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Bulk Copolymerization of Acrylonitrile with Allyl Chloride and Thermal Analysis of the Products

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The bulk copolymerization of acrylonitrile (M_1) with allyl chloride (M_2), carried out at 40 °C, was initiated by 0.05 mol% of α,α'-azobisisobutyronitrile under nitrogen. The compositions of six copolymers were in the range of allyl chloride units, 0.63—6.32 mol%. The monomer reactivity ratios r_1 and r_2 were calculated to be 6.04 and 0.035, respectively. Only three copolymers were soluble in *N,N*-dimethylformamide and their intrinsic viscosities were found to be greater than 4.5 dL g^{-1}. The chlorine contents, although 0.42, 0.87, and 1.03 wt%, were sufficiently effective to cause a change in the behavior of the thermal degradation of polyacrylonitrile (PAN). In DTA curves measured at a rate of 5 °C min^{-1} under nitrogen for copolymers containing ca. 1 wt% of chlorine, a sharp exotherm due to the polymerization of cyano groups shifted to the higher-temperature side (ca. 40 °C) and the differential temperature decreased to about 1/6. Moreover, the weight loss at 350 °C decreased from 19 wt% for PAN to 13 wt%. A similar thermal-degradation behavior was also observed for acrylonitrile-α-chloroacrylonitrile (CAN) copolymers. However, there was a great difference between allyl chloride and CAN units concerning the effect on the thermal degradation of PAN. Namely, only 1.5 mol% of allyl chloride units corresponded to 10 mol% of CAN units.

In a preceding study[1)] hydrogen chloride (HCl) accelerated the rate of polymerization of cyano groups at 220 °C in an isothermal heat treatment of polyacrylonitrile (PAN). The acceleration was thought to be the result of the action of chlorine atoms which were formed by the reaction of thermally degraded polymer radicals with HCl. Moreover, it was demonstrated that in both DTA curves for the PAN samples heat-treated under an HCl atmosphere and for acrylonitrile-α-chloroacrylonitrile (CAN) copolymers, a sharper exotherm due to the polymerization of cyano groups appeared more at the higher-temperature side than that for pure PAN. The differential temperature ΔT decreased upon increasing the chlorine content. This type DTA behavior was also considered to be attributable to the action of chlorine atoms. Grassie and McGuchan[2)] have already observed similar behavior for copolymers of acrylonitrile with vinyl chloride, vinylidene chloride, and CAN (comonomer units, more than 5 mol%). Acceleration effects on the polymerization rate of cyano groups are thought to appear even for a low content of comonomer units by changing its chemical component. In order to clarify the abovementioned problem, we tried to prepare acrylonitrile (M_1)-allyl chloride (M_2) copolymers. So far, it has been reported that this system should be ideal and the relative reactivity of allyl chloride toward the acrylonitrile-type radical is 0.18 at 60 °C.[3)] Since this indicates $r_1=1/0.18$ and $r_2=0.18$, it was expected that favorable copolymers will easily be obtained.

Experimental

Preparation of Copolymers. Commercial acrylonitrile and allyl chloride were distilled in a nitrogen atmosphere. Bulk copolymerization carried out at 40 °C was initiated by 0.05 mol% of AIBN under nitrogen. Polymerization conditions are listed in Table 1. The reaction vessel was sealed to prevent the loss of both monomers during copolymerization. After 1.25—36 h, the copolymerization was terminated by adding of a small amount of hydroquinone. The copolymer was filtered, washed thoroughly with methanol, and finally dried in a vaccum at 30 °C.

Chlorine Analysis. The method was reported in a previous paper.[4)]

Determination of Intrinsic Viscosity. The intrinsic viscosity $[\eta]$ was measured in *N,N*-dimethylformamide (DMF) at 35 °C.

Measurement of IR Absorption Spectra. IR spectra were measured by a Shimadzu IR-435 spectrophotometer using a pellet method.

Differential Thermal Analysis (DTA). The method was reported in a previous paper.[1)] Samples were heated to 350 °C at 5 °C min^{-1} rate under nitrogen.

