2460 *Macromolecules* **1990,** *23,* 2460-2465

Structural Study of Polyacrylonitrile Fibers during Oxidative Thermal Degradation by Pyrolysis-Gas Chromatography, Solid-State ^{13}C Nuclear Magnetic Resonance, and Fourier Transform Infrared Spectroscopy

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ABSTRACT: The structural changes during the oxidative thermal degradation of poly(acrylonitrile) (PAN) fibers were studied by high-resolution pyrolysis-gas chromatography (PyGC), solid-state ^{13}C nuclear magnetic resonance (NMR), and Fourier transform infrared (FT-IR) spectroscopy. The main stabilization mechanism of the PAN fibers to form cyclic ladder structures was confirmed by PyGC, ^{13}C NMR, and FT-IR. Furthermore, the contribution of dehydrogenation and/or dehydrocyanide reactions to form conjugated polyene structures suggested by the data of PyGC, especially for the PAN fibers stabilized at relatively higher temperatures, was also supported by those of ^{13}C NMR and FT-IR.

Carbon fibers from poly(acrylonitrile) (PAN) are ordinarily prepared through the following three steps: (a) stretching to get raw oriented fibers of PAN below 200 °C, (b) stabilization in air at moderately high temperatures between 200 and 300 °C, and (c) final carbonization of the stabilized fibers between 900 and 1500 °C.[1] Among these, (b) is the most time-consuming step, often taking more than 1 h. In order to increase the industrial productivity of the carbon fibers, the optimization of the thermal treatments especially during step (b) is critical. However, it is not an easy task to clarify the correlation between the treating conditions and the resulting microstructures of the stabilized fibers, which in turn affect the mechanical properties of the final carbon fibers chiefly because of their insoluble nature in any solvents and their extremely low transparency.

Among various spectroscopic methods, Fourier transform infrared (FT-IR) and solid-state ^{13}C nuclear magnetic resonance (NMR) spectrometry have been most effectively utilized for the structural studies of the intractable carbon fiber samples.[2-6] The confirmed common mechanisms for the stabilization process at high temperatures in air involve competitive thermal reactions such as cyclization, dehydrogenation, and oxidative degradation. The associated structural changes during the process are also elucidated to some extent. However, these are still not enough to explain the subtle differences caused by different stabilization conditions, such as the processing temperature, time, atmosphere, etc.

Recently, high-resolution pyrolysis-gas chromatography (PyGC) has been extensively utilized to characterize various cross-linked intractable polymer samples such as epoxy resins, vulcanized rubbers, and styrene-divinylbenzene copolymers.[7-9]

In this work, various PAN fiber samples treated under different stabilization temperatures and various treating times were subjected to the structural characterization by PyGC, solid-state ^{13}C NMR, and FT-IR. Thus structural information obtained was related to the mechanical properties of the final carbon fibers prepared after carbonization to elucidate the optimum stabilization conditions.

Table I
PAN Fiber Samples

sample no.	treating time in air, min at 215 °C	at 235 °C	at 265 °C	total treating time, min
		Precursor		
P-1				0
		Stabilized Fiber		
S-1	20	15		35
S-2	20	30		50
S-3	20	60		80
S-4	20	90		110
S-5	20	120		140
S-6	20	180		200
S-7	20	240		260
S-8	20	1800		1820
S-9	20	15	10	45
S-10	20	15	40	75
S-11	20	15	60	95

Experimental Section

Materials. A copolymer type PAN which contains less than a few percent of methyl methacrylate and itaconic acid comonomers was used to prepare the precursor fiber, which was thermally stabilized in air under different conditions. Thus prepared fiber samples are listed in Table I together with the stabilization conditions. The precursor fiber sample was also used as the reference material. The precursor and the stabilized fiber samples were kindly offered from Nikkiso Co., Ltd.

PyGC Conditions. A gas chromatograph (Shimadzu, Model 7AG) equipped with a vertical microfurnace type pyrolyzer[8] (Yanagimoto, Model GP-1018) and a high-resolution fused-silica capillary column (0.25 mm i.d. × 30 m) coated with 1 μm thickness of immobilized 5% phenylmethylpolysiloxane was used. The separation column was operated under a temperature programming mode from 50 to 280 °C at 5 °C/min. Various stabilized PAN fiber samples weighing about 0.1 mg were pyrolyzed at 700 °C under a flow of N_2 carrier gas. Most of the characteristic peaks on the resulting pyrograms were identified by a quadrupole mass spectrometer (Shimadzu, Model QP-1000) directly attached to the PyGC system.

