0.53	72.32
M8	0.46	70.14

[a] Sample heat-treated at 240°C for 1 h.
[b] Sample heat-treated at 240°C for 2 h.

Thermal and Cyclization Behavior of Copolymers

The DSC thermograms of copolymers containing various amount of MA were shown in Figure 7. to investigate their exothermic behavior. If we considered the exothermic onset and peak temperatures on the DSC thermograms of copolymers correspond to the starting and the maximum temperatures of cyclization, respectively, both the starting and maximum cyclization temperatures were increased with the MA content in the copolymers. The copolymers thermally treated at 240°C also showed a similar trend, as shown in Figure 8. Therefore, the control of the amount of MA in copolymers is very important to reduce the cost to produce carbon fiber.

Since the increasing trend of starting and maximum cyclization temperatures was more serious for the M4 sample, which copolymerized with about 3.0 mol % of MA, the critical concentration of MA for suitable cyclization was believed to be the MA content in M2 sample.

As tabulated in Table II, the shift of exothermic onset temperature to lower temperature with the heat treatment temperature and time suggested that the cyclization was easily initiated even at a lower temperature due to the more active sites produced by a longer heat treatment at high temperature. However, the change of maximum exothermic temperature with heat treatment condition was different from that of the onset exothermic temperature.

The increase of the maximum exothermic temperature of M0 to M2 samples with heat treatment temperature and time was caused by the improvement of thermal stabilization through more cyclization after heat treatment of copolymers, as shown in Table III. However, the maxi-
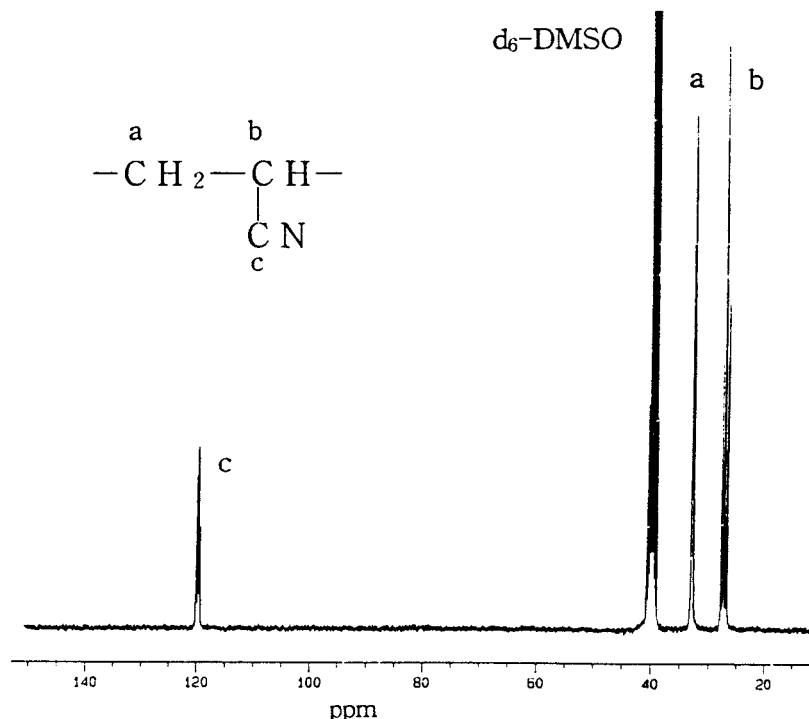
Figure 9 ^{13}C-NMR spectrum typical of a PAN polymer: (a) methylene, (b) methine, and (c) nitrile carbon resonances.

mum exothermic temperature of M4 to M8 samples containing higher MA than critical content was not much changed due to no improvement of thermal stability through less cyclization after heat treatment.

Table III shows the AI of copolymers with different amounts of MA heat treated under different conditions. Even though AI, which was known as the indicator of the degree of cyclization, could be generally determined by X-ray diffraction, Tsai reported for the oxidized PAN fiber that the differential scanning calorimetry (DSC) experiment could be another useful method for this purpose.[15] So, we also applied DSC data to determination of AI. The degree of cyclization was decreased with the amount of MA in copolymers regardless of thermal treatment temperature. This shows that MA that inhibits the initiation and propagation of cyclization.

