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Chlorination of Polyacrylonitrile and Analysis of Its Products

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Chlorination of polyacrylonitrile (PAN) was carried out by passing dried chlorine gas through a tetrahydrothiophene 1,1-dioxide (sulfolane) solution of PAN or a powdery mixture of PAN with sodium chloride. The chlorinated products were examined by comparison with acrylonitrile–α-chloroacrylonitrile (CAN) copolymers corresponding to α-chlorinated PANs. In solution the reaction proceeded easily below 100 °C, but due to side reactions analysis of the products was difficult. In the powdery mixture hardly any reaction took place below 100 °C, but in the range 120—140 °C, the reaction proceeded smoothly and its rate became *ca.* 2.7 times in proportion as its temperature was raised by 10 °C. The chlorinated products were investigated by means of infrared and thermal analyses. The chlorinated moiety consists mainly of α,β-dichlorinated units, which seem to result from the addition of chlorine to the double bonds produced by dehydrochlorination after β-chlorination. These chlorinated products were dehydrochlorinated at lower temperature than acrylonitrile–CAN copolymers, but in many respects they resemble each other in the behavior of thermal degradation.

Grassie and McGuchan[1] carried out bulk copolymerization of acrylonitrile with α-chloroacrylonitrile (CAN) and recognized from the favorable thermoanalytical behavior of the copolymers obtained that the copolymers can be used for carbon fiber processing. They correspond to the partially α-chlorinated polyacrylonitrile (PAN). Chlorination of PAN remains to be investigated. However, if it proceeds preferentially on the α-carbon of the PAN molecule, its products should assume the same thermal behavior as copolymers.

Chlorination of PAN was studied in three different states: (1) dispersed powder in carbon tetrachloride, (2) solute in tetrahydrothiophene 1,1-dioxide (sulfolane), and (3) dispersed powder in sodium chloride powder. The reaction did not proceed in the first state but the chlorinated products could be obtained in the second and third states. In this work, these products were examined in comparison with acrylonitrile–CAN copolymers.

Experimental

Preparation of PAN. Two hundred and ninety grams of freshly distilled acrylonitrile was dissolved in 400 cm^3 of *N,N*-dimethylformamide (DMF). This solution and 0.8 g of α,α′-azobisisobutyronitrile (AIBN) dissolved in 40 cm^3 of DMF were put into a three-necked flask which had been evacuated with an oil pump and flushed with nitrogen several times. Stirring was started. The temperature inside the flask was maintained at 47 °C; it rose to 52 °C immediately after addition of AIBN. After 11.5 h, the reaction mixture was diluted with 400 cm^3 of DMF containing 0.01 g of hydroquinone, and then poured into 20 dm^3 of distilled water. The precipitate was filtered, washed with methanol and distilled water at 70 °C, and dried in a vacuum at 50 °C to constant weight. The yield was 92.7 g. The intrinsic viscosity, $[\eta]$, in DMF at 35 °C was 2.54.

Preparation of Acrylonitrile–CAN Copolymers. The method was reported in a previous work.[2]

Chlorination of PAN in A Solution State. Sulfolane (bp 122 °C at 4 mmHg (1 mmHg≈133.3 Pa)) was used as a solvent. Chlorination was carried out by passing dried chlorine gas at *ca.* 25 cm^3/min through a polymer solution consisting of 0.2 g of PAN and 40 cm^3 (at 100 °C) of sulfolane. The solution was bubbled with nitrogen for 15 min prior to the admission of chlorine gas. A magnetic stirrer was used and the solution was illuminated with a 100-W National Electric street lamp. After the lapse of reaction time (Table 1), the reaction system was purged with nitrogen and the solution was poured into 1 dm^3 of methanol. The precipitate was filtered, washed with methanol for 18 h using a Soxhlet extractor, and dried at 30 °C in a vacuum oven to constant weight.

