Differential Thermal Analysis of Polyacrylonitrile in the Presence of Chlorine-Containing Polymers

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A differential thermal analysis (DTA) of polymer blends of polyacrylonitrile (PAN) with poly (α-chloroacrylonitrile) (PCAN) and poly (vinyl chloride) (PVC), prepared by coprecipitation from a solution containing both polymers, was carried out under nitrogen. Even if a small amount of PCAN or PVC was added to PAN, the exotherm peak position due to violent polymerization of the cyano groups, which appears at ca. 260 °C in pure PAN, shifts to the higher-temperature side by ca. 40 °C and its intensity becomes lower. Moreover, a new generation of heat is observed above ca. 220 °C and ca. 260 °C in the case of PAN–PCAN and PAN–PVC, respectively. These results were associated with the HCl generated during the heating process, since the chlorine atom formed by the reaction of a thermally degraded PAN polymer radical with HCl can both initiate polymerization of the cyano groups in PAN and terminate progress in polymerization by combination. Namely, DTA behavior could be explained by the effect of initiation (in the case of PAN–PCAN) and termination (in the case of PAN–PVC) upon the polymerization of cyano groups both below and above the temperature, respectively, at which PAN begins to be subjected to a sharp transition.

Hydrogen chloride has the effect of changing the thermal degradation behavior of polyacrylonitrile (PAN).[1)] This effect is observed even when differential thermal analysis (DTA) is carried out under nitrogen for copolymers of acrylonitrile with chlorine-containing monomers; the exothermic polymerization of cyano groups is delayed and the differential temperature is reduced, as compared with the DTA curve for pure PAN.[1—3)] However, there is a great difference between comonomers concerning the effect.[3)] This proved to be caused by a difference in the temperature at which each comonomer unit is dehydrochlorinated; HCl accelerates and retards the polymerization of cyano groups below and above the temperature, respectively, at which pure PAN begins to be subjected to a sharp transition.[1,4)]

The purpose of the present paper is to report on the DTA behavior of the two binary polyblends, namely, PAN–poly(α-chloroacrylonitrile) (PCAN) and PAN–poly(vinyl chloride) (PVC), and then to verify the above-mentioned conclusion on the effect of HCl. So far the DTA behavior of a 1:1 by weight of the PVC–PAN mixture has been reported by McNeill et al.[5)] Their result shows that when HCl evolution has almost ceased, polymerization of the cyano groups begins to reach a significant rate; this is in accordance with our expectation, since the degradation of the two homopolymers suggests a considerable overlap in their main volatilization reactions.

Experimental

Preparation of Polymer Blends. A polymer blend was prepared by the coprecipitation of two polymers from a solution containing PAN[6)] and PCAN[7)] or PAN and PVC (Geon 103 EP-8). The powder mixture given in Table 1 was dissolved in 26 cm^3 of *N*,*N*-dimethylformamide (DMF); the solution obtained was then poured into 520 cm^3 of methanol at −60 °C. The precipitate was filtered, washed with methanol and dried in a vacuum at 50 °C for eight days to constant weight.

Chlorine Analysis. The method was reported in a previous paper.[7)]

Thermogravimetry (TG). A Shimadzu DTG-20 was used. Five milligrams of PAN, PCAN, and PVC were packed in quartz sample holders measuring 5 mm in diameter and 2 mm deep; the measurement was carried out under dynamic nitrogen flow (60 cm^3 min^{-1}) at a heating rate of 5 °C min^{-1}.

Differential Thermal Analysis (DTA). A Rigaku CAT. No. 8001 Thermoflex was used. Fifty milligrams of powdered samples were employed and heated to 320 °C at a rate of 5 °C min^{-1} under nitrogen.

