M-AM-B7 ^{1}H-NMR INVESTIGATION OF THE CONFORMATION OF CHARGED AND ZWITTERIONIC α- and β-PHOSPHOLIPIDS IN SONICATED VESICLES. Andreas Plückthun, Jacqueline deBony and Edward A. Dennis, Department of Chemistry (M-001), University of California at San Diego, La Jolla, California 92093 U.S.A.

The two fatty acyl chains of α-phospholipids are conformationally distinct when the phospholipids are in aggregated structures such as micelles. These differences can also be detected in sonicated vesicles by ^{1}H-NMR spectroscopy (360 MHz) of the α-methylene group using resolution enhancement techniques [J. deBony and E.A. Dennis, Biochemistry 20, 5256-5260 (1981)]. In vesicles with anionic phospholipids or PE at high pH, the spectra of the α-methylene region can be well resolved and fully accounted for. Zwitterionic α-PC, however, shows a more complicated pattern. On the other hand, β-phospholipids such as β-PE, N-methyl-β-PE, and N,N-dimethyl-β-PE give rise to two signals in sonicated vesicles (although both acyl chains are equivalent by symmetry) but only one signal in mixed micelles with detergent. Zwitterionic β-PC, however, shows only one peak in either case. Since this behavior is paralleled by the signals of the N-methyl groups, it probably derives from inside-outside differences of the β-phospholipids in the vesicle. The unusual spectra of both α- and β-PC compared to their charged analogues will be discussed in terms of packing differences within the bilayer. (NSF 79-22839)

M-AM-B8 NATURAL ABUNDANCE CARBON-13 NMR T_1 STUDIES OF LIPID BILAYER MOLECULAR DYNAMICS: EFFECT OF ACYL CHAIN LENGTH AND UNSATURATION. M.F. Brown, G.D. Williams,* and A.A. Ribeiro,†* Dept. of Chemistry Univ. of Virginia, Charlottesville, VA 22901, and †Stanford Magn. Res. Lab., Stanford, CA 94305

Natural abundance ^{13}C T_1 measurements have been made for unilamellar vesicles in which the phospholipid acyl chain length and unsaturation have been varied in a systematic manner. At present, ^{13}C T_1 values have been obtained as a function of temperature for DLPC, DMPC, DPPC, DSPC, and DOPC bilayers, in the liquid crystalline state, at resonance frequencies of 15, 25, 45, and 90 MHz. At superconducting magnetic field strengths, the data clearly reveal a "plateau" in plots of $1/NT_1$ vs. chain position, in agreement with ^{2}H T_1 studies.[1,2] A surprising feature is that $1/NT_1$ is approximately independent of acyl chain length, in spite of the vastly different phase transition temperatures. For the unsaturated DOPC bilayer, $1/NT_1$ of the CH=CH segment is almost twice that of the chain CH_2 segments. These new experimental results will be discussed in terms of theoretical models for molecular dynamics in lipid bilayers. The ^{13}C and ^{2}H T_1 data for the DPPC bilayer can be quantitatively described by a relaxation law of the form $1/T_1 = A\tau_f + BS_{CD}^2\omega_0^{-\frac{1}{2}}$, where A and B are constants, S_{CD} the segmental order parameter, and ω_0 the resonance frequency. The first (A) term corresponds to thermally activated trans-gauche isomerizations of the lipid acyl chains, while the second (B) term describes collective bilayer modes (director fluctuations) which predominantly influence the relaxation frequency dependence. The value of $\tau_f \sim 10^{-11}$ sec suggests that the microviscosity of the bilayer hydrocarbon region is not appreciably different from that of simple paraffinic liquids.
(Supported by NIH Grant RO1 EY 03754 and by the Cystic Fibrosis Foundation).
1) M.F. Brown et al., J. Chem. Phys. 70, 5045 (1979), 2) M.F. Brown, J. Magn. Res. 35, 203 (1979).

M-AM-B9 X-RAY DIFFRACTION AND CALORIMETRIC STUDIES OF N-PALMITOYLGALACTOSYLSPHINGOSINE (NPGS) (CEREBROSIDE) AND DIPALMITOYLPHOSPHATIDYLCHOLINE MIXTURES. M.J. Ruocco*, D.M. Small, R. Skarjune, E. Oldfield and G.G. Shipley, Biophysics Institute, Boston Univ. Schl. of Med., Boston, Mass. and Schl. of Chem. Sci., Urbana, Ill.

Differential scanning calorimetry and x-ray diffraction show that up to 20 mol% NPGS can be incorporated into hydrated DPPC bilayer phases both below and above the gel → liquid crystal transition ($T_c \sim 42^\circ$C). Transition enthalpy measurements indicate complete miscibility of DPPC and NPGS; x-ray diffraction data demonstrate only minor differences in the DPPC bilayer parameters on incorporation of up to 20 wt.% NPGS. At > 20% mol% NPGS additional high temperature transitions indicate phase separation of NPGS. For example, at NPGS:DPPC (mol ratio 1:1), the transition at ∿ 42° C is followed by an exotherm at ∿ 50 C and an endotherm at ∿ 82 C. At 20 C, x-ray diffraction shows two lamellar phases, hydrated DPPC-NPGS ($d \simeq 64$ Å) and NPGS ($d \simeq 55$ Å); further heating to T > 82 °C melts the NPGS phase and a single NPGS-DPPC bilayer Lα phase is formed ($d \simeq 54$ Å). The observed phase behavior suggests that at molar ratios > 1:4 NPGS:DPPC, NPGS-NPGS lateral hydrogen bonding promotes phase separation of the cerebroside.