Crystal Structures and Polymorphism in Long-Chain Alkane-α,ω-Diols

Kenjiro UNO

Crystal structure determinations of long-chain alkane-α,ω-diols, HO-(CH$_2$)n-OH, with *n* = 15-24 have been achieved in this study. The crystal structures with a series of chain lengths, *n* = 10-24, have been determined in which our previous reports were included. The results showed a consistent distinction between the structures with odd and even numbers of carbon atoms. In the former group, the molecule had a *gauche* conformation at one of the terminal hydroxy groups. The molecules formed layers in which the long axes of the molecules were normal to the layer plane. In the latter group, the molecule including both terminal hydroxy groups had an all-*trans* conformation. The molecules formed layers in which the long axes were inclined with respect to the layer plane. The group of the even numbered alkane-α,ω-diols further divided into two groups in view of the unit cell and the methylene chain packing in the layer, forming the boundary between 18 and 20 carbon atoms. In addition, the even-numbered alkane-α,ω-diols with *n* = 16-24 showed a polymorphism depending on the crystallizing condition, which crystal structures were similar to those of the odd-numbered alkane-α,ω-diols.

The crystal structures were compared with that of the self-assembled multilayer film formed on the water surface, derived by Popovits-Biro *et al*. from grazing incidence synchrotron X-ray diffraction data. As a result, we suggested that there is room for improvement in the proposed model of the multilayer film. On the other hand, the carbon number starting to exhibit a polymorphic form coincides with that starting to show a rotator phase which are observed just below their melting points. From the viewpoint of the epitaxial crystal growth at the surface, of the calculated density, and of the structures between polymorphic form and rotator phase, it is found that the crystal structure of polymorphic form has an advantage in exhibiting the rotator phase.