Solid-State ^{13}C NMR Conditions. The cross-polarization/magic angle spinning (CP/MAS) solid-state ^{13}C NMR spectra of the stabilized PAN fiber samples were measured by a Bruker AT-250 NMR spectrometer operating at 62.86 MHz. The optimal CP contact time of 1 ms, 1K data points in a spectral width

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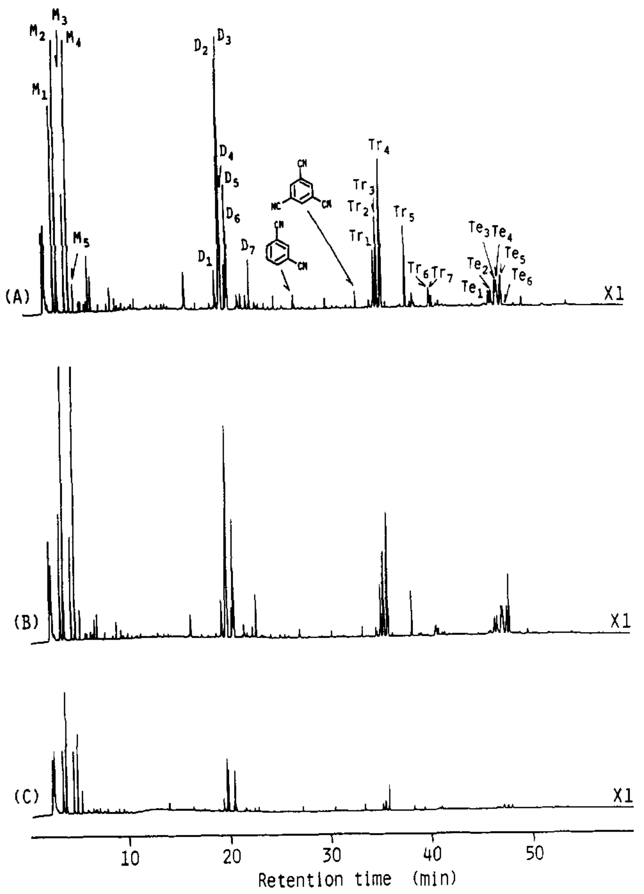


Figure 1. Typical pyrograms of a precursor and two differently stabilized PAN fiber samples at 700 °C: (A) precursor PAN (P-1); (B and C) stabilized PANs (S-1 and S-5, respectively); attenuation, ×1. Notations correspond to those in Table II.

of 31 250 Hz, 5-ms acquisition time, and 1.5-s delay time between acquisitions were employed. Aluminum oxide rotors were spun at 4 kHz. The sample size was about 0.1 g, and 1300–1600 scans were needed to obtain a good signal-to-noise ratio. The chemical shifts relative to TMS were determined by using the carbonyl peak of glycine at 176.1 ppm.

FT-IR Conditions. A FT-IR spectrometer (Digilab, Model FTS-15C) was used with a resolution of 4 cm^{-1} and an accumulation of 100 scans. The transmission spectra were measured for the KBr disks prepared for the finely powdered fiber samples.

Results and Discussion

Pyrolysis–Gas Chromatographic Studies. Figure 1 shows typical pyrograms of a precursor PAN fiber (P-1) and two differently stabilized PAN fibers (S-1 and S-5) at the pyrolysis temperature of 700 °C. The main common degradation products on the pyrograms are the peaks of acrylonitrile (AN) monomers (M_1–M_5), dimers (D_1–D_7), trimers (Tr_1–Tr_7), and tetramers (Te_1–Te_6), which reflect the AN sequences in the polymer chain.[10] The assignment of these peaks is summarized in Table II. Among the trimer peaks, Tr_2 and Tr_3, and Tr_5 and Tr_7 are assigned to the corresponding diastereoisomers and geometrical isomers, respectively. These monomers and oligomeric products are mainly formed through thermal chain scissions along the original polymer chain. In addition, minor peaks of CN-substituted aromatic compounds such as *m*-dicyanobenzene and 1,3,5-tricyanobenzene are also observed. These are probably formed through dehydrogenation and/or dehydrocyanide reactions followed by cyclization. However, the contribution of this stepwise thermal reaction to the production of aromatic products is not so significant during the pyrolysis. Furthermore, the fact that about 12 wt % of the original precursor fiber sample (ca. 0.1 mg) is found as the residue in the sample holder after the pyrolysis at 700 °C suggests that cyclization reactions to form thermally stable structures are also occurring to some extent. Therefore, as summarized in Figure 2, the PAN fiber undergoes more or less the following types of the competitive thermal reactions during the pyrolysis at 700 °C.