Results and Discussion

Chlorine Content of Polymer Blends. PAN–PVC samples were white, but PAN–PCAN samples became light purple. Figure 1 shows the relationship between

Table 1. Preparation of Polymer Blends

Sample	Composition			Chlorine content
	PAN	PCAN	PVC	
	mg	mg	mg	wt%
PAN	500.2			
PAN–PCAN-1	504.2	15.4		1.06
PAN–PCAN-2	501.9	30.8		1.92
PAN–PCAN-3	502.8	60.7		3.67
PAN–PCAN-4	501.0	120.5		6.71
PAN–PVC-1	500.6		5.1	
PAN–PVC-2	500.4		10.1	
PAN–PVC-3	505.0		18.4	1.77
PAN–PVC-4	509.0		30.1	2.94
PAN–PVC-5	500.8		61.0	6.12
PAN–PVC-6	508.5		120.2	10.98

the actual chlorine content given in Table 1 and the value calculated on the basis of a composition of each sample. Though the two values, Cl_A and Cl_C, in Fig. 1, in the PAN–PVC system agreed with each other, in the case of the PAN–PCAN system the actual value of Cl_A was smaller by ca. 15% than the calculated value of Cl_C. This indicates that PCAN is partially dehydrochlorinated in the course of the preparation of polymer blends. The fact that PCAN is dehydrochlorinated in DMF has been reported before.[7,8] It is clear that coloration in PAN–PCAN samples is caused by such dehydrochlorination.

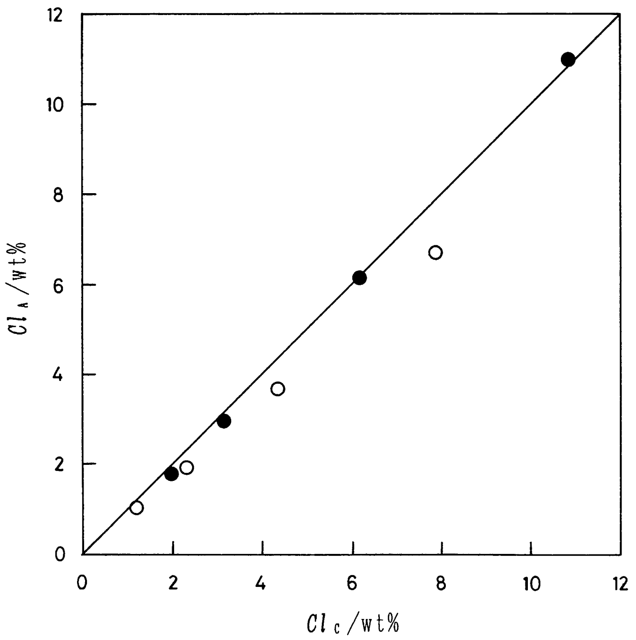


Fig. 1. Actual chlorine content ($\mathrm{Cl_A}$) vs. calculated content ($\mathrm{Cl_C}$). ○: PAN–PCAN, ●: PAN–PVC.

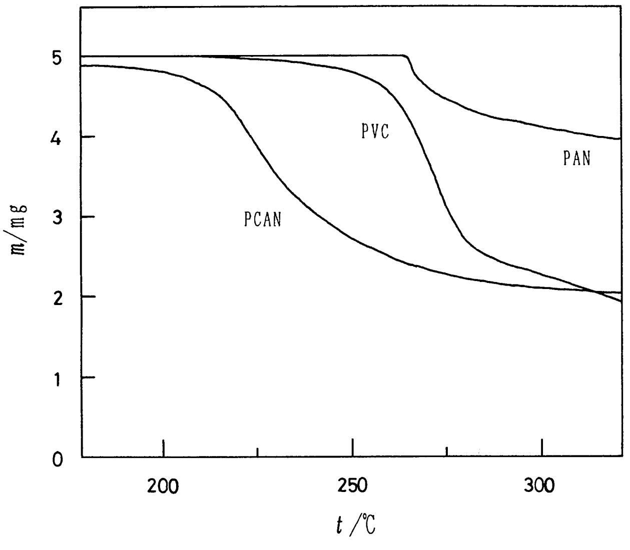


Fig. 2. TG curves for PAN, PVC, and PCAN.

