ALCOTEX-1017 FH was oxidised with hypochlorite solution, oxidised samples were obtained at different time intervals. Their tacticity was measured by infrared spectra and crystallinity by X-ray diffraction technique. Weights of the 80:20 alcohol-water insoluble high molecular weight oxidised polymer are given in Table XXVII. Infrared spectra of the oxidised samples are already discussed in Chapter III, Figures 14, 15 and 16. Density ratio D916/D849 have been calculated and are listed in Table XXVII.

ESTIMATION OF DEGREE CRYSTALLINITY (DC)

Estimations of DC in polyvinyl alcohol are generally reported using infrared spectroscopy\(^{251}\), but suitable X-ray methods for its evaluation are hard to find in literature. Since the principles of various X-ray methods of crystallinity evaluation are well-known, a particular procedure can be adapted for obtaining relative crystallinity of PVA samples. The correlation\(^{252}\) method which provides a numerical comparison of an unknown sample with the most crystalline and most amorphous extremes (standards) that can be physically obtained for the polymer species in the laboratory. The correlation methods have been widely employed for the estimation
of DC in variety of polymers\textsuperscript{255-256}. Some of the pioneering work leading to the success of this method has been carried out earlier by Radhakrishnan and Co-workers\textsuperscript{256-258}. Since the procedures for collection of polymer X-ray data and computation of DC have already been standardised in the laboratories of ATIRA, the problem of estimation of DC in various PVA samples reduces to that of developing the appropriate crystalline and amorphous standards for this particular polymer.

**PREPARATION OF INTERNAL STANDARDS**

Amorphous standard was prepared by dissolving PVA-057 in water and rapidly precipitating it by the addition of acetone. Crystalline standard was prepared by heating ALCOTEX-1017 FH in triethylene glycol until dissolution occurred at around 180°C. The solution was cooled slowly to room temperature, resulting in precipitation of crystalline PVA which was filtered and washed with methanol. Crystalline PVA standard thus obtained is insoluble in boiling water.

**COLLECTION OF X-RAY INTENSITY DATA**

X-ray scans were obtained by chart recording between 10° and 50° (2\(\theta\)) angular range. CuK\(\alpha\) X-rays were employed as incident beam and monochromatization of diffracted intensities was achieved electronically. The X-ray system consisted of a vertical Philips X-ray diffractometer set-up to collect transmitted intensities from any sample using a Curved
Crystal Focalizer accessory to reduce the broadening caused by the instrument. A 4° divergence slit and a 0.3 mm receiving slit were employed.

**COMPUTATION OF THE DEGREE OF CRYSTALLINITY**

X-ray intensities from the polymer sample (S), crystalline standard (C) and amorphous standard (A) were read from chart scans at 0.25° increments in 2θ. These values formed the input for a computer programme written in FORTRAN IV and executed on an IBM 360 computer. The programme carries out a normalization of diffraction data so that the areas under the curves between 10° and 50° (2θ) are the same for all samples and computes differential intensities (S-A)_i and (C - A)_i at each incremental position i in 2θ. It then calculates the linear regression of (S - A) on (C - A) and the degree of crystallinity is defined by the slope of this regression line.

Normalized X-ray diffractograms of crystalline and amorphous standards of PVA are compared in Figure 35. The crystalline peaks have been indexed on the basis of an orthorhombic unit cell\textsuperscript{259} for PVA.

The X-ray diffractograms of control unoxidized starting material and oxidized PVA samples are shown in Figure 36. The results of the X-ray crystallinity evaluation of various PVA samples are listed in Table XXVII.
POLY (VINYL ALCOHOL)
- Crystalline Standard
- Amorphous Standard

FIG. 35: X-RAY DIFFRACTOGRAMS OF CRYSTALLINE AND AMORPHOUS STANDARDS PVA SAMPLE.
FIG. 36: X-RAY DIFFRACTOGRAMS OF CONTROL UNOXIDISED AND OXIDISED PVA SAMPLES.
TABLE XXVII
CRYSTALLINITY AND TACTICITY OF OXIDISED POLYVINYL ALCOHOL SAMPLES

