



Photographic

SCIENCE AND ENGINEERING

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The Microstructure of Photographic Gelatin Binders

J. E. JOLLEY, *E. I. du Pont de Nemours & Co., Inc., Photo Products Department, Wilmington, Delaware 19898*

Review of measurements made on gelatin solutions and dried layers indicates a structural behavior similar to other semicrystalline polymeric materials. In aqueous solution, the gelatin molecules exist as single chains in random configurations, sheathed by water molecules. This random structure persists under conditions of "hot" drying, e.g., at 50°C, but partial crystallization (i.e., gelation) occurs on "cold" drying, e.g., at 10°C. A new method of estimating the degree of crystallinity from measurement of the heat of melting of an anhydrous gelatin layer is proposed. This gives an estimate of 20% for the maximum crystallinity. This concept of gelatin structure is related to published reports on properties important for a binder of silver halide grains in a photographic emulsion.

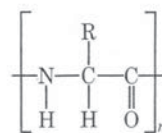
Gelatin has been used in photographic emulsions for about 100 years and plays a variety of important roles. Its chief functions are as a protective colloid, ripening agent, sensitizer, halogen acceptor, and binder, and much research has been directed at understanding how and why it functions in each of these roles.¹⁻⁴ Gelatin's binder properties have probably received least attention, and this paper will concentrate on this aspect. The author will show that when viewed from the point of view of polymer physics, the characteristics of gelatin film structure and gelation fit conventional theories. It is the purpose of this paper to present a unified picture of the microstructural features and properties of gelatin films that hopefully will provide a useful framework for photographic scientists in all fields, although some aspects will necessarily be simplified because of the limitations of time. Much of the information presented is from the literature, but some original data is included.

The general properties that are desired in a photographic binder are that it forms transparent films, strong enough to be handled in both the wet and dry state, which are insoluble, yet highly permeable, to both water and ionic solutions. These are the kind of physical properties that typically depend upon the microstructure of a material, that is to say, the way in which the molecules are arranged in the material. Most solid materials such as plastics

and metals have microstructures that are greatly influenced by thermal treatments, e.g., in quenching and annealing operations. Although it is not generally thought of as such, gelatin is a thermoplastic polymer, and it would be surprising if its microstructure did not also depend upon its thermal history.

The Molecular Structure and Origin of Gelatin

The gelatin molecule is a long chain polymer molecule made up of amino acids joined together by CO—NH linkages called peptide bonds. Its empirical formula is deceptively simple:



In a typical photographic gelatin there may be 500–1000 amino acid units, or residues, in the chain. There are 18 different amino acids in gelatin, and although their precise sequence in the chain has not been elucidated, the general arrangement is clear. Three amino acids make up about 55% of the gelatin molecule. They are Glycine (G), Proline (P), and Hydroxy proline (H), and each gives a non-polar residue. They occur frequently in the terpolymer sequence $(\text{G—P—H})_m$. Glycine appears to occur at every third site along the whole chain with amino acids filling in. About 20% of the amino acids are ionizable, some being acidic and some basic, giving rise to an amphoteric character to the

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1. H. W. Wood, *J. Photogr. Sci.*, **9**: 151 (1961) (78 references).
2. H. Irie, *J. Soc. Sci. Photogr. Japan*, **25**: 59 (1962) (35 references).
3. C. E. K. Mees and T. H. James, *The Theory of the Photographic Process*, 3rd ed., Macmillan, New York, 1966, Chapter 3.
4. H. Borginon, *J. Photogr. Sci.*, **15**: 207 (1967) (105 references).

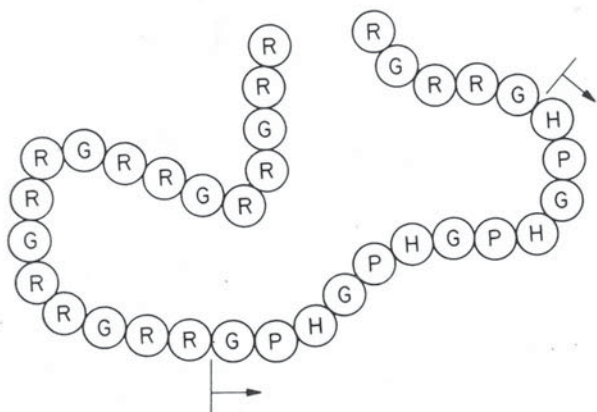


Figure 1. Gelatin molecule.
 G = Glycine
 P = Proline
 H = Hydroxyproline
 R = Other amino acid residues

over-all molecule. Figure 1 illustrates a portion of a gelatin molecule schematically, showing a non-polar $(G-P-H)_m$ sequence and polar $(G-R-R)_p$ sequences.