Table II
Assignment of Main Peaks on Pyrogram of PAN

peak notation	structure
	Monomers
M_1	$\underset{CN}{CH_3}$
M_2	$CH_2{=}\underset{CN}{CH}$
M_3	$CH_3\underset{CN}{CH_2}$
M_4	$CH_2{=}\underset{CN}{C}CH_3$
M_5	$CH_3\underset{CN}{CH}CH_3$
	Dimers
D_1	$CH_3\underset{CN}{CH}CH{=}\underset{CN}{CH}$ and $CH_2{=}\underset{CN}{C}CH_2\underset{CN}{CH}CH_3$
D_2	$\underset{CN}{CH_2}CH_2\underset{CN}{CH_2}$
D_3	$CH_2{=}\underset{CN}{C}CH_2\underset{CN}{CH_2}$
D_4	$CH_2{=}\underset{CN}{C}CH_2\underset{CN}{C}{=}CH_2$
D_5	$CH_3\underset{CN}{CH}CH_2\underset{CN}{CH_2}$
D_6	$\underset{CN}{CH_2}CH{=}CHCH_2\underset{CN}{CH_2}$
D_7	$CH_2{=}\underset{CN}{C}CH_2CH{=}CH\underset{CN}{CH_2}$ or $CH_2{=}\underset{CN}{C}CH{=}CHCH_2\underset{CN}{CH_2}$
	Trimers
Tr_1	$CH_2{=}\underset{CN}{C}CH_2\underset{CN}{CH}CH_2\underset{CN}{CH_2}$ and $\underset{CN}{CH_2}CH{=}CHCH_2\underset{CN}{CH}CH_2\underset{CN}{CH_2}$ or $\underset{CN}{CH_2}CH_2CH{=}CH\underset{CN}{CH}CH_2\underset{CN}{CH_2}$
Tr_2, Tr_3	$CH_3\underset{CN}{CH}CH_2\underset{CN}{CH}CH_2\underset{CN}{CH_2}$
Tr_4	$\underset{CN}{CH_2}CH_2\underset{CN}{CH}CH_2\underset{CN}{CH_2}$
Tr_5, Tr_7	$CH_3\underset{CN}{CH}CH_2\underset{CN}{CH}CH{=}\underset{CN}{CH}$
Tr_6	not identified
	Tetramers
Te_1–Te_6	$CH_3\underset{CN}{CH}CH_2\underset{CN}{CH}CH_2\underset{CN}{CH}CH_2\underset{CN}{CH_2}$ $\underset{CN}{CH_2}CH_2\underset{CN}{CH}CH_2\underset{CN}{CH}CH_2\underset{CN}{CH_2}$