The Effect of Polymer Tacticity on Cyclization

In the research on cyclization of PAN with the tacticity, Coleman reported that tacticity is a crucial factor to control the rate of cyclization, especially one much faster with isotactic PAN than

with a syndiotactic one, through computer modeling calculation.[16] Chen, however, reported that the cyclization was independent of PAN tacticity.[17] In our research, we investigated the relationship between tacticity and cyclization by analyzing the ^{13}C-NMR spectra of thermally treated PANs containing various amounts of MA.

As shown in Figure 9, the chemical shift of methine carbons of PAN homopolymers was around 27 ppm with 3 separated peaks, which was generally used to determine the triad tacticity, due to the triad chemical shift sensitivity. As shown in Figure 10, we separated the strong peaks of free nitrile carbons before and after cyclization at around 120 ppm into a pentad sequence, which was already known by Turska et al.[18] Since the direct analysis of NMR spectra was not so precise, we applied the computational estimation to obtain the relative integration values for triad and pentad abundances, as shown in Tables IV and V. If we assume that the cyclization takes place first in isotactic or syndiotactic chains, the integration values of NMR peaks of nitrile carbons in isotactic or syndiotactic chains must be reduced after cyclization. However, we found the relative integration values of nitrile peaks for iso-
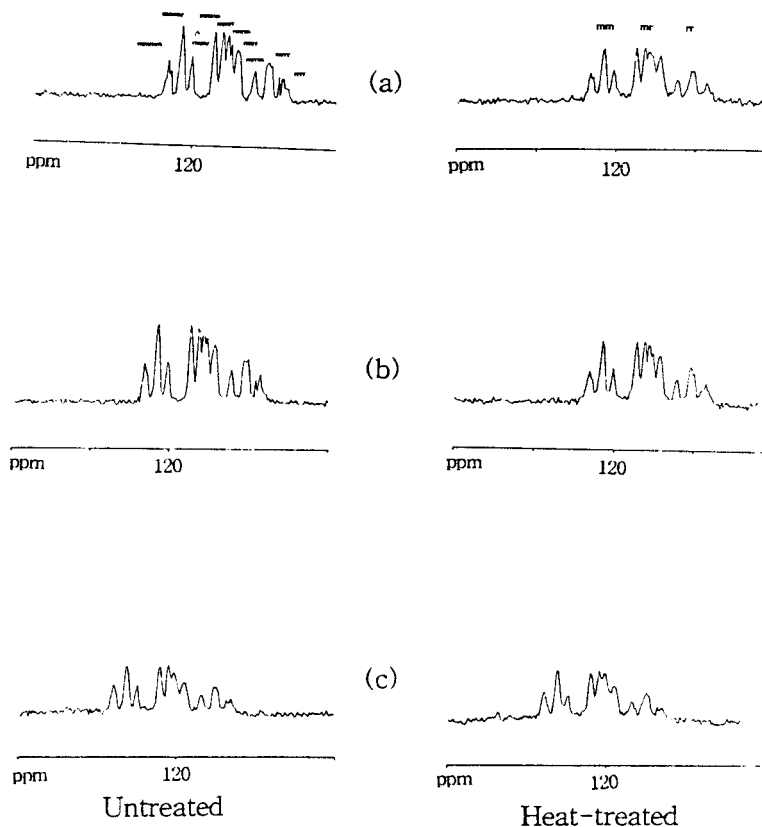
Figure 10 ^{13}C-NMR spectra showing nitrile carbon resonances: (a) M0, (b) M2, and (c) M8.

tactic, syndiotactic, and heterotactic chains, regardless of the content of MA in copolymers. This result means that even though we do not exactly know whether it may control the rate of cyclization, the tacticity of copolymers is not a crucial factor for total cyclization.

CONCLUSION

Considering the effect of the composition of poly-(acrylonitrile-co-methyl acrylate) on the cycliza-

tion and fine structural change in polymer chains under various heat treatment conditions, we obtained the following conclusions.