Dehydrochlorination of Chlorine-Containing Polymers during Heating Process. TG curves for PAN, PVC, and PCAN are shown in Fig. 2. The temperature range in which PVC is dehydrochlorinated corresponds to that of the sharp PAN breakdown transition, whereas PCAN shows a weight loss due to dehydrochlorination in a much lower temperature range than PVC. As mentioned in the preceding section, PCAN is partially dehydrochlorinated in the course of preparation of polymer blends. Such PCAN is more easily dehydrochlorinated than the original PCAN.[9] Thus, in the case of the PAN–PCAN system, HCl exists below the temperature at which pure PAN begins to be subjected to a sharp transition, accompanied by an exothermic polymerization of the cyano groups.

Effect of the Composition in PAN–PCAN System on the Exothermic Polymerization of Cyano Groups. DTA curves for PAN–PCAN samples are shown in Fig. 3. As the composition increases in PCAN, the exotherm peak position due to violent polymerization of the cyano groups shifts to the higher-temperature

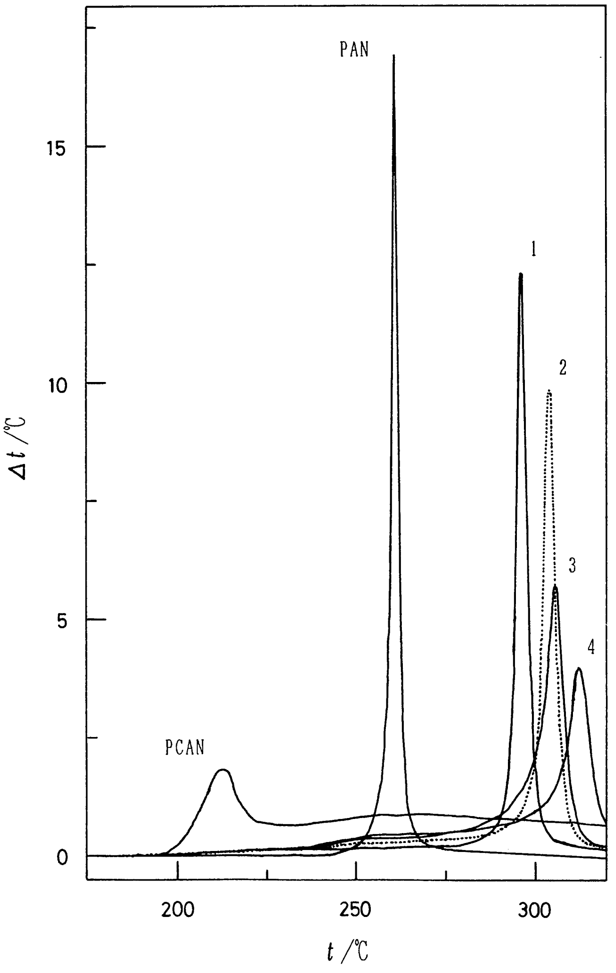
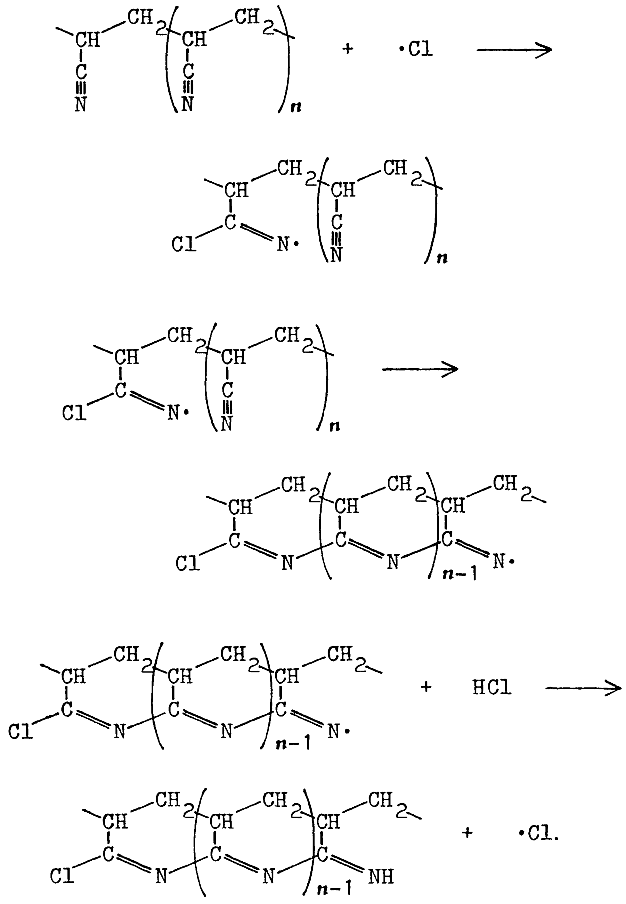