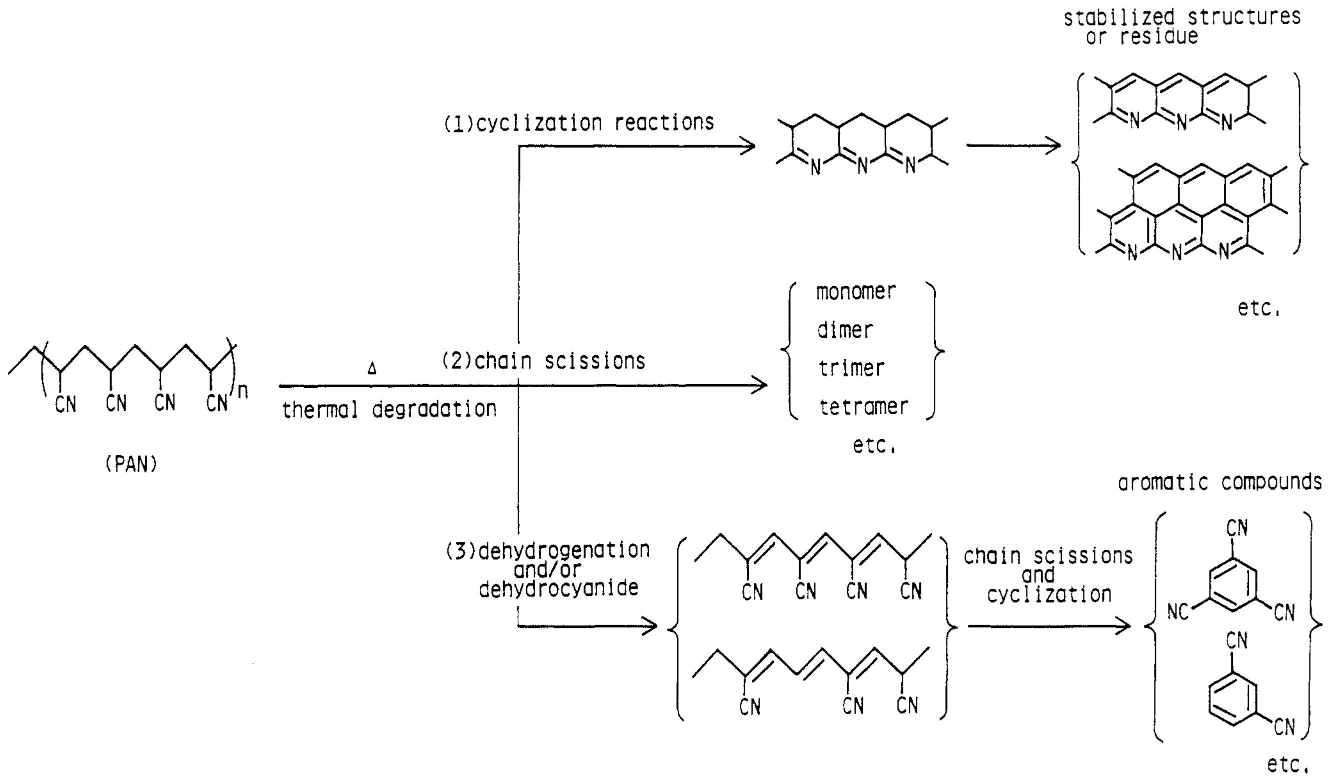


Figure 2. Competitive thermal reactions for PAN fibers during the pyrolysis.

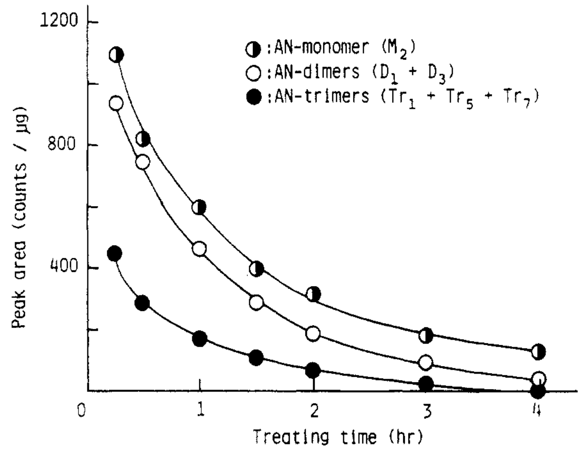


Figure 3. Relationships between the peak intensities per unit sample weight for monomer, dimers, and trimers formed at 700 °C and the treating time at 235 °C after the pretreatment at 215 °C for 20 min.

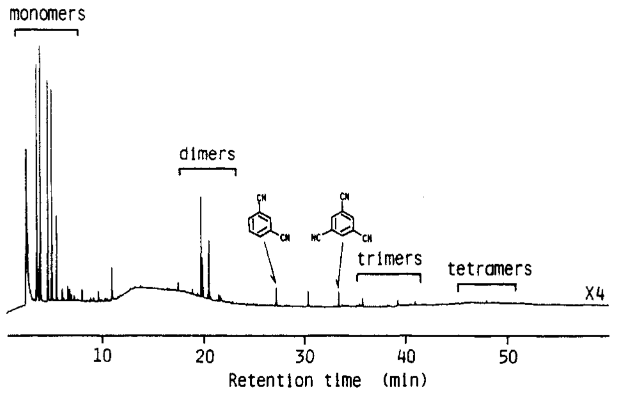


Figure 4. Pyrogram of a highly stabilized PAN fiber sample at 700 °C: sample, S-10; attenuation, ×4.

Table III
Relative Peak Intensity of CN-Substituted Aromatic Compounds

fiber sample[a]	relative peak intensity to AN monomer,[b] %	
	dicyano-benzene	tricyano-benzene
P-1	3.7	2.1
S-1	3.6	2.8
S-5	7.6	10.0

[a] Sample numbers are the same as those in Table I. [b] AN monomer: M_2 in Table II.

Figure 3 shows the relationships between the observed total peak intensities per unit weight (μg) for the monomer [C_3H_3N (M_2)], dimers [$C_6H_6N_2$ (D_1 + D_3)], and trimers [$C_9H_9N_3$ (Tr_1 + Tr_5 + Tr_7)] on the pyrograms at 700 °C and the treating time for the stabilization at 235 °C including the pretreatment at 215 °C for 20 min. In general, the peak intensities of all the cluster peaks decrease as a monotonous function of the treating time. However, the fact that the decrements of the bigger products become more significant suggests that the average AN-sequence length in the stabilized fibers becomes shorter after longer treating time.

Figure 4 shows a pyrogram at 700 °C for a highly stabilized PAN fiber sample (S-10), which is treated at 215 °C for 20 min, then at 235 °C for 15 min, and finally at 265 °C for 40 min. Here, the intensities of all the characteristic peaks on the pyrogram are negligibly small. However, it should be noted that the peaks of the CN-substituted aromatic compounds remain with relatively strong intensity.

