

Temperature Scanning Structural Study on Stratum Corneum

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The outermost layer of skin, stratum corneum (SC), is composed of corneocytes and intercellular lipid matrix. The matrix works as not only the main barrier but also as the pathway of water, drug, etc. In mammalian SCs, long and short lamellar structures with a repeat distance of about 13 nm and about 6 nm, respectively, have been observed by small-angle X-ray diffraction (SAXD) [1,2]. Independently a hexagonal and an orthorhombic hydrocarbon chain packings have been observed by wide-angle X-ray diffraction (WAXD) [1,3]. In the present study we performed the simultaneous small- and wide-angle X-ray diffraction measurements as a function of temperature. The purpose of this study is to make clear the correspondence between the lamellar structure (long or short) and the hydrocarbon chain packing (hexagonal or orthorhombic) from the structural behavior at the phase transitions which have been obtained by our DSC [4].

We carried out the X-ray diffraction measurements with special attention to the correlation of the SAXD and WAXD intensities at 32 and 39 °C where phase transitions take place [4]. In the SAXD the diffraction peaks associated with the long lamellar structure start to bend to higher angle at 32 °C. In the WAXD a new broad peak which seems to be a precursor of a liquid state in the hydrocarbon chain packing. This is consistent with the behavior predicted by the DSC study, that is, the phase transition from the low-temperature hexagonal to liquid-like phase takes place at 32 °C. From these results it was found that the long lamellar structure is composed of the low-temperature hexagonal hydrocarbon chain packing at room temperature. The short lamellar structure generally is broad and is hardly detected by the SAXD at room temperature since its peak appears behind the strong SAXD due to the long lamellar structure, but above 51 °C it becomes evident because the SAXD due to the long lamellar structure disappears. In the SAXD the peak of the short lamellar structure shifts to higher angle with increasing temperature and at the same time the peak for the high-temperature hexagonal packing, which takes the orthorhombic hydrocarbon chain packing below 39 °C, shifts to lower angle. This behavior indicates that the short lamellar structure is composed of the orthorhombic hydrocarbon chain packing at room temperature.

In conclusion, we propose that there are two domains in the intercellular lipid matrix; one is the long lamellar structure with hexagonal hydrocarbon-chain packing and the other the short lamellar structure with orthorhombic packing. As pointed out in our previous paper [3], the long lamellar structure has hydrophobic nature and on the other hand the short lamellar structure has hydrophilic nature. Then, based upon these structural evidences we can thoroughly elucidate the mechanisms of cosmetic function, percutaneous transport, etc.

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