Fig. 3. DTA curves for PAN, PCAN, and PAN–PCAN samples. 1, 2, 3, and 4: PAN–PCAN-1, -2, -3, and -4 shown in Table 1, respectively.

side, and its intensity becomes lower than in the case of PAN. Moreover, in the cases of PAN–PCAN-3 and -4, a broad exotherm appears clearly above ca. 220 °C. This exotherm is due to a polymerization of the cyano groups which is closely associated with HCl generated during the heating process.[1] The mechanism has been explained by the action of a chlorine atom, which was formed by the reaction of thermally degraded polymer radical (P·) with HCl:

$$\mathrm{P\cdot} + \mathrm{HCl} \longrightarrow \mathrm{PH} + \mathrm{\cdot Cl}$$



Since the chlorine atom is much more mobile at ca. 220 °C than the polymer radical, polymerization of the cyano groups is promoted in the presence of HCl. When the moieties subjected to such polymerization exist in the polymer chain, they should prevent the progress of a rapid polymerization of the cyano groups with which fragmentation[10] in PAN is usually accompanied. This effect is expected to increase in proportion to the PCAN content, since the more HCl that is generated, the more are chlorine atoms formed. Actually, the exotherm peak position due to violent polymerization of the cyano groups shifts to the higher-temperature side with increasing PCAN content (Fig. 3). Such behavior corresponds to that found in DTA curves for the acrylonitrile–α-chloroacrylonitrile copolymers in which the mole fraction of α-chloroacrylonitrile units is below 0.1.[1]

Thermal Degradation Behavior of PAN in PAN–PVC System. DTA curves for PAN–PVC-1— -3 and -4— -6 are shown in Figs. 4 and 5, respectively. Even the DTA behavior of PAN–PVC-1 (the chlorine content being ca. 0.6 wt%) changed remarkably. Namely, the exotherm peak position due to a violent polymerization of the cyano groups shifted to the higher-temperature side than that for pure PAN by ca. 40 °C; its intensity became about 1/3 compared with that for pure PAN. This change is similar to that for PAN–PCAN-3 (the chlorine content being ca. 3.7 wt%), although no broad exotherm was observed below 260 °C. It is evident that there is a great difference between PVC and PCAN concerning the effect on the thermal degradation of PAN. This seems to have been caused by a difference in the temperature range associated with dehydrochlorination. In the case of PAN–PVC-2, -3, or -4, the exotherm peak position is identical with that for PAN–PVC-1 and its intensity