Table III summarizes the observed relative peak intensities of the characteristic aromatic products when the precursor (P-1) and two stabilized PAN fiber samples (S-1 and S-5) are pyrolyzed at 700 °C. The fact that the relative yields of the CN-substituted aromatic compounds for the precursor PAN (P-1) and lightly stabilized PAN (S-1) are almost comparable suggests that the characteristic aromatic compounds are mostly produced during the pyrolysis step at 700 °C and that the formation of the conjugated polyene structures along the poly-

Table IV
Peak Intensity of Characteristic Products for Two Comparably Stabilized PAN Fiber Samples under Different Treating Conditions

	peak intensity (counts)[b] per unit weight sample (μg)				
fiber sample[a]	monomers	dimers	trimers	dicyano-benzene	tricyano-benzene
S-6	640.4	338.2	90.4	16.8	21.0
S-10	638.1	264.3	25.9	19.2	22.4

[a] Sample numbers are the same as those in Table I. [b] Monomers: $\sum_{i=1}^{5} M_i$. Dimers: $\sum_{i=1}^{7} D_i$. Trimers: $\sum_{i=1}^{7} Tr_i$.

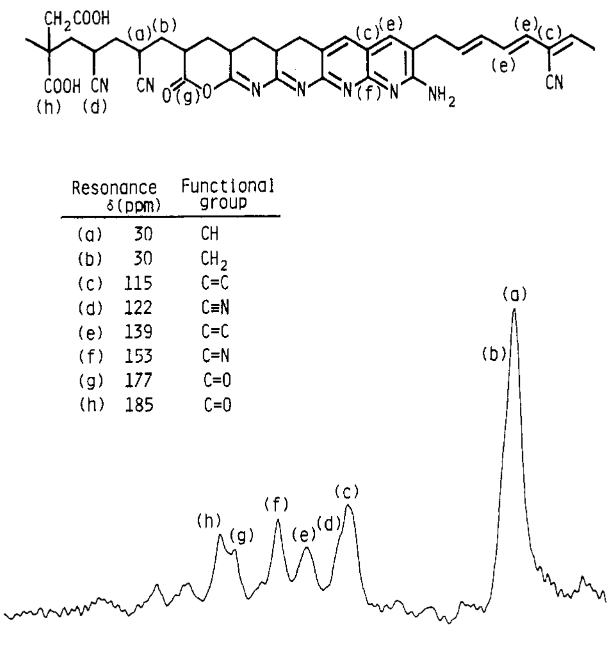
mer chain is not so significant during the given soft stabilization conditions. However, the fact that the relative yields of these aromatic compounds for the fully stabilized PAN fiber (S-5) prepared under the prolonged treating time at 235 °C are significantly stronger than those for the precursor (P-1) and the softly stabilized fiber (S-1) indicates that the conjugated polyene structures along the PAN fiber molecules should be preliminarily formed to some extent during the prolonged stabilization treatment at 235 °C. In other words, during the stabilizing treatment of PAN fibers mainly to form the stable ladder structures, the dehydrogenation and/or dehydrocyanide reactions to form the conjugated polyene structures along the backbone chain also participate to some extent depending on the stabilization conditions.

Table IV summarizes the observed relative yields of the characteristic products through the pyrolysis of two almost comparably stabilized PAN fiber samples (S-6 and S-10) prepared under different treating conditions: (a) milder conditions for longer time at 215 °C for 20 min and then at 235 °C for 180 min (200 min in total), and (b) severer conditions for shortened time at 215 °C for 20 min, then at 235 °C for 15 min, and finally at 265 °C for 4 min (75 min in total). Although the peak intensities of the main monomer peaks (M_1–M_5) for both samples are almost comparable, the yields of the dimers (D_1–D_7) and the trimers (Tr_1–Tr_7) for the sample S-6 are significantly stronger than those for the sample S-10. On the other hand, the yields of the CN-substituted aromatic products show an opposite tendency. These observations suggest that the stabilized fibers treated under the severer conditions have the shorter AN sequences and the much more amount of the conjugated polyene structures. Moreover, the fact that the carbonized final fibers from the sample S-6 have much more superior mechanical properties than those from the sample S-10 suggests that the conjugated polyene structures introduced by excess heating might cause undesirable final structures for the carbonized fibers.

CP/MAS ^{13}C NMR Studies. Recently the CP/MAS ^{13}C NMR spectra of thermally treated PAN fiber samples taken at 15.1[4] and 25.1 MHz[5] were assigned, and the structural change of the PAN fiber samples during the thermal treatment was studied.

Figure 5 shows the observed typical CP/MAS ^{13}C NMR spectrum taken at 62.9 MHz for a stabilized PAN fiber sample (S-10). Possible model structures of the PAN fiber sample under the stabilization process are also shown in Figure 5 to make the corresponding assignment of the characteristic resonance signals. The overall resolution of the spectrum is much improved because of the higher magnetic field (5.872 T) utilized.