The gelatin molecule is the basic building block of collagen, the most abundant protein in the animal kingdom, where it occurs in the skin, bone, and connective tissue of mammals. Collagen is an insoluble fibrous protein, with a high degree of order as indicated by its x-ray diffraction pattern. From the x-ray diffraction pattern, it has been deduced^{5,6} that the highly ordered crystalline regions of collagen contain basic crystalline units that consist of three gelatin molecules wound around each other in a ropelike fashion to form what is known as a triple-stranded helix, illustrated in Fig. 2. Not all of the gelatin molecule can participate in such a highly organized crystalline structure, however, but the nonpolar $(G-P-H)_m$ sequences can, and fit perfectly to give a structure that accounts exactly for the observed x-ray pattern. The three chains are held together in the helical conformation by lateral interchain hydrogen bonds, although agreement has not been reached over whether there is one H bond per $(G-P-H)$ unit,⁵ or two.⁶ In the one bonded structure, the H bond is between the amide hydrogen (NH) of the glycine residue on one chain, and the carbonyl oxygen (CO) of the proline residue on the neighboring chain. The highly ordered regions of collagen fibers contain bundles of such triple-stranded helical units, which in polymer terminology are called crystallites. In the non-crystalline regions of collagen, the unordered single-stranded gelatin chains are joined at various points via covalent crosslinks formed between their polar groups, giving collagen its toughness and insolubility.

The gelatin molecule then contains segments that can crystallize into triple-stranded crystallites

(the neutral, $(G-P-H)_m$ sequences) and segments that do not crystallize (the polar sequences).

In the manufacture of most photographic gelatin, bone collagen (ossein) is broken down by alkaline hydrolysis. If done carefully, this yields predominantly single-stranded gelatin molecules, but too vigorous hydrolysis leads to products in which the gelatin backbone is broken in preference to the interchain crosslinks, leading to highly branched structures. For simplicity I will refer to single chains throughout the discussion, but the same principles apply to the more highly branched gelatins. For more detailed information on the molecular structures of gelatin and collagen, and the manufacture of gelatin, those interested are referred to three recent books.⁷⁻⁹

The Microstructural Features of Gelatin Films

In aqueous solution gelatin molecules exist as single chains, completely sheathed by water molecules. The segments of the chain are in a continual state of rapid motion, rotating about the backbone bonds to various degrees depending on the chemical nature of the bonds, the pH, and the temperature. This conformation is known as the random coil configuration. On drying down a thin layer of a solution of gelatin, a clear film is obtained, and it is well known that the film has different microstructure and properties depending upon the temperature of drying.^{10,11} In the subsequent discussion I will consider two extreme examples, "hot dried" film, dried at 50°C, and "cold dried" film, dried at 10°C.

On x-ray examination, the hot dried film gives only a broad diffuse diffraction pattern typical of liquids or glassy materials, indicating no ordering of the gelatin molecules. The gelatin molecules are randomly arranged, essentially like their configuration in solution except that the motion is frozen out. Hot dried films thus have a relatively simple random coil, or amorphous, structure.

In contrast, cold dried gelatin films give an x-ray pattern with a series of diffracted arcs and spots indicating the presence of a definite crystalline species with a high degree of order. The spacings are identical to those found in collagen but have different orientations, indicating the same crystal structure, but a different alignment of the crystallites. If the film is stretched during the cold drying step, the diffraction pattern obtained is essentially identical to that of a natural collagen fiber. This is illustrated in Fig. 3, where the x-ray diffraction pattern of a gelatin film stretched to 3 times its length during drying is compared to that of a piece of natural collagen fiber (kangaroo tail tendon,

7. A. Veis, *The Macromolecular Chemistry of Gelatin*, Academic Press, New York, 1964.
8. G. N. Ramachandran, Ed., *Treatise on Collagen*, Vol. 1, Academic Press, New York, 1967.
9. R. J. Croome and F. G. Clegg, *Photographic Gelatin*, The Focal Press, London, 1965.
10. E. M. Bradbury and C. Martin, *Proc. Roy. Soc.*, **A214**: 183(1952).
11. D. W. Jopling, *J. Appl. Chem.* (London), **6**: 79(1956).

5. A. Rich and F. H. C. Crick, *J. Mol. Biol.*, **3**: 483(1961).
 6. G. N. Ramachandran and G. Kartha, *Nature*, **176**: 593(1955).

KTT). Thus, the ordered gelatin molecules in this stretched film are not only organized in the same triple-stranded helical structure found in natural collagen, but the stretching process oriented them, as in the fiber. In a gelatin film dried on a support-base, as is usually the case, the x-ray diffraction pattern shows the presence of the triple-stranded crystallites arranged so that they lie in the plane of the film, with random orientation in that plane, i.e., in a planar orientation.

It has been noticed by numerous workers in the field that whenever the conditions of film preparation are such that the gelatin solution passes through the gel stage, the resultant dried film contains gelatin crystallites. We can, therefore, anticipate that crystallite formation is intimately connected with gelation, but I will defer detailed discussion of the mechanism of crystallite formation until the next section.

