Detection of End-groups in Polyacrylonitrile by Differential Infrared Spectroscopy

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The differential infrared spectroscopy, which is useful for the identification or quantitative estimation of minor constituents in organic substances¹⁾, has been applied to the detection of the end-groups in polyacrylonitrile. As O'Connor et al.²⁾ have described, the infrared measurements of polymers can be successfully performed with the potassium bromide disk technique, particularly when the samples are obtained in the form of a fine powder or fibers. In the present study the differential analyses of polymers have been carried out with success in combination with the potassium bromide disk technique.

Fig. 1 shows the infrared spectra obtained from the potassium bromide disks of some different polyacrylonitrile samples. The disks were prepared from the mixtures of 400 mg. of potassium bromide and 4 mg. of the sample material, both screened through 250-mesh stainless-steel cloth, by applying a pressure of 8 tons for 10 min. in the evacuated die mount. The infrared spectra were obtained using a Perkin-Elmer model 21 spectrophotometer (with NaCl optics). Samples A and B are polyacrylonitriles of different degrees of polymerization ($\overline{M}_n=49500$ and 11000, respectively)*, both being polymerized by using ammonium persulfate-sodium bisulfite redox system as initiator. Sample C is one polymerized using azo-bis-isobutyronitrile as initiator ($\overline{M}_n=7000$). By inspection of the spectra of samples A and B it has been found that the intensities of the weak shoulder band at 1041 cm^{-1} and the one around 1200 cm^{-1} increase remarkably with the lowering of the degree of polymerization. On the contrary, as is evident from the spectrum of sample C, no such absorption bands of variable intensities are observable at the corresponding frequencies in the case of polyacrylonitrile polymerized using azo-bis-isobutyronitrile as initiator, while the situation is the same for the sample obtained by γ-ray initiated polymerization. Therefore, it seems that these bands are characteristic of the polymer obtained

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1) See for example, D. Z. Robinson, *Anal. Chem.*, **24**, 619 (1952); H. Powell, *J. Appl. Chem.*, **6**, 488 (1956).

2) R. T. O'Connor, E. F. DuPré and E. R. McCall, *Anal. Chem.*, **29**, 998 (1957).

* Measured according to the method of P. F. Onyon, *J. Polymer Sci.*, **22**, 13 (1956).

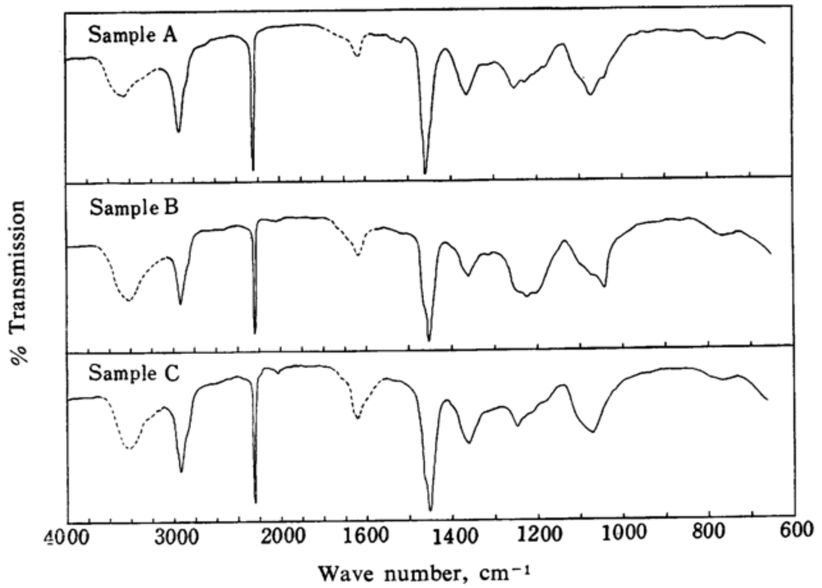

Fig. 1. Infrared spectra of some polyacrylonitriles. Sample A and B were polymerized using ammonium persulfate-sodium bisulfite redox system as initiator ($\overline{M}_n=49500$ and 11000, respectively). Sample C was polymerized using azo-bis-isobutyronitrile as initiator ($\overline{M}_n=7000$). (Dashed lines indicate the absorptions due to water adsorbed by potassium bromide).

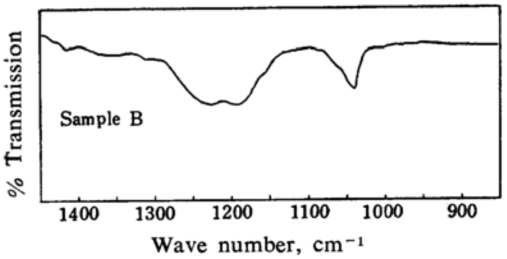

Fig. 2. Differential spectrum of polyacrylonitrile sample B (initiator=ammonium persulfate-sodium bisulfite redox system) against sample C (initiator=azo-bis-isobutyronitrile).