Roughly speaking, the spectrum consists of two regions, namely the upfield aliphatic sp^3 region between 20 and 40 ppm and the downfield sp^2 and sp regions between 100 and 200 ppm. The former involves the resonance peaks of CH (a) and CH$_2$ (b), which are not resolved even on this spectrum. The latter comprises various resonance peaks (c–h) for C=C, C=O, C=N, and C≡N, whose possible assignments are shown in the model structures in Figure 5.



Resonance δ(ppm)		Functional group
(a)	30	CH
(b)	30	CH$_2$
(c)	115	C=C
(d)	122	C≡N
(e)	139	C=C
(f)	153	C=N
(g)	177	C=O
(h)	185	C=O

Figure 5. Typical solid-state ^{13}C NMR spectrum of a stabilized PAN fiber sample: sample, S-10.

Figure 6 shows the CP/MAS ^{13}C NMR spectra for the precursor PAN (P-1) and various PAN fiber samples differing in the treating conditions. On the spectrum of the precursor (A), in addition to the unresolved aliphatic CH and CH$_2$ peaks (a + b) around 30 ppm and the C≡N peak (d) at 122 ppm, a fairly strong C=O peak (h) at 185 ppm mainly originating from the comonomer components such as methyl methacrylate and itaconic acid are observed. However, it should be noted here that the spinning sideband from the resonance peak at 122 ppm (122 + 64 = 186 ppm) is also overlapping at the C=O peak (h).

As the stabilization reactions proceed, the spectra show drastic change. For example, as can be seen on the series of the spectra from (A) to (D), all the peaks (a + b, d, and h) characteristic of the precursor PAN decrease in their intensity monotonously with the lapse of the treating time, while various new peaks (c and e–g) appear between 115 and 177 ppm. As shown in Figure 6C, when the stabilization is reasonably attained, the resulting spectrum shows not only the newly appearing peaks of c and e–g, which reflect the cyclization reactions to form the stabilized structures, but also the fairly strong peak of a + b, which corresponds to the residual CH + CH$_2$ in the stabilized fiber sample. However, as shown in Figure 6D, on the spectrum of the excessively stabilized PAN fiber sample (S-8), the aliphatic resonance peak (a + b) becomes no more observable. Here, it is interesting to note that the C≡N signal at 122 ppm is still observed as a shoulder peak even on the spectra C and D. The residual nitrile groups in the fully stabilized PAN fiber samples should be mostly attributed to those bonded to the conjugated polyene structures, which are suggested to exist from the PyGC data mentioned above.

Here, it is worthwhile to compare the subtle differences in the two spectra C and F, which are confirmed to have an almost comparable degree of the stabilization