Results and Discussion

Composition of Copolymers. The chlorine content and $[\eta]$ of copolymers are shown in Table 1. It was found from these results that the copolymers obtained in Expt Nos. 2, 3, and 4 contained little chlorine and that the molecular weights were sufficiently high. The content of allyl chloride units incorporated in each copolymer was calculated from the chlorine content (Table 1). Figure 1 shows the IR spectra of PAN and copolymers obtained in Expt Nos. 6 and 8. It was supposed from the spectra that a side reaction would proceed simultaneously with copolymerization in Expt Nos. 8 and 9, because a strong absorption appeared at 1738 cm^{-1}. Accordingly, these two copolymers were not analyzed in the present research. Although two new absorptions appeared at 685 and 725 cm^{-1} in all copolymers, they

Table 1. Copolymerization of Acrylonitrile (M_1) with Allyl Chloride (M_2) by AIBN at 40 °C

Expt	Reaction conditions			Analytical data of product			
No.	M_2 mol%	M_1+M_2 g	Time h	Yield wt%	Chlorine content wt%	M_2 units mol%	[η] dL/g
1	0	22.46	1.25	2.70	0	0	8.0
2	3.73	24.01	2.5	3.94	0.42	0.63	9.2
3	7.31	23.52	3	4.76	0.87	1.31	5.9
4	8.68	23.73	7	4.95	1.03	1.55	4.5
5	13.23	25.81	8	6.62	1.64	2.48	—[a]
6	20.28	25.64	8.75	—	2.31	3.51	—
7	29.57	23.68	11.25	4.32	4.11	6.32	—
8	35.04	25.19	16.2	1.12	5.45	—	—
9	41.49	27.65	36	0.07	7.19	—	—

a) The products in Expt Nos. 5—9 were insoluble in DMF.

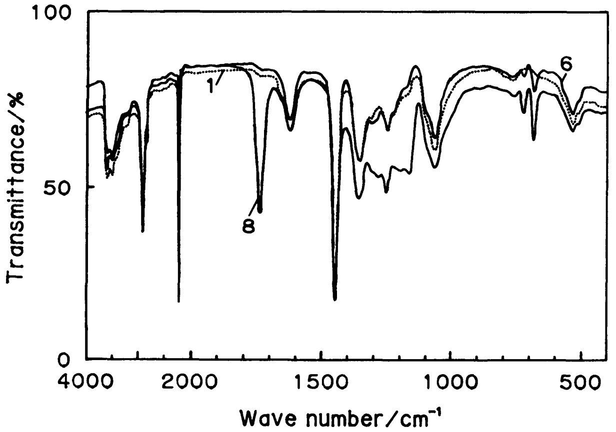

Fig. 1. IR absorption spectra of PAN and acrylonitrile-allyl chloride copolymers.
Arabic numerals used here are the same as Expt Nos. in Table 1. Concentration: Sample/KBr (mg/mg) = 1: 2.3/300, 6: 2.5/300, 8: 2.7/300.

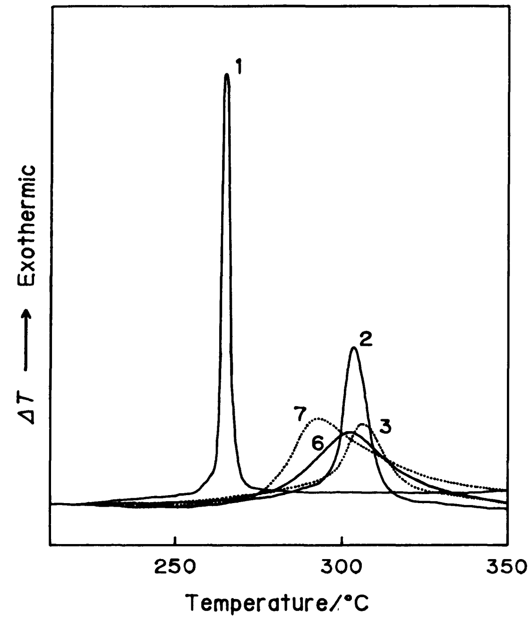

Fig. 2. DTA curves for PAN and acrylonitrile-allyl chloride copolymers.
Arabic numerals used here are the same as Expt Nos. in Table 1.

could be assigned to C–Cl stretching vibrations in allyl chloride units since their normalized absorbances[5] increased in proportion to the chlorine content.

During the present copolymerization the conversions were low as shown in Table 1. Therefore, the monomer reactivity ratios could be determined by the method of Fineman and Ross[6] using the composition of copolymers obtained in Expt Nos. 2—7. The values of r_1 and r_2 were calculated to be 6.04 and 0.035, respectively. Although the present copolymerization system was not ideal at 40 °C, it proved that favorable copolymers were obtained.