Chlorination of PAN in a Solid State. One gram of PAN powder was dispersed in 50 g of sodium chloride powder. The mixture was thoroughly dried and then charged in a U tube

Table 1. Chlorination of PAN in a solution state

Reaction temperature °C	Reaction time h	Chlorine content of product wt%
55	10	9.17
80	10	16.10
110	10	22.20
120	3	9.84
120	10	23.70
135	2	6.64
135	3	9.70
135	10	23.10

Table 2. Chlorination of PAN in a solid state

Reaction temperature °C	Reaction time h	Chlorine content of product wt%
100	20	4.49
120	4	4.03
120	7	7.32
120	10	9.85
130	2	2.70
130	3	4.35
130	5	10.81
130	10	20.82
140	2	5.73
140	3	10.84
140	5	22.45
140	8	34.84
140	10	42.11
140	20	49.54

The process of chlorination was similar to that for solution state. The reaction temperature and time are given in Table 2. After the reaction, the mixture was washed with distilled water until no chloride ion could be detected. The product obtained was dried in a vacuum at 30 °C to constant weight.

Chlorine Analysis and Measurement of Infrared Absorption Spectra. The methods were reported in a previous work.[3]

Thermomechanical Analysis (TMA). The measurement was carried out under tension at a heating rate of 10 °C/min with a Shimadzu TMA-20 Thermomechanical Analyzer. The sample was cut from the casting film (15—40 μm thick), the measurement being carried out with 5 g load.

Differential Thermal Analysis (DTA). A Rigaku CAT. No. 8001 Thermoflex was used. Fifty milligrams of sample was employed in each experiment and heated at a 5 °C/min rate under nitrogen.

Results and Discussion

Infrared Absorption Spectra of Acrylonitrile–CAN Copolymers. Acrylonitrile–CAN copolymers,[2] corresponding to α-chlorinated PANs, were studied before examining the chlorination of PAN. The infrared spectrum of a copolymer, shown in Fig. 1, is similar to the combination of spectra of PAN[2] and poly(α-chloroacrylonitrile)[3] (PCAN). In the copolymers, the bands at 2240 and 500 cm^{-1} were chosen as the characteristic bands of acrylonitrile and CAN[4] units, respectively. The absorbances and whether the molar extinction coefficients were affected by copolymerization were determined. Each absorbance was normalized by the equation

$$A = \frac{a}{w} \times \left(1+\frac{34.445\,x}{3545.3-34.445\,x}\right), \qquad (1)$$

where A is the normalized absorbance, a the observed absorbance for w mg of sample, and x the chlorine content of sample.

The relationship between the number of chlorine atoms in 100 monomer units (N_{Cl}) and the absorbances at 2240 and 500 cm^{-1} (A_{2240} and A_{500}) is shown in Figs. 2 and 3 by solid lines. N_{Cl} was calculated by the equation

$$N_{\mathrm{Cl}} = \frac{53.064\,x}{3545.3-34.445\,x} \times 100. \qquad (2)$$

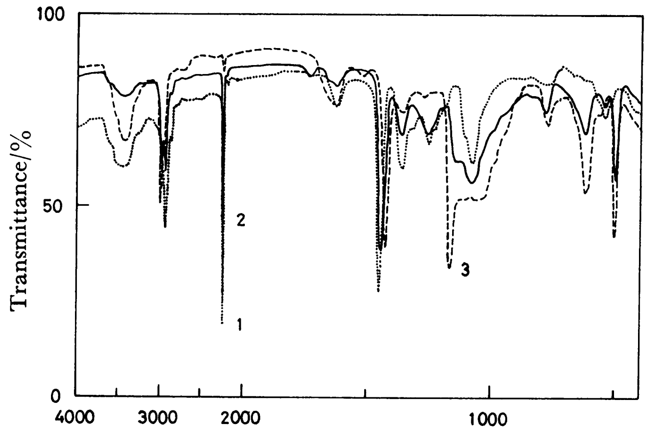


Fig. 1. Infrared absorption spectra of (1) PAN, (2) acrylonitrile–CAN copolymer (chlorine content: 20.25 wt%), and (3) PCAN.

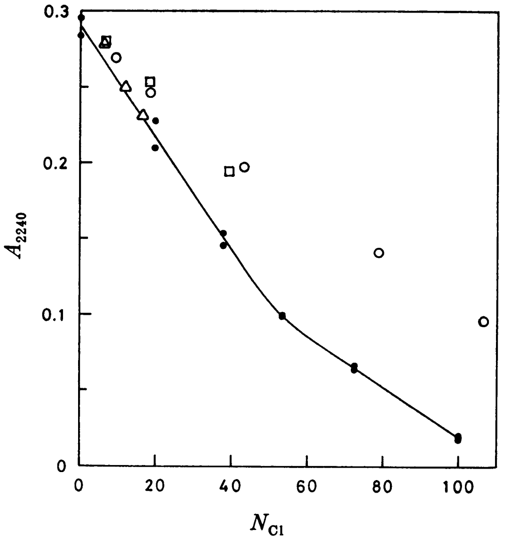


Fig. 2. Relationship between the number of chlorine atoms in 100 monomer units and the absorbance at 2240 cm^{-1}. ●: Acrylonitrile–CAN copolymers. △, □, and ○: Products chlorinated at 120, 130, and 140 °C, respectively, in a solid state.