Having established the presence of triple-stranded crystallites in cold dried gelatin films, now let us try to estimate their size and amount. As in most semicrystalline polymers, it is difficult to determine directly the size of the crystallites. From low angle x-ray diffraction measurements, we deduce that their lateral dimensions are quite small, of the order of a hundred to a few hundred angstroms in size. This is typical of polymer crystallites, for example, in nylon, polyethylene terephthalate, polyethylene, etc., and is to be expected because of the interferences from the long tangled

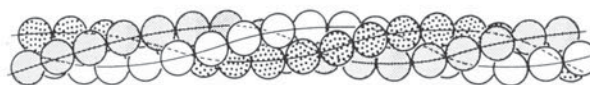
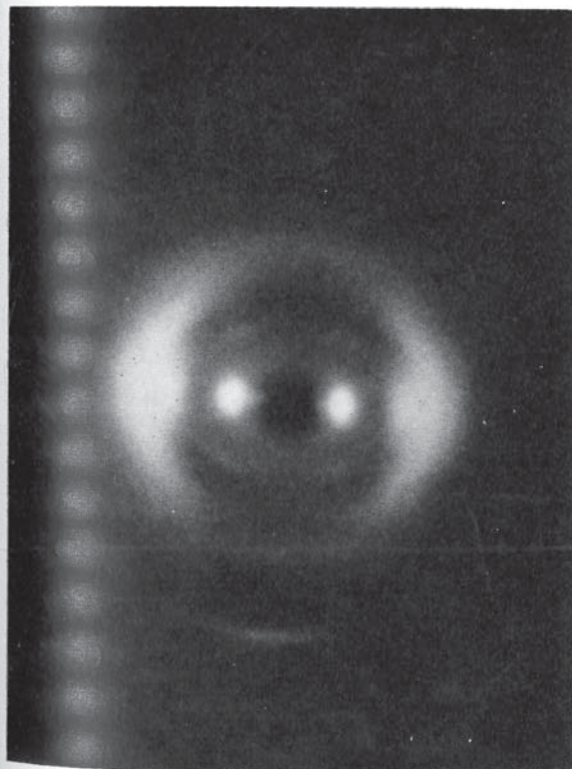


Fig. 2. Collagen structure.

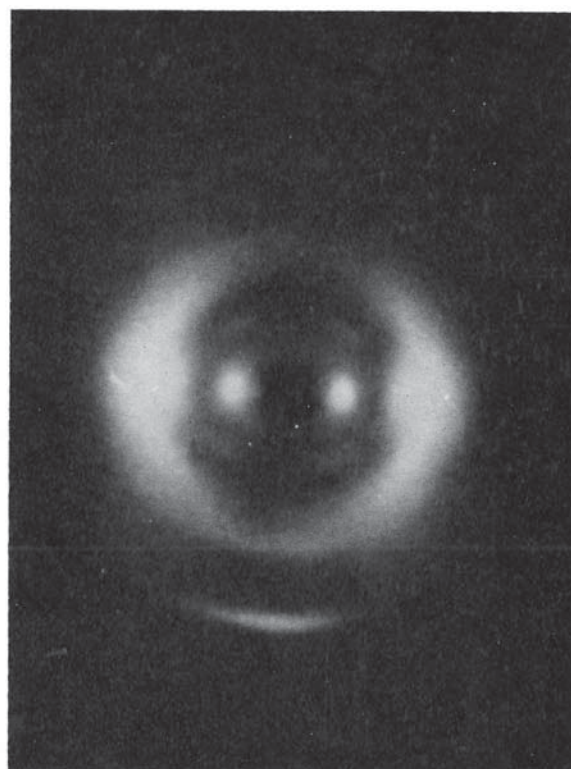
chain ends that only allow perfect crystallization over relatively short distances.

A fundamental characteristic of a crystalline material is that it has a well defined melting point and heat of fusion. By studying the melting behavior of anhydrous cold dried gelatin and collagen we have been able to obtain for the first time an approximate, but direct estimate of the total amount of their crystallinity. It is well known that on heating collagen or cold dried gelatin film the material melts or shrinks rapidly at some temperature, and it has been established by a number of workers that this is due to the melting of the ordered triple-stranded crystallites to disordered single-stranded gelatin molecules.¹²⁻¹⁴ Most studies of this phenomenon have been on materials containing more or less water, which complicates interpretation. We carefully dried samples of cold dried gelatin film and two kinds of natural collagen (ossein and KTT) and measured their melting

12. P. J. Flory and R. R. Garrett, *J. Amer. Chem. Soc.*, **80**: 4836(1958).
13. P. J. Flory and E. S. Weaver, *J. Amer. Chem. Soc.*, **82**: 4518(1960).
14. J. Naghski, A. Wisniewski, E. H. Harris, Jr., and L. P. Witnauer, *J. Amer. Leather Chem. Assoc.*, **61**: 64(1966).



NATURAL COLLAGEN



STRETCHED GELATIN

Fig. 3. X-Ray diffraction patterns.

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