Electron Diffraction Study of Thin Films of Polymers of Para-Halogeno-Styrene

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Amorphous thin films of polymers of p-Cl-, p-Br- and p-I-styrene were studied by electron diffraction, using a sector-camera. A model was proposed for the intra- and intermolecular structures.

Thin films of polymers of p-Cl-, p-Br- and p-I-styrene were studied by electron diffraction, using a sector-camera. The diffracted intensity was measured by the usual microphotometric technique for the Cl-derivative, but the intensities were visually estimated for the Br- and I-derivatives because of the difficulty in preparing films thin enough to produce diffraction patterns with high contrast. Ten to thirteen halos were observed for each case, but the features of the patterns differ among the different kinds of

Fig. 1. Comparison between the intensity calculated from the best model and the observed intensity. $(s=(4\pi/\lambda)\sin(\theta/2))$.

derivatives, especially for $4<s<12$Å^{-1}, as shown in Fig. 1.

The intensity formula used for the correlation analysis is

$$I(s)=\sum_i^{\text{unit}} \sum_j'^{r_{ij}<l_{AB}} Z_i Z_j$$
$$\times \exp(-\Delta_{ij}s^2)\sin sr_{ij}/sr_{ij}$$
$$-(N/V)\sum_A \sum_B n_A n_B Z_A Z_B$$
$$\times \int_0^{l_{AB}} 4\pi r^2 \sin sr/sr dr ,$$

where N is the number of repeating units of the sample in the effective volume V, n_A the number of atoms of the A-type in a unit, l_{AB} the value of r beyond which the A—B component in the radial distribution function has no fluctuation, $\sum_i^{\text{unit}}$ indicates the summation over all atoms in a unit, $\sum_j'^{r_{ij}<l_{AB}}$ the summation over all atoms for which $0<r_{ij}<l_{AB}$, irrespective as to whether the j-th atom may be in or not in the unit where the i-th atom lies, and $\sum_A$ the summation over all types of atoms. The above formula represents the structure sensitive intensity per repeating unit and corresponds to the intensity function derived from the deviation of the radial distribution function from its average function.

Four models of a linear molecule and three types of lateral arrangement of neighboring molecules were considered, and two styrene residues, $C_{16}H_{14}X_2$, were taken as a repeating unit, where X is a halogen atom. Normal values for the bond distances and bond angles were assumed, and the value of l_{AB} was assumed to be equal to the van der Waals' distance of the A—B pair, except for $l_{XX}=$ 6.0Å. In the cases of Br- and I-derivatives the complex atomic scattering factors for electrons were used for the intensity calcu-
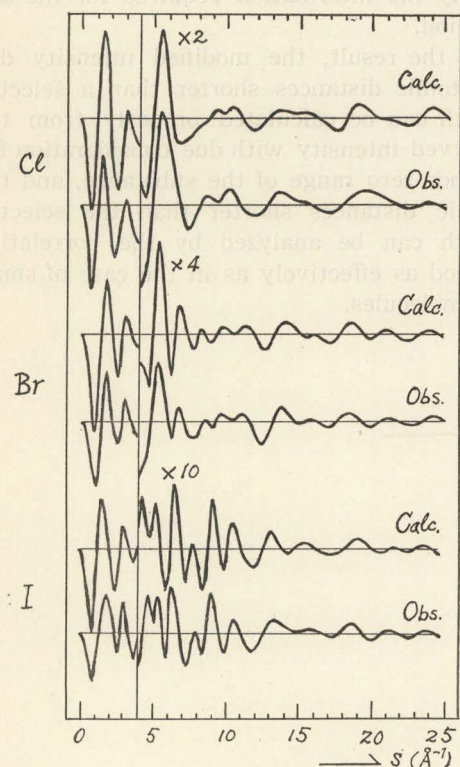
lation. Intensities calculated for these models from the above equation were compared with the observed intensity for each derivative. Such intra- and intermolecular structures as shown in Fig. 2 were found to be the best in common to the three kinds of derivatives. Fig. 1 shows the comparison between the intensity calculated from the best model and the observed intensity.

The radial distribution analysis was carried out for the Cl-derivative. The first and the second peaks of the radial distribution curve were decomposed into individual peaks for each distance with the consideration of the effect of non-nuclear scattering. It was found that the assumptions used in the calculation
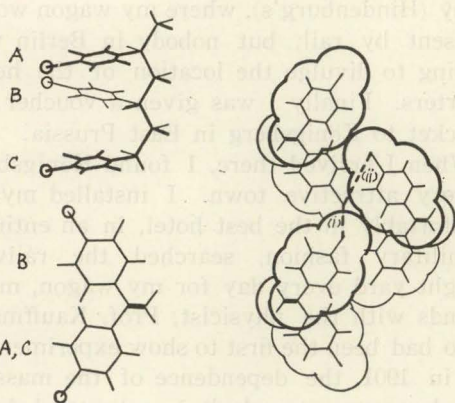

Fig. 2. The best model. Left: side view and plane of a molecule. Right: lateral arrangement of molecules.

of intensities were reasonable.

The samples used here are polymers synthesized by the method of radical polymerization, and the films are expected to be in an amorphous state. Some regularities in the structure however, were found as shown in Fig. 2. In this model, styrene residues connect in a "head to tail" arrangement, their benzene rings being located alternately on each side of the plane of the paraffin chain. Neighboring molecules are closely packed in a "face to face" configuration in a plane vertical to the chain. These regularities should be maintained only among the nearest neighboring residues, and the orientation of the next nearest neighboring and farther residues should be practically at random, because the observed patterns are well reproduced by the intensities calculated only with the interatomic distances shorter than those between the nearest neighbors and the radial distribution curve shows no appreciable fluctuation beyond $r=4\sim6$Å. Moreover, the values of C-X bond distances were found to be shorter than the sum of covalent bond radii and to be equal to the values of the distances in the halogen derivatives of benzene.

It is very significant that the observed intensity features of the three kinds of halogen derivatives differing considerably from each other can be well explained with one common model.

Details of this study will be published in Acta Crystallographica.