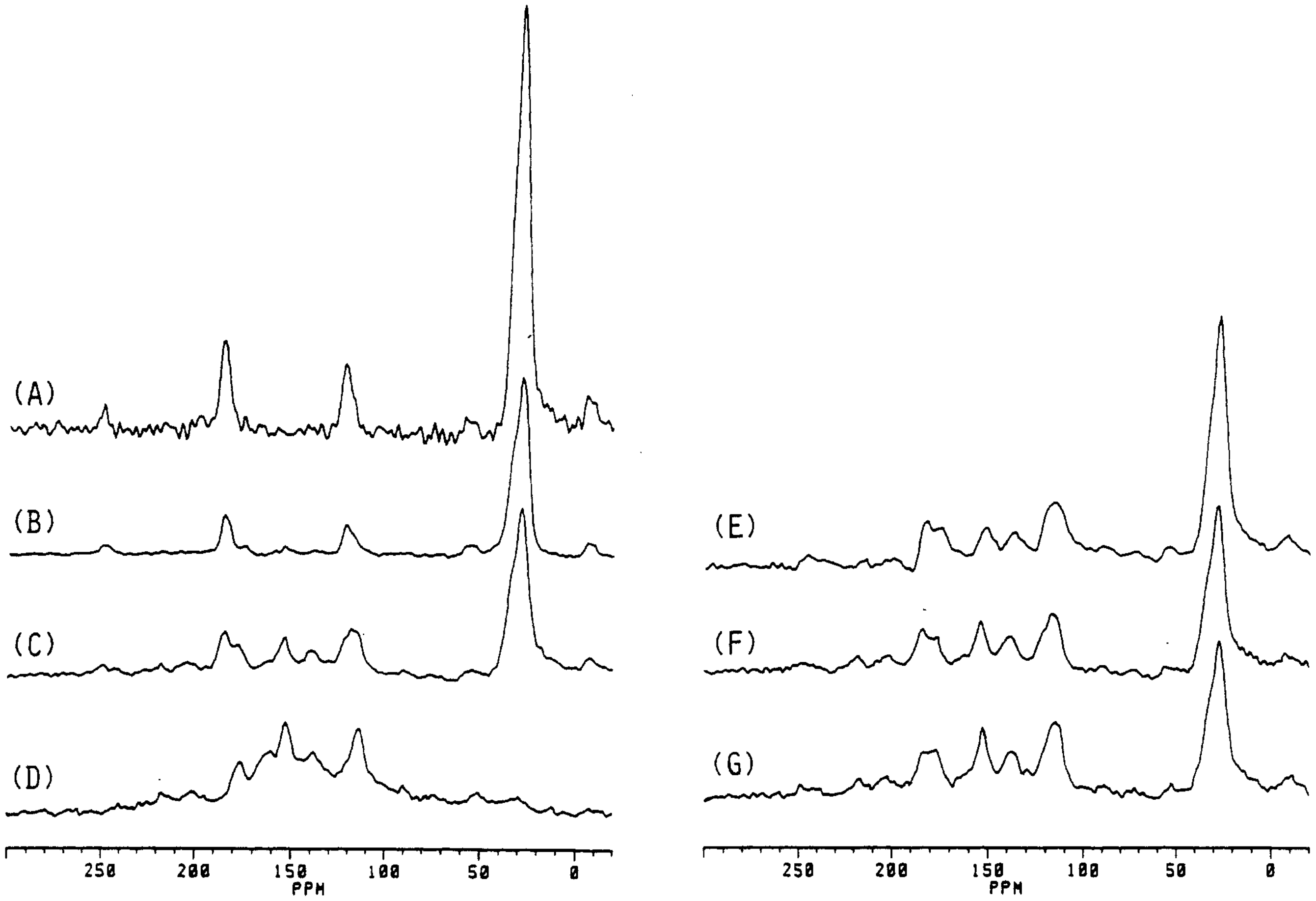


Figure 6. Solid-state ^{13}C NMR spectra of a precursor and various PAN fiber samples differing in the treating conditions: (A) P-1, (B) S-1, (C) S-6, (D) S-8, (E) S-9, (F) S-10, (G) S-11.

by PyGC. Although the whole spectra closely resemble each other, the relative intensities of the peak e at 139 ppm against the peak a + b at 29 ppm, which are good measures for the cyclization reactions and dehydrogenation and/or dehydrocyanide reactions to form the conjugated double bonds, were 0.07 for C and 0.13 for F. This observation also supports the possibility for the much abundant formation of the conjugated double bonds when the PAN fiber sample is stabilized finally at the higher temperature of 265 °C to shorten the total treating time.

FT-IR Studies. Figure 7 shows a series of the transmission FT-IR spectra for the precursor PAN (P-1) and the differently stabilized PAN fiber samples (S-1, S-6, and S-8). As was reported in the previous paper,[2,3,5,6] the most prominent changes observed are the decrease in the intensities of the C≡N band for saturated nitriles at 2240 cm^{-1} and those for aliphatic C–H ones around 2900 and 1450 cm^{-1} and the growth of the C=N, C=C, and cyclic C=O bands between 1580 and 1700 cm^{-1}. The fairly intense absorption at 1740 cm^{-1} for the precursor, which is assigned to the C=O band for the comonomer components such as methyl methacrylate and itaconic acid, also decreases as the degradation proceeds.

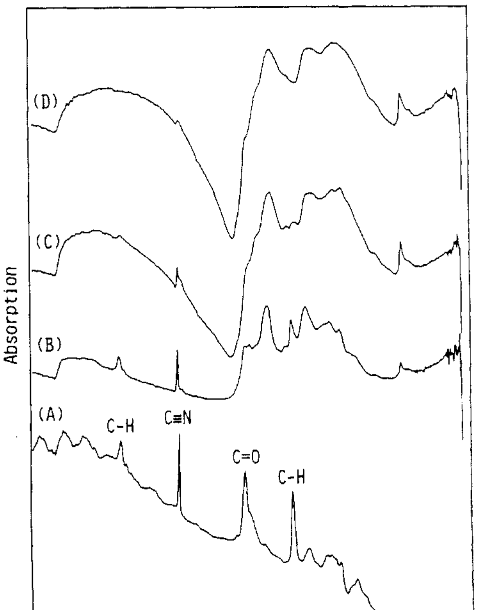


Figure 7. Series of transmission FT-IR spectra for a precursor and three differently stabilized PAN fiber samples: (A) P-1, (B) S-1, (C) S-6, (D) S-8.

