Structural Change of Polyacrylonitrile by Iodine Sorption

Iodinated polymer complexes for enhancing electrical properties in polymer materials have been extensively investigated in recent years. It has been shown by Hsu et al.[1] that the iodine derivatives are charge transfer complexes in which the derivative structures are best viewed as a perturbation of the structures of the parent polymers. The sorption of iodine species into a polymer, therefore, can affect the degree of crystallinity and structural order of parent polymer. An investigation on the lattice conversion of parent polymer by iodine doping was carried out recently in some polymers such as polyacetylene (PA), polyvinyl alcohol (PVA), and Nylon-6. Consequently, the iodine sorption has been reported to produce significant structural changes in these polymers.

In equatorial x-ray diffraction of iodinated PA, Baughman et al.[2] found the appearance of a diffraction line (d = 7.9 Å) which was identified with the (100) reflection of PA–iodine cocrystal, whose x-ray structure factor is zero in pure PA. Murthy et al.[3] also obtained a 15.6 Å reflection in a Nylon-6–iodine complex film. Similar work on polyvinyl alcohol[4] was reported. These papers regarding the x-ray diffraction of polymer–iodine complexes report about 3 Å meridional spacing which is attributed to iodine ions intercalated between parent polymer chains.

On the other hand, polyacrylonitrile (PAN) is a well-known polymer which has a strong dipolar group per monomer unit. Therefore, it is also possible that PAN forms the charge transfer complex with iodine. Early studies[5-7] for the iodine sorption behavior in PAN have not dealt with the investigation of a structural change of PAN, which probably is due to the indefinite crystal structure of PAN.

We confirmed a structural change of PAN by iodine sorption as in the case of the above-mentioned polymers.

PAN homopolymer, having a viscosity-average molec-

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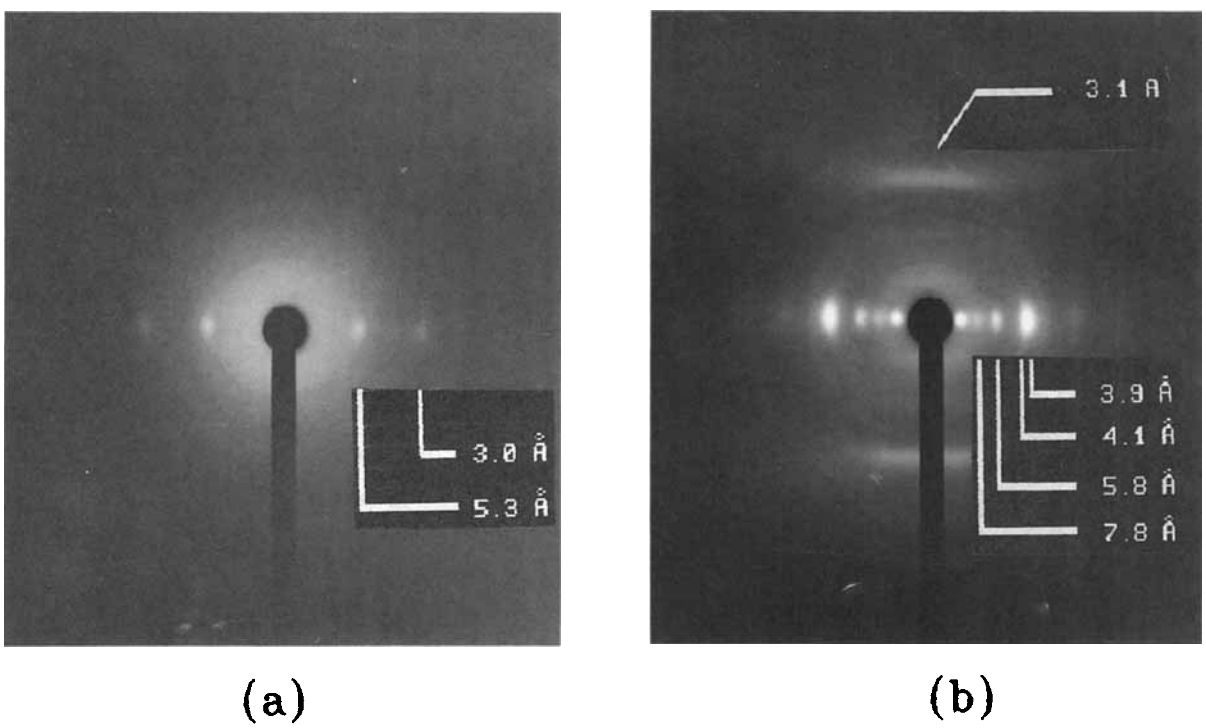

Figure 1 Wide-angle x-ray diffraction photographs of PAN films: (a) pure PAN, (b) iodinated PAN.

