temperature (25.0 ± 1.0 °C) was regulated by a Varian temperature controller interfaced to an air-flow system. The product yield was obtained by NMR integration of the *tert*-butyl resonances of DTBP and BQ or DPQ.[8] The reproducibility of the reaction was within NMR integration error limits (±3%).[9]

Figure 1 illustrates the effect of a magnetic field on the relative rate, k(rel), of the catalytic oxidation of DTBP. The relative rate is the ratio of the rate at magnetic field (H) to the rate at zero-field. The complicated k(rel) vs. magnetic field strength profile in Figure 1 is analogous to photochemical investigations where the magnetic field alters the intersystem crossing rate between a triplet radical pair and a singlet state product.[1] The observed dependence of k(rel) is between a maximum value of 2.0 in a weak magnetic field and a minimum of $^1/_3$ in an infinite magnetic field.[1,10,11] By use of the procedure developed by Doubleday and Turro, the relative contribution of spin–orbit (SOC) and hyperfine coupling (HFC) to intersystem crossing can be determined.[1c,d] If it is assumed that a radical pair reaction is responsible for the observed magnetochemistry, the ratio of SOC to HFC is estimated to be 77/23 ($H = 0$), 65/35 ($H = 1000$), and 92/8 ($H = 7.0 \times 10^4$) for the cobalt-catalyzed oxidation and 53/47 ($H = 0$), 15/85 ($H = 1390$), and 84/16 ($H = 7.0 \times 10^4$) for the manganese-catalyzed oxidation. As the separation between the unpaired electron spins in a triplet radical pair increases, the contribution from the magnetic field dependent HFC process increases.[11a,b] Spin-sorting reactions involving higher spin states will exhibit a similar trend between electron spin separation distance and the range in k(rel).[11c]

The proposed mechanism[4b,c] of the cobalt-catalyzed oxidation of DTBP is illustrated in Figure 2. In principle, any process that alters the concentration of the active catalyst, Co(*S*MDPT)(O_2) ($S = {}^1/_2$) (steps a and f of Figure 2), the phenoxy radical concentration (steps c and f), or the rate-determining step (step d or e)[4a] will affect the reaction rate. Step a can be eliminated from consideration because its forward rate constant is reported to be on the order of $k = 3.4 \times 10^3$,[12] $>10^5$ times faster than the rate-determining step. Moreover, a 10 000-G magnetic field imparts only a fraction of a kilocalorie to the free energy of the equilibrium. Step b involves the hydrogen bonding of the substrate to the catalyst[13] and cannot be responsible for the spin-sorting process observed. The importance of step c was tested by examining DTBP deuteriated in the phenol position. Since the nuclear magnetic moment of ^2H is smaller than ^1H,[14] the HFC process will be less efficient if step c contributes to the observed effects. The oxidation rate of deuteriated DTBP–OD by either catalyst is within experimental error limits (±3%) of the DTBP–OH rate at $H \geq 0$. Hence, steps a–c are not implicated in the observed magnetic field effect. On the other hand, steps d–f might be responsible for the observed magnetic field effect. Either step d or step e can be interpreted as rate limiting,[4a] and both could involve a spin-sorting process. Step d describes the approach of two doublet molecules to form a radical pair that combines to form the metal peroxide.[4a] If subsequent decomposition of the metal peroxide to BQ and diamagnetic-oxidized catalyst involves homolytic bond cleavage, then step e could be influenced by a magnetic field. Finally, the perturbation of step f, the rate of catalyst regeneration, can alter the reaction rate by changing the steady-state concentration of the phenoxy radical. Therefore, steps d–f singly or collectively can be responsible for the magnetic field behavior.