On the other hand, the fact that the decreasing saturated nitrile band at 2240 cm^{-1} has a shoulder around 2200 cm^{-1} suggests that some different types of C≡N structures are formed during the thermal degradation. In the previous paper, these were tentatively attributed to the formation of the conjugated and/or β-amino type C≡N.[3-5] Here, it is interesting again to compare those bands for the comparably stabilized PAN fiber samples (S-6 and S-10) of which comparative studies by PyGC and solid-state ^{13}C NMR were mentioned above. Figure 8 shows the partial FT-IR spectra in the C≡N region for the two samples. Although the whole absorbances of the C≡N bands are almost comparable for the two samples, the absorbance ratios at 2200 and 2240 cm^{-1} (A_{2200}/A_{2240}) of 0.53 for S-6 and 0.70 for S-10 also suggest that

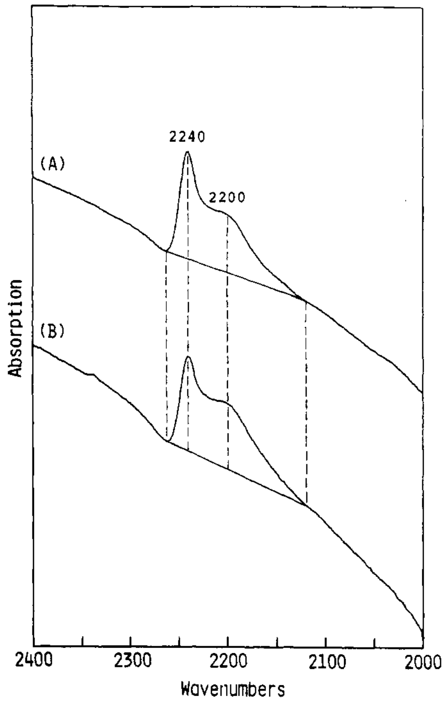


Figure 8. Partial FT-IR spectra in the $C{\equiv}N$ region for two comparably stabilized PAN fiber samples: (A) S-6, (B) S-10.

the latter severely but shortly treated PAN sample (S-10) has much more conjugated nitrile content than the former softly and slowly treated one (S-6).

In conclusion, the main stabilization mechanism of PAN fibers under oxidative thermal degradation to form cyclic ladder structures was indirectly and directly confirmed by PyGC and CP/MAS ^{13}C NMR and FT-IR, respectively. In addition, the contribution of dehydrogenation and/or dehydrocyanide reactions to form the conjugated polyene structures suggested by the data of PyGC especially for the PAN fibers treated at relatively higher stabilization temperatures was also supported by those of CP/MAS ^{13}C NMR and FT-IR.

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Registry No. PAN (copolymer), 26202-14-2.

Microstructural Analysis of Polysilapropynylene Copolymers by ^{13}C and ^{29}Si Nuclear Magnetic Resonance

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Received August 23, 1989;
Revised Manuscript Received November 21, 1989

ABSTRACT: The sequence distribution of poly(dimethylsilapropynylene-*co*-diphenylsilapropynylenes) $[[(Me_2SiC{\equiv}C-)_x(Ph_2SiC{\equiv}C-)_y]_n]$ has been studied by NMR spectroscopy. It is shown that the silylethynyl units are randomly distributed within the copolymer cyclic and linear chains at equilibrium. The distributions of triad and pentad sequences in the ^{29}Si NMR and of diad and tetrad sequences in the ^{13}C NMR have been determined theoretically and compared with experimental spectra. Rearrangement reactions leading to the randomized products occur and have been shown to compete with condensation reactions. This randomization process is independent of the nature of substituents on the silicon atom and temperature. The ratio of specific copolymerization equilibrium constants has been calculated, and the whole process of copolymerization is shown to be entropy driven.

Introduction

Silicon-containing polymers are finding an increasing number of applications in many areas of technology and research. The particular electronic structure of the silicon atom compared to that of carbon atom gives special properties to these polymers. The ability of the silicon atom to transmit electronic effects in silicon ethynyl derivatives has been known for many years.[1,2] We have recently reported the synthesis of pericyclynosilanes,[3] a class of cyclic compounds of the type $[(R_2SiC{\equiv}C-)_x(R'_2SiC{\equiv}C-)_y]_n$. These compounds are synthesized by the addition of a diorganodichlorosilane to a dilithium derivative of a diorganodiethynylsilane (Scheme I).

When $R = R'$, homopolymers can be prepared using this procedure, and when $R \neq R'$ copolymers containing equimolar quantities of the two silylethynyl units are formed. Single-crystal X-ray diffraction analysis confirmed the cyclic nature of $(Me_2SiC{\equiv}C-)_6$, which adopts a chair conformation similar to cyclohexane.[4] Copolymers containing different mole ratios of silylethynyl units, $-R_2SiC{\equiv}C-$ to $-R'_2SiC{\equiv}C-$, may be prepared by a coequilibration process (Scheme II).

Herein we describe the sequencing of (dimethylsilyl)-

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