Bull. Chem. Soc. Jpn., 56, 2802—2804 (1983)

Assignment of a Characteristic Infrared Absorption Band at 810 cm^{-1} in Heat-treated Polyacrylonitrile

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(Received August 10, 1982)

When polyacrylonitrile (PAN) was heat-treated at about 250 °C under nitrogen, a violent exothermic reaction took place. PAN lost weight and the infrared absorption at 2240 cm^{-1} disappeared, but there was little change in the atomic ratios of carbon, hydrogen, and nitrogen. This indicates that fragmentation is accompanied by rapid polymerization of cyano groups. The sample obtained after the completion of the exothermic reaction seems to be liable to oxidation, because a strong exothermic reaction and weight gain occur immediately if air is admitted to enter. During the oxidation the percentages of carbon and nitrogen did not change, but that of hydrogen largely decreased, indicating the occurrence of oxidation and subsequent dehydration in the moieties subjected to polymerization of cyano groups. Therefore, the tri-substituted carbon-carbon double bonds are formed in the six-membered ring systems. A new infrared absorption band which appears at 810 cm^{-1} is assigned to the C–H out-of-plane bending vibration in such a double bond.

Polyacrylonitrile (PAN) fiber is changed into flame-proof fiber by heat treatment in air at 200—300 °C.1) Carbon fiber is produced by heating the flame-proof fiber in an inert atmosphere at 1000—1500 °C.2) Thus a prior oxidative treatment is necessary in the preparation of carbon fiber from PAN fiber. In infrared absorption spectrum of PAN subjected to such an oxidative treatment, a strong absorption appears at 810 cm^{-1}. This was assigned to C–H out-of-plane bending vibration in $-CH{=}C(C{\equiv}N)-$,3–8) but no absorption appeared at 810 cm^{-1} in the spectra of the products obtained by dehydrochlorination of poly(α-chloroacrylonitrile).9) This fact is not consistent with the assignment.

Experimental

Preparation of PAN. The preparative method was reported in a previous work.10)

Isothermal Heat Treatment. Heat treatment of PAN was carried out in a differential thermal analyzer (Rigaku CAT. No. 8001 Thermoflex) to observe the change of the sample temperature. The rate of the temperature rise is 20 °C/min.

Infrared Absorption Spectra. A Hitachi EPI-G$_2$ diffraction grating infrared spectrophotometer was used. Samples were examined as KBr disks. Normalized absorbance (A) of an absorption band was calculated by the equation:

$$A = \frac{a}{w} \times \frac{W}{W_0},$$

where a is the observed absorbance for w mg of the sample, and W (mg) is the amount left after heating W_0 (mg) of PAN. The yield given in Table 1 was calculated by

$$\text{Yield} = \frac{W}{W_0} \times 100\ (\%).$$

Results and Discussion

Observation of an Exotherm in the Course of Heat Treatment. Change of the sample temperature was measured during the isothermal heat treatment (Fig. 1). Under nitrogen an exotherm due to polymerization of cyano groups was always observed when the heat-treatment temperature was above 230 °C. The differential temperature increases with the treatment temperature. Especially, generation of heat was very sharp for the heat treatment at *ca.* 250 °C. In air an exotherm due to both polymerization of cyano groups and oxidation was observed at *ca.* 220 °C, but the peak was broad and weak even at 250 °C. This indicates that oxygen can retard a rapid polymerization of cyano groups at *ca.* 250 °C.

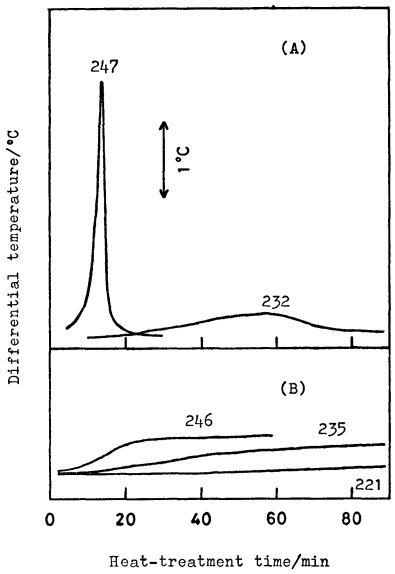


Fig. 1. Observation of an exotherm during isothermal heat treatment of 50 mg of PAN (A) under nitrogen and (B) in air. The heat-treatment temperature (°C) is given in the figure.