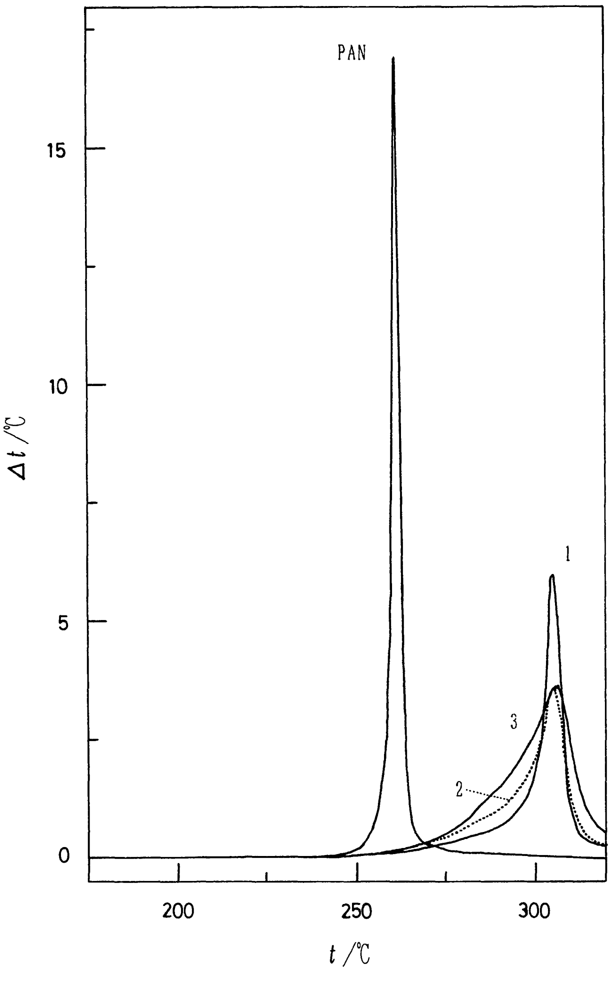


Fig. 4. DTA curves for PAN and PAN–PVC samples. 1, 2, and 3: PAN–PVC-1, -2, and -3 shown in Table 1, respectively.

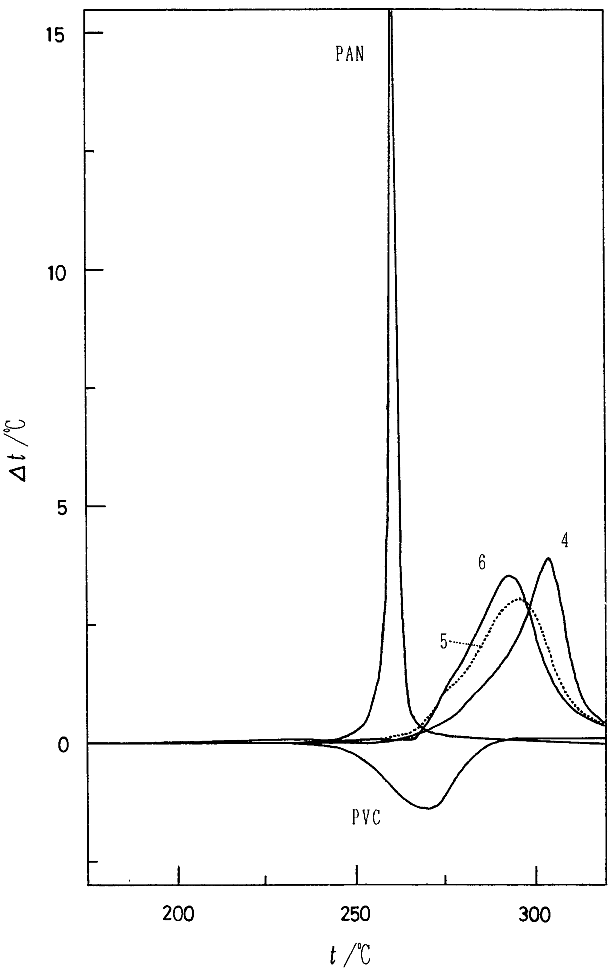
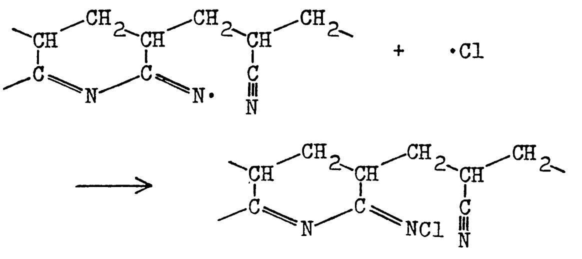