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Time (min.)</th>
<th>Wt. of Insoluble Polymer g per gram</th>
<th>IR Density Ratio D916/D849</th>
<th>Crystallinity %</th>
<th>Correlation Coefficient</th>
<th>mmoles of Available Cl₂ Consumed per PVA Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>-</td>
<td>0.33</td>
<td>88</td>
<td>0.75</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>0.90</td>
<td>0.29</td>
<td>46</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.85</td>
<td>0.26</td>
<td>42</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>0.65</td>
<td>0.26</td>
<td>29</td>
<td>0.43</td>
<td>170</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>-</td>
<td></td>
<td>38</td>
<td>0.53</td>
<td>192</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>0.55</td>
<td>0.25</td>
<td>29</td>
<td>0.43</td>
<td>220</td>
</tr>
<tr>
<td>7</td>
<td>150</td>
<td>-</td>
<td></td>
<td>30</td>
<td>0.46</td>
<td>247</td>
</tr>
<tr>
<td>8</td>
<td>180</td>
<td>-</td>
<td></td>
<td>36</td>
<td>0.53</td>
<td>247</td>
</tr>
<tr>
<td>9</td>
<td>360</td>
<td>0.32</td>
<td>0.26</td>
<td>42</td>
<td>0.60</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>720</td>
<td>0.25</td>
<td>0.30</td>
<td>43</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>1440</td>
<td>0.30</td>
<td>0.31</td>
<td>41</td>
<td>0.59</td>
<td>-</td>
</tr>
</tbody>
</table>

* Fraction insoluble in 80:20 alcohol-water mixture.

Figure 37 shows a semi-log plot of crystallinity and infrared density ratio D916/D849 as a function of oxidation time. The minimum value of crystallinity and density ratio both occur at around 120 minutes. It is not possible to relate crystallinity to tacticity, as has been well-known from earlier work reported on PVA. Figure 38 shows X-ray diffraction photographs of crystalline, amorphous standards, untreated controlled PVA-1017 FH and oxidised polyvinyl alcohol sample.

As the oxidation proceeds the polymer gets oxidised and there appears a considerable depolymerization of PVA as shown by decrease in weight of oxidised polymer in Table XXVII. This
OXIDATION REACTION TIME (min.)

FIG. 37: PLOTS OF CRYSTALLINITY AND INFRARED DENSITY RATIO (D916/D849) OF OXIDISED PVA AS A FUNCTION OF OXIDATION REACTION TIME.
Crystalline Standard  
Amorphous Standard

Untreated Control  
(PVA-1017 FH)
Oxidised-PVA

Fig. 38: X-Ray Diffraction Photographs of Polyvinyl Alcohol Samples
reduces the interchain hydrogen bonding and crystallinity of the polymer.

After about 150 to 180 minutes reaction period, little oxidation takes place, but surprisingly, the weight of polymer obtained has decreased considerably. This indicates possibility of faster depolymerization of the highly oxidised samples. Regarding reactivity/tacticity, it is noticed distinctly that initially syndiotacticity of the polymer (density ratio 0.33) favours much faster reaction. As a result density ratio decreases to 0.29, 0.26 and 0.25 in 15, 30-60 to 120 minutes consuming progressively about 247 m moles of oxidant out of 310 m moles initially present. Thus syndiotacticity decreases and atacticity increases. Weight of the polymer obtained after oxidation also follows a trend of gradual decrease upto about 150 minutes. Noteworthy, the sooner the oxidation reaction slows down or level off, the degradation reaction (or depolymerization reaction) gains speed, thus yielding progressively much lower yields of the oxidised products. Tacticity of the degraded products obtained after about 180 minutes, is though atactic but changes gradually to syndiotacticity. X-ray crystallography data reveal initial very fast decrystallization of polyvinyl alcohol changing DC from 88% to 46% in first 15 minutes of the oxidation. DC decreases, then, gradually to about 30%, when oxidation reaction is virtually complete after 180 minutes. Correctly then, the crystallinity increases gradually on further prolonging the period of oxidation to 360 to 720 minutes. The
increase is significant and characteristic. The polymer is considerably lower molecular weight, with atactic nature after 180 minutes. Both this factors favour crystallization, which is noticed to take place predominantly. Earlier studies on film have shown that low molecular weight polyvinyl alcohol crystallizes more favourably than the high molecular weight ones\textsuperscript{261-265}. Syndiotacticity and atacticity also favour crystallization more than isotacticity. In film method, results have possed problem due to anisotropy nature of film\textsuperscript{266}. In the present powder diffraction method, such an interference due to anisotropy is absent. Therefore, the trends and conclusions lend greater reliability.