Compositions of Samples Heat-treated under Different Conditions. Samples 1, 2, 3, and 4 were heat-treated at 250 °C under the conditions given in Fig. 2. The yields and compositions are shown in Table 1. The percentage changes in carbon, hydrogen, and nitrogen due to the heat treatment are given in Table 2.

When PAN was heat-treated for 29 min under nitrogen, and for additional 10 min under reduced pressure, there was little change in the atomic ratios of carbon, hydrogen, and nitrogen although the weight loss was 6.3 wt%. This indicates fragmentation accompanied

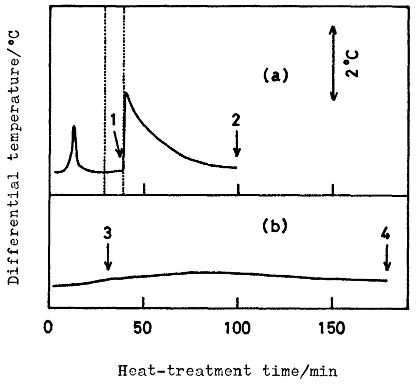


Fig. 2. Preparation of samples 1, 2, 3, and 4 by the isothermal heat treatment of 30 mg of PAN at 250 °C. The arrows indicate the end of heat treatment. Sample 1 was cooled by admitting nitrogen. Samples 2, 3, and 4 were cooled in a desiccator.
Atmosphere for heat treatment: (a) Nitrogen (0—29 min), reduced pressure (29—39 min), and air (39—99 min). (b) Air.

Table 1. Yields and analytical data of samples 1, 2, 3, and 4

Sample	Yield/%	Chemical compositions (%)				
		C	H	N	Ash	O (+Errors)
PAN	100	67.6	5.9	25.7	0.3	0.5
1	93.7	65.9	5.5	24.4	0.5	3.7
2	98.3	62.9	3.2	22.5	0.9	10.5
3	98.7	—	—	—	—	—
4	94.3	60.1	3.4	22.1	1.0	13.4

Table 2. Changes in weights of carbon, hydrogen, and nitrogen by heat-treating PAN

Sample	Residual weights (%)		
	C	H	N
PAN	100	100	100
1	91.3	87.3	88.9
2	91.5	53.4	86.1
4	83.8	54.4	81.1

by rapid polymerization of cyano groups. Sample 1 seems to be liable to oxidation, because a strong exothermic reaction and weight gain occur immediately if air is admitted to enter. Since weight loss of sample 2 obtained by heat-treating sample 1 in air for 60 min was 1.7 wt%, it is clear that oxygen combined with sample 1 to give weight gain of at least 4.6 wt%. During the oxidation the percentages of carbon and nitrogen did not change, but that of hydrogen decreased remarkably. This indicates that sample 1 was easily oxidized and subsequently dehydrated.

Sample 4 obtained by heat-treating PAN in air for 179 min resembles sample 2 and flame-proof fibers[1,11] in composition. Further there was no difference between the weight losses of hydrogen for a flame-proof fiber[11] and samples 2 and 4. The weight losses of carbon and nitrogen for a flame-proof fiber[11] and sample 4, however, were much higher than those for sample 2. This indicates that the degree of degradation for a flame-proof fiber[11] and sample 4 is much higher than that for sample 2.

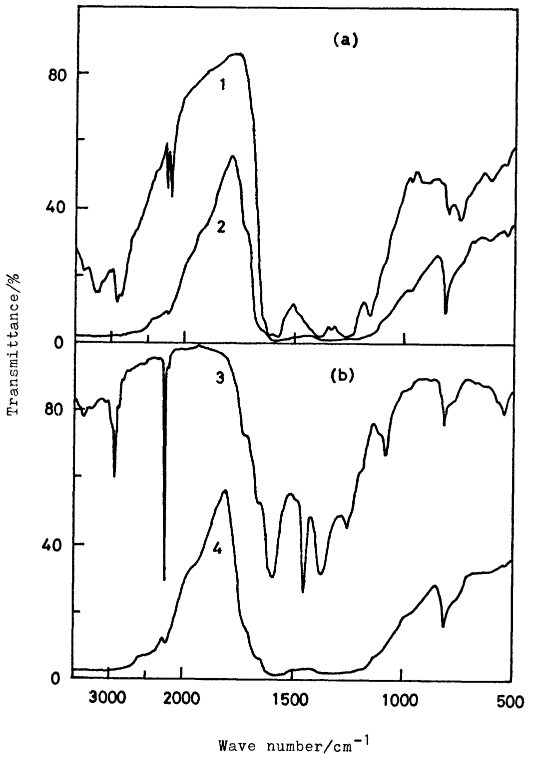


Fig. 3. Infrared absorption spectra of samples 1, 2, 3, and 4.