Fig. 5. DTA curves for PAN, PVC, and PAN–PVC samples. 4, 5, and 6: PAN–PVC-4, -5, and -6 shown in Table 1, respectively.

decreases to about 1/5 in comparison with that for pure PAN. This indicates that a very small amount of PVC in the PAN–PVC system is sufficient to change the behavior of the thermal degradation of PAN. It also proved that polymerization of the cyano groups cannot make rapid progress until HCl generated from PVC escapes out of the PAN–PVC system.

The generation of heat was observed in the 260—300 °C range, and increased in proportion to the PVC content (Fig. 4). We cannot conclude that this is due to only polymerization of the cyano groups. In PAN the thermally degraded polymer radicals are much more in number and are much more mobile at 260 °C than at 220 °C. Therefore, in the case of pure PAN, polymerization of the cyano groups progresses rapidly at ca. 260 °C. In the PAN–PVC system, since HCl exists in PAN above 260 °C, chlorine atoms are formed along with the disappearance of an equal number of polymer radicals. At this time although the number of active centers which initiate polymerization of the cyano groups does not change, chlorine atoms can also terminate progress in the polymerization of the cyano groups:



Since this reaction can take place frequently with increasing concentration of chlorine atoms, polymerization of the cyano groups should progress slowly with increasing the PVC content. Therefore, if the generation of heat in the 260—300 °C range is due to only polymerization of the cyano groups, it must decrease in proportion to the PVC content. This is contrary to the facts.

It is clear that the above-mentioned termination reaction is exothermic because of a combination of two active species. The heat of reaction must become larger as the composition increases in PVC. This is not contrary to the results shown in Figs. 4 and 5. In DTA curves for PAN–PVC-5 and -6, the exotherm peak is not observed at ca. 305 °C, but ca. 295 °C (Fig. 5). The magnitude of this broad exotherm is worth noticing. It was not reduced in spite of both a diminished content of PAN and an enlarged influence of the endotherm due to PVC. It can thus be concluded that the termination reaction is considerably exothermic.11)

The DTA behavior of the PAN–PVC system is similar to that of acrylonitrile–allyl chloride copolymers.3) This is thought to be attributable to a close resemblance between the two dehydrochlorination behaviors.4)

Chlorine Content of Polymer Blends Heated to 320 °C. After DTA of polymer blends, a chlorine analysis of the residual products was carried out. The values obtained from PAN–PCAN-4 and PAN–PVC-5 were 0.35 and 2.32 wt%, respectively. These original chlorine contents are 6.71 and 6.12 wt%, respectively, (Table 1) and though they nearly resemble each other, there is a very great difference between the chlorine contents of residual products. In the case of the PAN–PVC system, as mentioned in preceding section, chlorine atoms terminate progress in the polymerization of the cyano groups. Since the termination reaction takes place frequently in the case of PAN–PVC-5 or -6 (Fig. 5), chlorine atoms combined as terminal points are the prime consideration with an increase in residual chlorine. The chlorine content of PAN–PVC-6 heated to 320 °C was 3.07 wt%, and more than that in the case of PAN–PVC-5. This comes up to our expectations, because the generation of heat in the

260—300 °C range is larger than that for PAN–PVC-5 (Fig. 5). Such a change in the residual chlorine is similar to that of the acrylonitrile–allyl chloride copolymers heated to 350 °C.[3] This indicates that these copolymers were also subjected to the abovementioned termination reaction.

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11) McNeill et al.[5] thought, in the case of a 1:1 PVC–PAN mixture, the heat of polymerization of cyano groups is increased by some 50% compared to PAN alone; we believe that the termination reaction is, however, the prime consideration with an increase in the heat of reaction.