Orientational order in oriented lipid membranes. A fluorescence and Raman spectroscopic study.

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Oriented multilayers of dipalmitoylphosphatidylcholine (DPPC) were prepared to work out a method for determination of both the mean orientation of membrane components and the fluctuations around the mean orientation described by orientational order parameters. Polarized fluorescence and Raman spectroscopy is applied to detect orientational order. For the fluorescence studies diphenylhexatriene (DPH) is used as the fluorophore to monitor lipid chain order.

Theoretically the steady-state fluorescence anisotropy of DPH for high orientational order is given by  $r = S (3\cos^2\theta - 1)/2$ , with  $\theta$  the angle between the mean orientation of the fluorophore and the polarization of the incoming light, and S the orientational order parameter. For the ordered phase of DPPC at low water content this angular dependence has been verified, with the result that the mean orientation of the lipid chains is parallel to the membrane normal and S = 0.95.

Polarized Raman spectra of the same system were obtained for different scattering geometries. They correspond to those of single crystals of DPPC (1), if the tilt of the lipid chains in single crystals is taken into account. The band intensities for the different geometries are evaluated for the polarizability tensors of different vibrations, e.g. the C-C stretch vibrations of the lipid chains. This knowledge allows determination of the usual order parameter S and a higher order parameter from polarized Raman spectroscopy.

1) Asher, S.A., Stearns, R., Urabe, T., and Pershan, P.S. (1981) Mol.Cryst.Liq.Cryst. 63, 193.