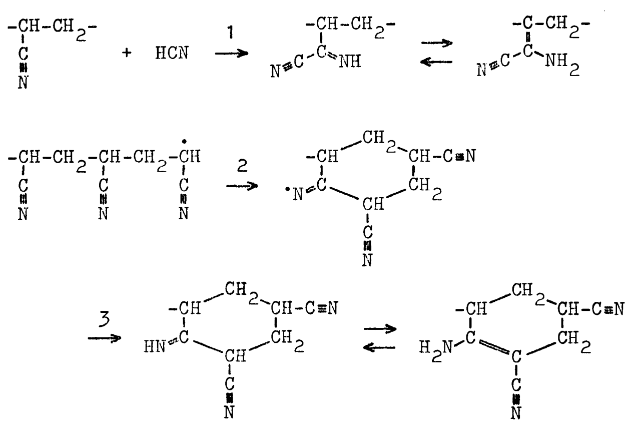
Table 3. Normalized absorbances at 2240, 2220, 2200, and 810 cm^{-1} in infrared absorption spectra of samples 1, 2, 3, and 4

Sample	Normalized absorbances			
	2240 cm^{-1}	2220 cm^{-1}	2200 cm^{-1}	810 cm^{-1}
PAN	0.300			
1	0.054		0.072	—[a]
2		0.034		0.221
3	0.254		0.010	0.036
4		0.050		0.121

a) Only observed as a shoulder of the band at 800 cm^{-1}.

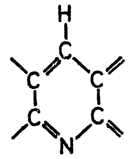
Infrared Spectra of Samples Heat-treated under Different Conditions. Infrared spectra of samples 1, 2, 3, and 4 are shown in Fig. 3. The normalized absorbances at 2240, 2220, 2200, and 810 cm^{-1} are given in Table 3.

Since sample 1 had rapid polymerization of cyano groups, the absorbance of the C≡N stretching vibration band at 2240 cm^{-1} was below 1/5 of the value for PAN. However, there is no reason why 4/5 of cyano groups are lost only by polymerization, because it is accompanied by the elimination of volatile fragments and the appearance of a band at 2200 cm^{-1}. The following reactions[12,13] will be related with the appearance of this band:



(A) (B)

In these reactions the atomic ratios do not change. The band at 2240 cm^{-1} disappears with reaction 1, but moieties A and B formed by six-membered ring formation 2 and subsequent hydrogen abstraction 3 have cyano groups which absorb at 2240 cm^{-1}. This explains why sample 1 obtained after the completion of rapid polymerization of cyano groups shows the band at 2240 cm^{-1}.

Sample 2 shows a strong absorption at 810 cm^{-1}, which is the characteristic band appearing in the spectra of PAN samples heat-treated in the presence of oxygen.[3-8,14] If this band is due to $-CH=C(C\equiv N)-$ formed by the oxidation and subsequent dehydration in acrylonitrile repeating units,[4] its absorbance for sample 4 must be higher than that for sample 2, because the amount of acrylonitrile repeating units for sample 1 is below 1/5 of that for PAN. Since the reverse is the case, the band at 810 cm^{-1} cannot be assigned to the C–H out-of-plane bending vibration in $-CH=C(C\equiv N)-$. A band at 2220 cm^{-1} can be assigned to the C≡N stretching vibration in such a moiety. As stated above, the moieties subjected to polymerization of cyano groups are readily liable to oxidation followed by dehydration. Therefore, when sample 1 is heat-treated in air,  should be easily formed. Since sample 2 should have such a moiety and shows a strong band at 810 cm^{-1}, this band is assigned to the C–H out-of-plane bending vibration in this moiety.

When PAN is subjected to slow polymerization of cyano groups in air, a band at 810 cm^{-1} will appear after completion of the exothermic reaction caused by polymerization and oxidation. Consequently sample 4 is expected to show such a strong band at 810 cm^{-1}. However, the normalized absorbance observed was only 0.121, much lower value than that for sample 2. This seems to be related with a higher degree of degradation for sample 4 than for sample 2.

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