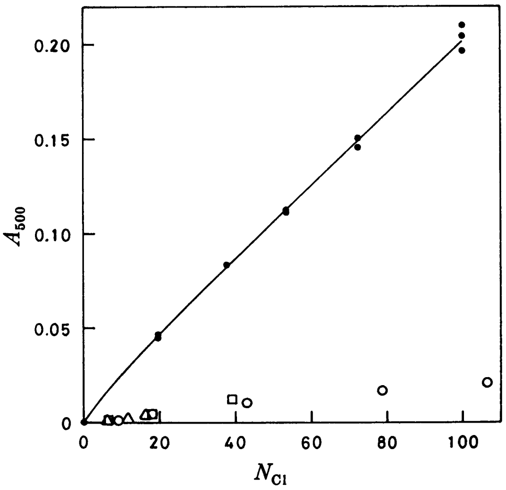


Fig. 3. Relationship between the number of chlorine atoms in 100 monomer units and the absorbance at 500 cm^{-1}. The symbols used here are the same as those in Fig. 2.

We see that the result for the band at 2240 cm^{-1} deviates considerably from the combination of absorbances of homopolymers, while at 500 cm^{-1} they are nearly equal. The chemical environment of acrylonitrile units in copolymer changes with position in the chain. In such cases, band broadening may occur. However, none was observed, indicating that the molar extinction coefficient of the 2240 cm^{-1} band in the copolymer is smaller than that in PAN, and that great care should be taken when using the absorbance of the band at 2240 cm^{-1} for determining the mole fraction of acrylonitrile units in a chlorinated PAN.

If only α-chlorination takes place during the course of chlorination of PAN, methylene groups do not change in number. However, with change in their chemical

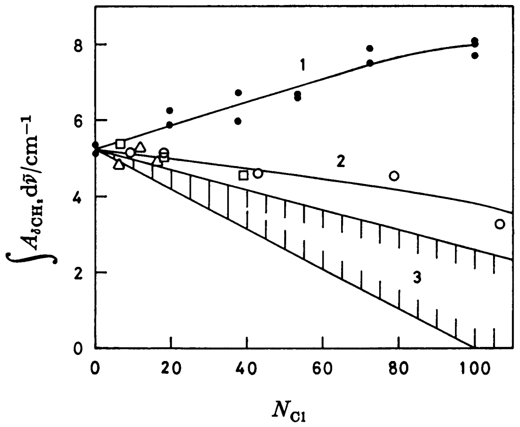


Fig. 4. Relationship between the number of chlorine atoms in 100 monomer units and the areal intensity of methylene scissoring vibration band. The symbols used here are the same as those in Fig. 2. Curves 1 and 2 express the changes which follow α-chlorination and the chlorination in a solid state, respectively. Area 3 is the expected one for β-chlorination (including β,β-dichlorination).

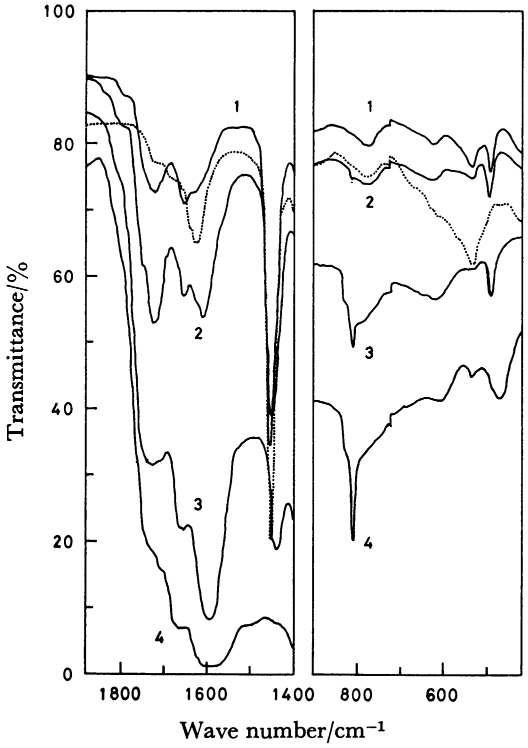


Fig. 5. Infrared absorption spectra of products chlorinated in sulfolane.

