# PHOTOGRAPHIC GELATIN II

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# Structure Formation in Gelatin Films

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ABSTRACT. The kinetics of structure formation during the setting and drying of gelatin films have been studied by means of optical rotation measurements on gelatin films prepared under widely varying conditions. The separate contributions of helical conformation and planar orientation to the optical rotation are resolved by analysis of the data obtained from measurements with the films tilted at various angles to the incident beam of polarized light.

The studies are made with model systems consisting of comparatively thick films cast on glass plates and monitored during drying at controlled temperature and humidity.

The effects of gelatin hardeners on structural changes are considered. The relationship between the structure of films and their physical properties is discussed.

## INTRODUCTION

The influence of drying conditions on the physical and sensitometric properties of photographic films is well established. However, the effects are known mainly in terms of empirical, use-oriented criteria, which are only of very limited value in assisting an understanding of the molecular processes involved. For studying the mechanism of structural change, optical rotation appears to be a suitable property, since gelatin possesses a high level of optical activity which is very sensitive to environmental change.

The molecular conformations of gelatin and collagen in solution have been thoroughly studied in recent years,[1,2] but the structure of gelatin films has received less attention. Infrared dichroism[3,4] and X-ray diffraction[5-7] indicated collagen-fold formation but the absence of the long-range order of native collagen. In gelatin sols and gels the optical rotation reflects the level of collagen-fold form-

ation, but in gel-dried films the optical rotation is much higher.[6,8,9] Hot-dried (45°) films show no structural order.[10] The optical rotatory dispersion curves of gelatin films are not significantly different from those of solutions, except in the magnitude of the rotation,[11] suggesting that there is no significant difference in molecular conformation; this conclusion is supported by Macsuga's study of thermal transitions in gelatin.[12] However, it has been observed that in films the major axis of the gelatin chains tends to be coplanar with film plane,[13,14] and this would appear to be the structural factor which causes the increased rotation.

The degrees of helical conformation and planar orientation both have an important influence on the properties of a gelatin film. The setting of a gelatin gel involves the formation of the triple chain collagen-fold structure.[15] Slow setting of the gel leads to the formation of larger helical segments. Gels formed under such circumstances have greater thermal stability than have gels formed by rapid chilling.[16,17] During the drying of a gelatin film the helical structure will remain intact if the temperature remains below the melting temperature of the helical segments. Under these conditions as the film contracts vertically, the major axes of the helical segments tend to become oriented in the plane of the film.

With gel-dried films, the closer the drying temperature is to the gel melting temperature, the higher the gelatin concentration at which the helical segments are formed. Hence the films dried at higher drying temperatures will swell less than those dried at lower temperatures, when immersed in water. The degree of orientation in the plane of the film should also be less. However, if the gel is allowed to mature before drying, it shows a much greater degree of swell than does a film dried immediately after coating.[18] The proportion of the gelatin molecule involved in the triple chain helical structure may not be very high, even in well matured gels. Jolley[19] estimates it is about 20%.

In practice it is necessary to increase the thermal stability of photographic films by the use of hardeners. Hardening appears to improve the stability of the helical structure in aqueous solutions.[20] However, if substantial hardening occurs prior to helix formation, the latter process may be significantly inhibited.[21] Thus the effect of hardening on film structure depends on the relative kinetics of the helix-forming and hardening processes.

A method of distinguishing between the contributors of the helical structure and planar orientation of collagen films has been proposed.[22] It is not self-evident that this approach is directly

applicable to gelatin films, which have a less complete and less stable helical structure. Consequently it was necessary to first of all test the theory with a model system consisting of a gelatin gel which was allowed to attain maximum helical structure prior to drying. The theory was then applied to films prepared under somewhat more realistic conditions, with concurrent helix formation and drying. These experiments were performed with model systems consisting of thick, slow drying films.

## EXPERIMENTAL

### Preparation of films

The thick films were cast on glass plates which were converted into moulds by attaching waterproof adhesive tape to the edges.

Into the mould 10 ml of a 50 g per litre gelatin solution was poured. A first extract, lime processed bone gelatin, pH 5·9, isoionic point 5·0, was used. Drying was carried out either under room conditions (20°C, 50% RH) or in a Kottermann Climatic Test Cabinet which could be adjusted to provide a wide range of temperature and humidity.

### Optical rotation measurements

The optical rotation measurements were performed with a Jasco ORD/UV5 Spectropolarimeter. The wavelength at which the measurements were made was 450 nm, as the rotation at lower wavelengths was too high to be measured by the instrument. The films were left on the glass plates during optical rotation measurements, as the plates showed no optical activity or absorption at the wavelength used.

## RESULTS AND DISCUSSION

In order to establish the relationship of the contribution to optical rotation of the helical structure and its orientation it is desirable to obtain independent values of these separate contributions. Yannas *et al.*[22] in their studies of collagen, could do this readily, since the collagen molecules form stable helical structures. The optical rotation of dilute solutions was measured, which provided an indication of the helical contribution, and the degree of orientation of the major axis of the helices in the film plane was determined by X-ray diffraction measurements.

With gelatin the problem is more difficult. At practical concentrations for coating (e.g. 50—100 g per litre) only very incomplete collagen helix structures can be formed, and these tend to rearrange during drying. This difficulty was surmounted by maturing the gel in a sealed container for 24 h, by which time the maximum degree of helical structure had been formed. Thus optimum conditions for stability of the helical content during drying were ensured. The film was set and dried at room temperature (20°C). Facilities for X-ray studies were not available, so it was necessary to deduce the degree of orientation entirely from optical rotation data. The optical rotation values obtained were as follows:

$$[\alpha_{11}]_r = [\alpha_{22}]_r = -1206^\circ$$

$$[\alpha_{33}]_r = +1506^\circ$$

where $[\alpha_{11}]_r$ and $[\alpha_{22}]_r$ are the rotations measured along the two molecular axes perpendicular to the axis of the helix, and $[\alpha_{33}]_r$ is the rotation measured parallel to the helical axis. The subscript $r$ indicates that the specific rotation values have been corrected for refractive index differences, and changes in path length and in the angle to the plane of polarized light which occur at different angles of incidence. The average angle of the helices to the plane of the film was found to be 18°.

Full details of this work have been published elsewhere.[23]

The next obvious step was to observe the differences in structure which arise when setting and drying occur concurrently. A film was cast on a glass plate and allowed to dry out under room conditions over a period of 24 h. The optical rotation of the film at various tilt angles was measured (Table 1). Yannas *et al.*[22] proposed the following relationship between optical rotation and angle of incidence:

$$\alpha_\theta = \alpha_{11} + \frac{(\alpha_{33} - \alpha_{11})}{2} \sin^2 \theta \qquad (1)$$

where $\theta$ is the angle of incidence and $\alpha_\theta$ is the optical rotation of the film for a given angle. By means of this equation and the data given in Table 1, the following optical rotation values were obtained:

$$[\alpha_{11}]_r = [\alpha_{22}]_r = -508^\circ$$

$$[\alpha_{33}]_r = +650^\circ$$

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