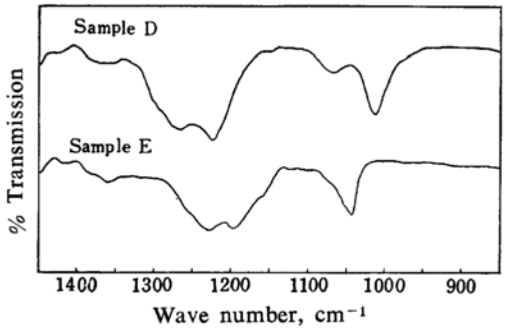

Fig. 3. Differential spectra of polyacrylonitrile sample D (initiator=ammonium persulfate, $\overline{M}_n=9600$) and sample E (initiator=Fe^{3+}-sodium bisulfite redox system, $\overline{M}_n=30300$) against sample C (initiator=azo-bis-isobutyronitrile).

using persulfate-bisulfite redox system as initiator. In order to make clear the nature of these bands, the differential method has been applied, in which the disk containing sample B is put in the sample beam of the spectrometer and the absorption bands due to polyacrylonitrile proper are cancelled out by placing the disk containing sample C in the reference beam. The differential spectrum is shown in Fig. 2, in which two independent bands have been separated; one at 1041 cm^{-1} and a doublet with peaks at 1227 and 1190 cm^{-1}. It has been predicted from the analyses by tracer methods[3] that, when the persulfate-bisulfite redox system is usedto initiate polymerization, both sulfate and sulfonate end-groups may be introduced into the polymer, and these groups are expected to show characteristic absorptions in the 1200~1000 cm^{-1} region[4]. Therefore, the above two bands are suspected to be due either to the sulfate or sulfonate end-groups. To clarify this point further, two other polyacrylonitrile samples have been examined by the differential method. Sample D was polymerized using ammonium persulfate as initiator ($\overline{M}_n=9600$), and it is expected that the sulfate end-groups

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[3] Y. Tsuda, *J. Appl. Polymer Sci.*, in press.

[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd Ed., Methuen & Co., Ltd., London (1958), Chapt. 22.

alone may be incorporated in this polymer. Sample E was polymerized using Fe^{3+}-sodium bisulfite redox system as initiator ($\overline{M}_n=30300$), so that the polymer may contain only the sulfonate end-groups. Fig. 3 shows the results of the differential measurements, in which the absorptions due to polyacrylonitrile have been cancelled out by placing sample C in the reference beam. In complete agreement with expectation, the spectrum of sample D corresponds well to those of aliphatic sulfates ($R-O-SO_3^-$), and we may ascribe the doublet with peaks at 1264 and 1224 cm^{-1} to the S–O degenerate stretching vibration, the band at 1065 cm^{-1} to the S–O symmetric stretching vibration of the sulfate ion, while the band at 1011 cm^{-1} may be ascribed to the C–O stretching vibration. In the same way, the spectrum of sample E agrees well with those of aliphatic sulfonates ($R-SO_3^-$)5), and the doublet with peaks at 1225 and 1195 cm^{-1} may be assigned to the S–O degenerate stretching vibration and the band at 1041 cm^{-1} to the S–O symmetric stretching vibration of the sulfonate ion. Liang and Krimm6) have reported that there exists a weak shoulder band at 1044 cm^{-1} in the spectrum of polyacrylonitrile and assigned this to a combination or overtone of some skeletal deformation vibrations of this molecule. Although they have not made mention of the initiator by which their polyacrylonitrile sample has been polymerized, it seems quite probable from the above results that this band corresponds to the vibration of the sulfonate end-groups. It is to be wondered why the spectrum of sample B, in which both sulfate and sulfonate end-groups are expected to exist, almost completely agrees with that of sample E and the absorptions due to sulfate end-groups are hardly observable. According to Tsuda's results3), however, in the polymerization initiated by persulfate-bisulfite redox system the ratio of the concentrations of the sulfate and the sulfonate end-groups produced varies depending on the initial concentrations of the salts and of the acrylonitrile monomer, so that the relative intensities of the absorption bands due to these groups may vary from sample to sample. Therefore, it seems not improbable that the sulfonate end-groups are predominant in the case of sample B.

Quantitative estimations of the end-groups by the differential method were also carried out using the polymers of known end-group contents, and the limit of detectability of both sulfate and sulfonate end-groups by this method is estimated to be about 0.002 millimol./g. polymer.

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5) K. Fujimori, This Bulletin, 32, 850 (1959).

6) C. Y. Liang and S. Krimm, *J. Polymer Sci.*, 31, 513 (1958).