1, 2, 3, and 4: Products chlorinated at 55, 80, 110, and 135 °C, respectively, for 10 h. ……: PAN heated at 150 °C for 10 h in sulfolane under nitrogen flow.

environment both methylene stretching and bending vibrations are affected (Fig. 1). The methylene scissoring vibration band appears at 1455 cm^{-1} in PAN and 1430 cm^{-1} in PCAN. In the copolymers, the integrated intensity of this band, $\int A_{\delta\mathrm{CH}_2}\mathrm{d}\bar{\nu}$, was calculated in the range 1540—1400 cm^{-1} (Fig. 4). Here, $A_{\delta\mathrm{CH}_2}$ is the absorbance of methylene scissoring vibration band at a wave number ($\bar{\nu}$). We see from Curve 1 that the integrated intensity increases with the progress of α-chlorination, being nearly equal to the combination of the intensities in PAN and PCAN.

Chlorination of PAN in a Solution State and Analysis of Its Products. The chlorine content and infrared spectra of chlorinated products are shown in Table 1 and Fig. 5, respectively. In the case of chlorination above 100 °C, there is a ceiling in the chlorine content (Table 1). Although the 500 cm^{-1} band appears, its intensity is weak in comparison with that in the copolymer which has a corresponding chlorine content (see Fig. 1). In addition, strong absorptions are observed in the range 1800—1500 cm^{-1}. The absorptions in the neighborhood of 1700 cm^{-1} show that cyano groups have been transformed into carboxyl or carbamoyl groups. Since the formation of these groups was hardly observed without the admission of chlorine gas (Fig. 5), some side reaction should proceed simultaneously with chlorination.[5] The absorption at *ca.* 1600 cm^{-1} shows the progress of polymerization of cyano groups. A conspicuous absorption appears at *ca.* 810 cm^{-1} which seems to correspond to the characteristic band appearing in the heat-treatment of PAN in the air.[7] Chlorination is accompanied by several side reactions, making the analysis of chlorinated products difficult. The side reactions seem to cause the above-mentioned ceiling in the chlorine content.

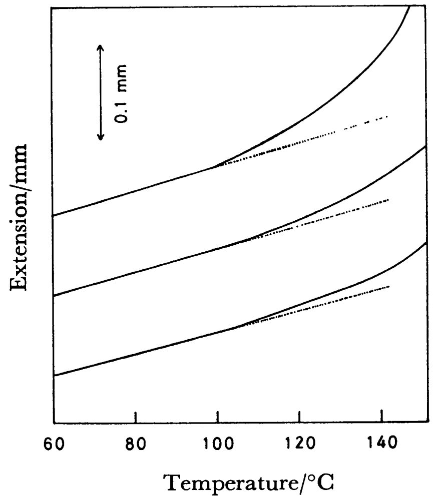


Fig. 6. TMA curves for PAN.

Chlorination of PAN in a Solid State and Analysis of Its Products. *Change of Chlorine Content Following Chlorination*: The chlorine content of chlorinated products is given in Table 2. It was found that the reaction scarcely proceeds at 100 °C. The reaction in a solid state should be accompanied by diffusion of chlorine into PAN granules. The rate of diffusion in a rubbery material is expected to be considerably higher than in a glassy one. Figure 6 shows TMA curves for original PAN. The rates of extension are equal below 100 °C but start to change at 100—110 °C, the glass transition temperature being *ca.* 100 °C. The reaction proceeded smoothly at 120, 130, and 140 °C. In the reaction at 140 °C, one chlorine atom per monomer unit was incorporated after *ca.* 10 h, chlorination proceeding further.

The degree of chlorination is proportional to the weight gain resulting from chlorination, since no side reaction which brings about the change in sample weight was observed during the course of chlorination. The weight gain is expressed by the following equation:

$$\text{Weight gain} = \frac{34\,445\,x}{3545.3-34.445\,x} \times 100(\%), \qquad (3)$$

where x is the chlorine content of chlorinated PAN. The relationship between chlorination time and weight gain is shown in Fig. 7. The rate of chlorination above 120 °C becomes *ca.* 2.7 times in proportion as the reaction temperature was raised by 10 °C.