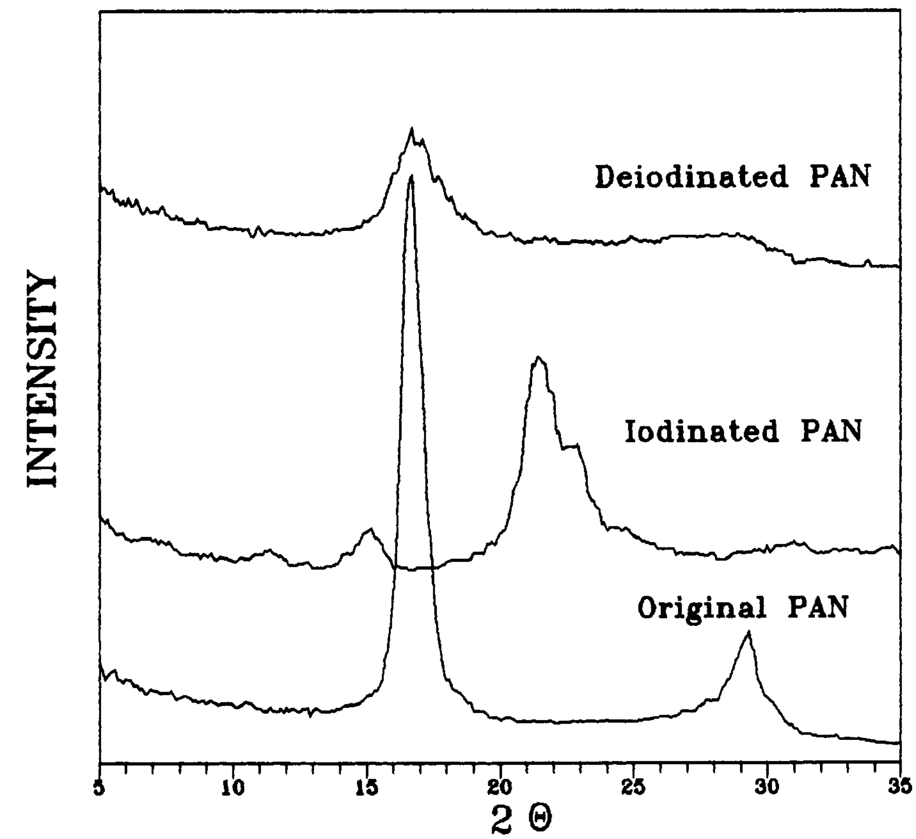

Figure 2 Equatorial x-ray diffraction profile of original PAN, iodinated PAN, and deiodinated PAN.

ular weight of 920,000, was prepared by suspension polymerization. The thin films used in the experiments were made by deposition from a 4% dimethylformide (DMF) solution and drawn 7 × uniaxially at 120°C. Aqueous iodine and potassium iodide (I_2/KI) solution with a mole ratio of 1 : 2 was prepared for sorption experiments. The film was soaked in aqueous I_2/KI solution (0.5 mol/L) over 24 h for equilibrium sorption. The iodinated film was dried between filter papers in a vacuum oven at 60°C for one day. X-ray diffraction photographs were obtained on a flat film using a Laue camera with a sample-to-film distance of 35 mm, and exposure times of 40 min. X-ray diffractometer scans were obtained on a Rigaku goniometer with nickel-filtered copper radiation, using a step size of 0.1 and count rate of 1000 cps.

The results are presented in Figures 1 and 2. Figure 1(a) is the x-ray diffraction photograph of pure PAN film, and shows a sharp spot with spacing ca. 5.3 Å, which indicates the hexagonal lattice of a typical PAN polymer. The diffraction photograph of iodinated PAN film shown in Figure 1(b) has new spots appearing on the meridian and the equator. In the diffraction pattern of iodinated film, the 3.1 Å spacing reflection was also found on the meridian, which is attributed to polyiodine parallel to PAN molecular rods, and the equatorial reflections at 5.3 Å and 3.0 Å of pure PAN disappeared completely. Instead, new reflections at 7.8, 5.8, 4.1, and 3.9 Å appeared along the equator.

This indicates that the sorption of iodine into PAN causes significant structural changes in PAN polymer films. Figure 2 shows the equatorial x-ray diffraction profile of pure PAN, iodinated PAN, and deiodinated PAN film. The iodinated PAN was washed with water in order to remove inorganic crystals formed on the surface of iodinated film just before applying x-ray. More striking changes were observed when the iodinated film was washed with acetone at ambient conditions. The reflection pattern of the deiodinated film recovers its original reflection pattern. These findings imply that the iodine which penetrates into the crystalline phase of PAN intercalates between the molecular rods, which have been formed by intramolecular repulsion of dipolar nitrile groups of PAN, without a remarkable change of molecular conformation of PAN. Further studies on sorption behavior, polyiodine, and fine structural aspects for PAN–iodine complex will be discussed with additional data in the future.

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