1. 2–3 mol % of MA in PAN copolymers was suitable for the carbon fiber precursor preparation.
2. MA was believed not to activate at all but to interfere the cyclization of PAN.
3. The tacticities of PAN copolymers were nearly the same regardless of the copolymer composition, and the tacticity of copolymers was not a

Table IV Measured Triad Abundance of Copolymers Calculated with ^{13}C-NMR Spectra

	Untreated Sample			Heat-Treated Sample		
Tacticity	M0	M2	M8	M0	M2	M8
mm (Isotactic)	27.62%	26.45%	30.50%	28.68%	29.48%	30.12%
mr (Heterotactic)	49.48	49.48	46.65	47.56	48.03	46.67
rr (Syndiotactic)	29.91	24.08	22.85	23.76	22.50	23.20

Table V   Measured Pentad Abundance of Copolymers Calculated with ^{13}C-NMR Spectra

Tacticity		Untreated Sample			Heat-Treated Sample		
		M0	M2	M8	M0	M2	M8
Isotactic	mmmm	7.322%	6.627%	6.176%	7.228%	8.657%	8.744%
	mmmr	13.372	12.747	13.610	12.465	13.317	13.110
	rmmr	7.000	6.889	6.529	7.665	7.738	6.668
Heterotactic	mmrm	12.145	12.145	13.194	11.848	13.761	12.991
	mmrr	9.547	8.908	9.880	8.523	9.784	10.617
	rmrm	14.960	15.548	11.659	14.699	10.131	13.396
	rmrr	12.670	12.995	12.401	13.376	12.905	10.882
Syndiotactic	mrrm	5.674	5.931	7.234	6.453	5.726	6.638
	mrrr	10.663	11.704	9.622	11.527	10.348	11.627
	rrrr	6.643	6.505	6.696	6.215	7.633	5.327

crucial factor for total cyclization under our conditions.

REFERENCES

1. H. Aotani and A. Ichimura, *Sen-I GaKKaish,* **33,** 72 (1977).
2. E. Fitzer and M. Heym, *Chem. Ind.,* **21,** 663 (1976).
3. A. K. Gupta, D. K. Paliwal, and Pushpa Bajaj, *Rev. Macromol. Chem. Phys.,* **C31,** 1 (1991).
4. C. Nakayama, K. Kamide, S. I. Manabe, and T. Sakamoto, *Sen-I Gakkaishi,* **33,** 23 (1977).
5. A. K. Kalshreshtha, V. N. Garg, and Y. N. Sharma, *J. Appl. Polym. Sci.,* **31,** 1413 (1986).
6. S. S. Chari, O. P. Bahl, and R. B. Mathur, *Fibre Sci. Technol.,* **15,** 153 (1981).
7. E.P. Pat., 0, 144, 793 (1984).
8. U.S. Pat., 4,535,027 (1985).
9. Y. H. Bang and H. H. Cho, *J. Korean Fiber Sci.,* **32,** 133 (1995).
10. P. Smith, *Colloid Polym. Sci.,* **259,** 1070 (1981).
11. Y. H. Bang, C. Y. Lee, and H. H. Cho, *J. Korean Fiber Sci.,* **32,** 471 (1995).
12. J. S. Tsai and C. H. Lin, *J. Appl. Polym. Sci.,* **42,** 3045 (1991).
13. A. K. Gupta and R. P. Singhal, *J. Polym. Sci., Polym. Phys. Ed.,* **21,** 2243 (1983).
14. J. Grobelny, M. Sokot, and E. Turska, *Polymer,* **30,** 1182 (1989).
15. J. S. Tsai and H. N. Hsu, *J. Mater. Sci. Lett.,* **11,** 199 (1992).
16. M. M. Coleman, G. T. Sivy, P. C. Painter, R. W. Snyder, and B. Gordon III, *Carbon,* **21,** 255 (1983).
17. S. S. Chen, J. Herms, L. H. Peebles Jr., and D. R. Uhlmann, *J. Mater. Sci.,* **16,** 1490 (1981).
18. E. Turska, J. Grobelny, A. Dworak, and H. Adoamowicz, *Acta Polym.,* **32,** 114 (1981).