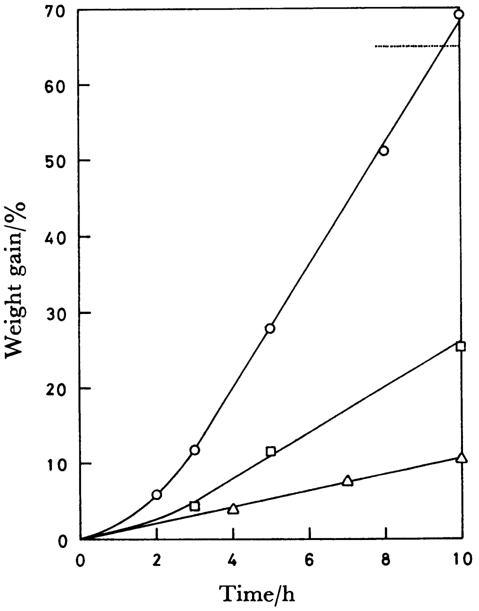


Fig. 7. Weight gain due to chlorination in a solid state. Chlorination temperatures are 120 (△), 130 (□), and 140 °C (○). A dotted line indicates the level of weight gain due to substitution of one hydrogen atom per monomer unit with one chlorine atom.

Infrared Analysis of Chlorinated Products: Infrared spectra of chlorinated products are shown in Fig. 8. No absorption related with side reactions was observed except in the neighborhood of 1600 cm^{-1}. New absorptions appearing in the neighborhood of 800 cm^{-1} and increasing with the progress of chlorination can be assigned to C–Cl stretching vibrations. A slight polymerization of the cyano groups proceeds simultaneously with chlorination but sample weight is changed by only chlorination. Thus each infrared absorption band can be quantitatively treated by means of the weight gain which follows chlorination.

A_{2240}, A_{500}, and $\int A_{\delta\mathrm{CH}_2}\mathrm{d}\tilde{\nu}$ were calculated using Eq. 1. The results shown in Figs. 2, 3, and 4, respectively, indicate that a preferential α-chlorination hardly occurs. Here, β-chlorination should be considered. In this case, $\int A_{\delta\mathrm{CH}_2}\mathrm{d}\tilde{\nu}$ is an effective measure. When only β-chlorination (including β,β-dichlorination) proceeds, the value should be in Area 3. However, Curve 2 expresses the change of this value which follows chlorination at 120, 130, and 140 °C. It is in agreement with the change in PAN which undergoes nearly equal chlorination on both CH_2 and CH groups. If the chlorination on CH groups proceeds independently of that on CH_2 groups, absorbance of the 500 cm^{-1} band should become much higher than that in Fig. 3. It seems that the chlorinated moiety consists mainly of α,β-dichlorinated units. Figure 2 is not contradictory, since the rate of decrease in the absorbance is about half of that in α-chlorination. Such a substitution of two chlorine atoms per monomer unit would still leave many monomer units even if 100 chlorine atoms per 100 monomer units were incorporated, making further chlorination possible.

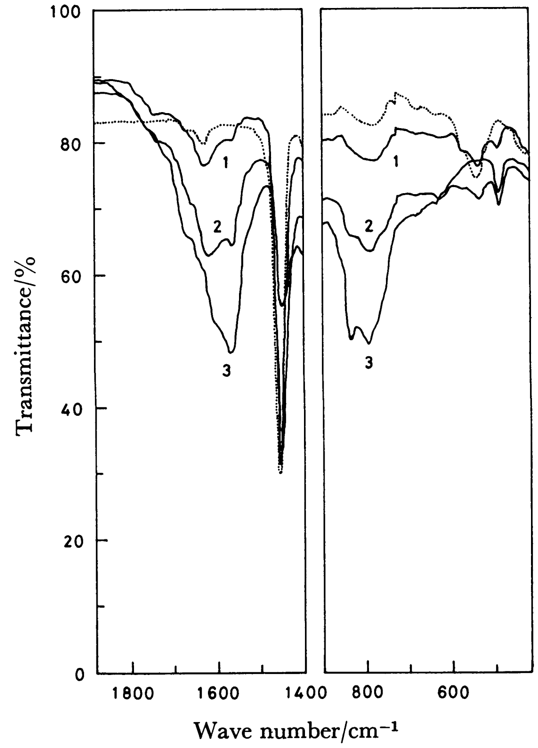


Fig. 8. Infrared absorption spectra of products chlorinated in a solid state.
1, 2, and 3: Products chlorinated at 120, 130, and 140 °C, respectively, for 10 h. ······: PAN heated at 130 °C for 10 h in sodium chloride powder under nitrogen flow.