Thermal Analysis of Copolymers. Figure 2 shows the DTA curves for PAN and copolymers obtained in Expt Nos. 2, 3, 6, and 7. The weight losses at 350 °C are shown in Fig. 3. Even the DTA behavior of the copolymer which contained 0.42 wt% of chlorine (the content of allyl chloride units corresponding to 0.63 mol%) changed remarkably. Namely, the exotherm peak position due to the polymerization of cyano groups shifted more to the higher-temperature side (ca. 40 °C) than that for pure PAN. The value of ΔT became to about 1/3 in comparison with that for pure PAN. But the weight loss at 350 °C was not different from that for pure PAN (Fig. 3). When the chlorine content of the copolymer was 0.87, 1.03, or 1.64 wt% (the content of allyl chloride units corresponding to 1.31, 1.55, or 2.48 mol%), the exotherm peak position showed a somewhat greater shift to the higher-temperature side than that obtained for a

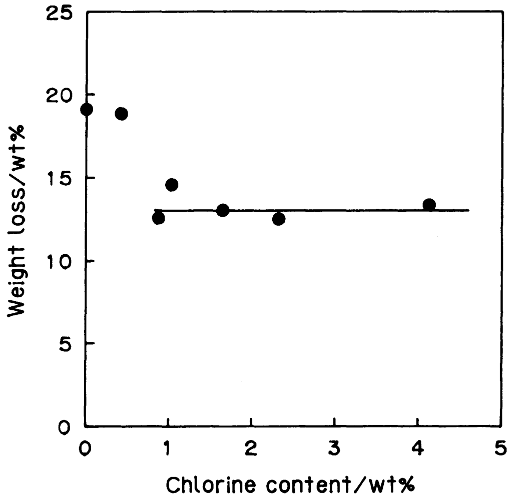

Fig. 3. Relationship between the chlorine content of copolymer and the weight loss at 350 °C.

copolymer containing 0.42 wt% of chlorine and ΔT decreased to about 1/6 in comparison with that for pure PAN. Moreover, the weight loss at 350 °C decreased from 19 wt% for PAN to 13 wt% for these copolymers (Fig. 3). Even if the chlorine content of copolymer was greater than 2 wt%, both ΔT and the weight loss didn't change again although the exotherm shifted to lower temperature side. Therefore, if allyl chloride is used as a comonomer, 1 wt% of chlorine is sufficient to change the behavior of the thermal degradation of PAN.

A similar behavior upon increasing the chlorine content has already been observed for acrylonitrile-CAN copolymers.[1,2] However, there was a great difference between allyl chloride and CAN units concerning the effect on the thermal degradation of PAN. When CAN was used as a comonomer, a sufficient chlorine content to change the behavior of thermal degradation of PAN was ca. 7 wt%. This indicates that regarding the effect of comonomer units, only 1.5 mol% of allyl chloride units corresponded to 10 mol% of CAN units. Consequently, HCl (and chlorine atoms) eliminated from the allyl chloride unit was more available than that eliminated from the CAN unit. This seems to have been caused by a difference in the temperature range in which each comonomer unit was dehydrochlorinated.

Finally, the chlorine and IR analyses of the copolymers which were heated to 350 °C at a rate of 5 °C min^{-1} were carried out. Since in every case both IR absorptions at 685 and 725 cm^{-1} disappeared after heating, it is clear that all allyl chloride units were dehydrochlorinated during heating. However, chlorine was detected in every case: after the heating of copolymers obtained in Expt Nos. 2—7, the chlorine contents were 0.11, 0.42, 0.44, 0.44, 1.06, and 1.35 wt%, respectively. The residual chlorine seems to have been combined as starting point of the polymerization of cyano groups.[1]

References

1) M. Okamoto, T. Ogura, R. Ashikawa, and O. Ishizuka, *Nippon Kagaku Kaishi,* **1983**, 566.

2) N. Grassie and R. McGuchan, *Eur. Polym. J.,* **9**, 507 (1973).

3) F. R. Mayo, F. M. Lewis, and C. Walling, *J. Am. Chem. Soc.,* **70**, 1529 (1948).

4) M. Okamoto, C. Aoki, and O. Ishizuka, *Nippon Kagaku Kaishi,* **1977**, 103.

5) The absorbance a for w mg of copolymer was normalized by $A=a/w$, where A is the normalized absorbance.

6) M. Fineman and S. D. Ross, *J. Polym. Sci.,* **5**, 259 (1950).