Thermal Analysis of Chlorinated Products: Figure 9 shows the DTA curves for products chlorinated at 130 and 140 °C for 10 h. The differential temperature, ΔT, is very small, exothermic reaction taking place at a temperature lower than that of the reactions in PCAN, acrylonitrile–CAN copolymers,[1] and PAN. When these two chlorinated products were heated at a rate of 5 °C/min under nitrogen in the DTA apparatus, their chlorine contents changed (Table 3). Since the number of chlorine atoms in 100 monomer units changes with dehydrochlorination following heating, its value, N'_{Cl}, was calculated by the following equation:

$$N'_{\mathrm{Cl}} = \frac{\left(53.064-2.016\times\frac{N_{\mathrm{Cl}}}{100}\right)x'}{3545.3-36.461\,x'} \times 100, \qquad (4)$$

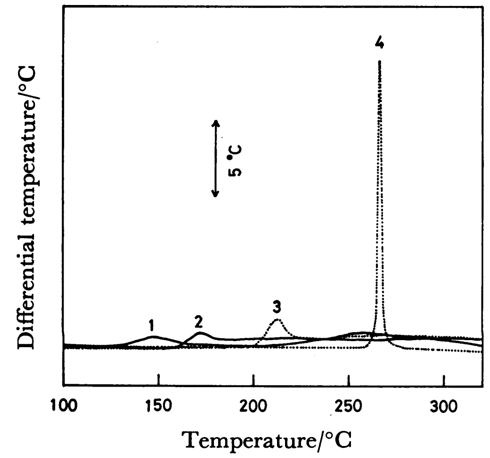


Fig. 9. Comparison in DTA curves between products chlorinated in a solid state (1 and 2) and PCAN (3) or PAN (4). 1 and 2: Products chlorinated at 130 and 140 °C, respectively, for 10 h.

TABLE 3. CHANGE OF CHLORINE CONTENT IN CHLORINATED PAN DURING HEATING PROCESS[a)]

Sample[b)]	Temperature °C	Chlorine content wt%
1	Before heating	20.82
	127	18.94
	149	15.68
	172	11.53
	197	8.27
	222	5.32
	259	3.25
	320	1.57
2	Before heating	42.11
	156	39.57
	185	35.03
	217	29.52
	251	22.03
	284	18.01
	320	11.71
	390	7.20

a) Heating was carried out at a rate of 5 °C/min under nitrogen in DTA apparatus. b) Samples 1 and 2 were chlorinated at 130 and 140 °C, respectively, for 10 h in sodium chloride powder.

where x' is the chlorine content of heated sample. The values obtained are shown in Fig. 10. From a comparison of Figs. 9 and 10, it was found that thermal dehydrochlorination starts at about the initiation temperature of exothermic reaction. The mode resembles that in PCAN and acrylonitrile–CAN copolymers.[1,4,8)] This indicates that, even in chlorinated PANs, the initiation of polymerization of cyano groups takes place as a side effect of the thermal dehydrochlorination.[1)] On the other hand, dehydrochlorination in chlorinated PANs occurs at a temperature lower than that in acrylonitrile–CAN copolymers[1)] and PCAN. This indicates that β-substituted chlorine atoms are easily dehydrochlorinated at lower temperature than α-chlorine atoms. It seems that α,β-dichlorinated units

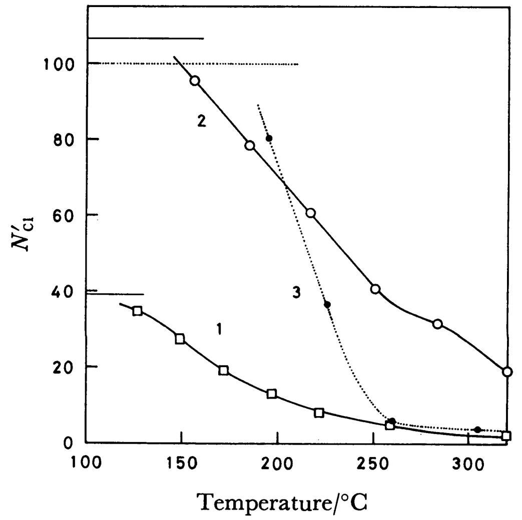
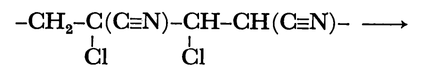


Fig. 10. Changes of the number of chlorine atoms in 100 monomer units during heating process.
1 and 2: Products chlorinated at 130 and 140 °C, respectively, for 10 h in a solid state, 3: PCAN.

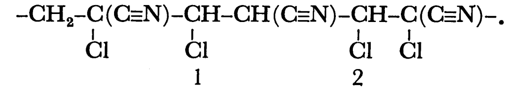
result from the addition of chlorine to the double bonds produced by dehydrochlorination after β-chlorination. The dehydrochlorination shown in Fig. 10 is nearly completed in both PCAN and slightly chlorinated PAN, but not in highly chlorinated PAN before the sample temperature reaches 300 °C. This can be interpreted by considering the α,β-dichlorinated unit as a chlorinated moiety. A chlorinated moiety is usually easily dehydrochlorinated. The reaction can be expressed by



$$-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{C}}(\mathrm{C{\equiv}N})-\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH(C{\equiv}N)}- \longrightarrow$$

$$-\mathrm{CH{=}C(C{\equiv}N)-CH{=}C(C{\equiv}N)}- + 2\,\mathrm{HCl}.$$

When dehydrochlorination took place, three new infrared absorption bands appeared, corresponding to the characteristic bands of dehydrochlorinated PCAN.[3)] However, complete dehydrochlorination is difficult in highly chlorinated PAN, since there should be chlorine atoms not subjected to intramolecular dehydrochlorination. An example is the case of chlorine atom 1 or 2 in



$$-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{C}}(\mathrm{C{\equiv}N})-\underset{\substack{\mathrm{Cl}\\1}}{\mathrm{CH}}-\mathrm{CH(C{\equiv}N)}-\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\substack{\mathrm{Cl}\\2}}{\mathrm{C}}(\mathrm{C{\equiv}N})-.$$

In order to examine the change of thermal behavior which follows chlorination, DTA curves were constructed for the products chlorinated at 130 °C (Fig. 11). In the case of the sample of low chlorine content, ΔT is still fairly high, the exothermic peak temperature

TABLE 4. CHLORINATION OF PCAN IN A SOLID STATE

Reaction temperature °C	Reaction time h	Chlorine content of product wt%
No chlorination		39.37[a)]
120	5	38.99
130	10	40.45
150	4	38.73

a) See Reference 9.

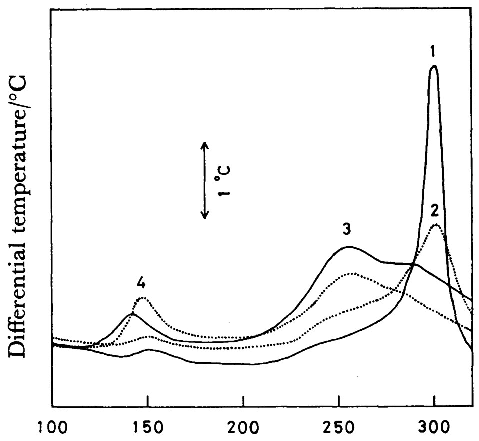


Fig. 11. DTA curves for products chlorinated at 130 °C in a solid state.
1, 2, 3, and 4: Products chlorinated for 2, 3, 5, and 10 h, respectively.

becoming higher than in PAN. Highly chlorinated samples exhibit broad complex exotherms at lower temperatures. Such DTA behavior is similar to that in acrylonitrile–CAN copolymers.[1] Although chlorinated PAN differs from acrylonitrile–CAN copolymer in chemical structure, they resemble each other as regards the mode of thermal degradation.

Possibility of The Chlorination or Hydrochlorination of Cyano Groups: There is a possibility that cyano groups in PAN undergo chlorination or hydrochlorination during the course of chlorination of PAN in a solid state. It is difficult to confirm whether cyano groups are chlorinated in the case of PAN; the groups in PCAN[9] are not chlorinated under similar conditions (Table 4). There might be a similarity in the case of PAN. If hydrochlorination takes place, a band would appear at *ca.* 1690 cm^{-1},[6] but no such band was observed (Fig. **9**).

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