The fact that Mn(5-NO_2*S*MDPT) and Co(SMDPT) exhibit similar magnetic field effects provides circumstantial evidence that step f is influenced. Mn(5-NO_2*S*MDPT) rapidly converts to the dimer, [Mn(5-NO_2SMDPT)]$_2$$O_2$ ($S = 2$),[5d] in the presence of O_2 and a proton source,[5] and this species generates phenoxy radicals which result in the formation of the coupled quinone, DPQ. Since the manganese catalyst does not form BQ, it appears unlikely that steps d or e in the cobalt-catalyzed oxidation are responsible for the magnetic effect. The manganese-catalyzed reaction exhibits a greater magnetic field effect than cobalt due to the increased importance of HFC.[11c] This is consistent with a manganese dimer and a cobalt monomer catalyst, since the greater separation between the unpaired electron spins in a triplet radical pair is expected for a dimer.

Previous investigations of magnetochemistry have focused on stoichiometric reactions where a triplet radical pair forms both cage and escape products. These reactions often exhibit a magnetically induced change in cage product yield between 5% and 15%.[1,2,10] In certain cases, the reported change is comparable to the error limits. In contrast, the Mn(5-NO_2*S*MDPT)-catalyzed oxidation produces a 27% change in product yield (1390 vs. 70 050G). Hence, the cumulative effect of long-term exposure to relatively weak magnetic fields could be observable because the rate of enzymatic reactions might be altered. The implication of this environmental effect on biochemically significant processes has yet to be investigated adequately.[2i]

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(7) Initial concentrations are DTBP (4.85×10^{-1} M) and either Co*S*MDPT or Mn(5-NO_2*S*MDPT) (8.1×10^{-3} M). The cobalt- and manganese-catalyzed reactions were measured after 36 and 23 h, respectively. Integration of the NMR spectrum requires 10 min and is insignificant compared to the total reaction time. In the case of Co*S*MDPT, formation of DPQ begins to be evident by 41 h. This product is formed by decomposed catalyst, and the rate of DPQ production increases as the catalyst decomposes. The rate of BQ formation catalyzed by Co*S*MDPT and of DPQ by Mn(5-NO_2*S*MDPT) is linear during the initial 36 and 23 h, respectively, and is a good estimate of the initial rate. Initial rates at zero-field are $k(\mathrm{Co}) = 1.2 \times 10^{-2}$ and $k(\mathrm{Mn}) = 1.8 \times 10^{-2}$ M^{-1} s^{-1}.

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Phospholipid Membranes from a Polymeric Phosphatidylcholine[†,1]

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In this report we show that a preformed phospholipid polymer (**2**), derived from 1,2-bis(2-mercaptohexadecanoyl)-*sn*-glycero-3-phosphocholine (**1**),[3] readily assembles into monolayer and bilayer membranes which (i) retain a natural phosphatidylcholine surface, (ii) display a phase transition, and (iii) exhibit compressibility behavior which is nearly identical with that of their monomeric analogue.

Phospholipid monolayers and multilayers represent powerful tools for probing structure–activity relationships of biomembranes.[4-6] Recently, polymeric analogues, having controllable

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[†] Dedicated to the memory of Professor Iwao Tabushi.

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(2) Heim Fellow, 1986–1987.

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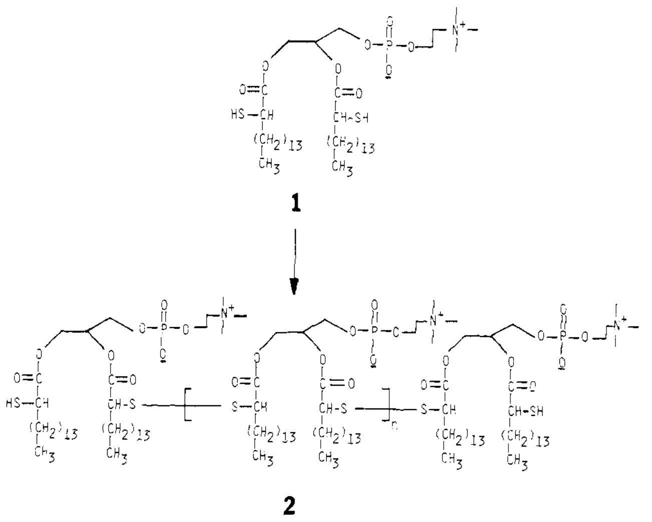
1

2

membrane stability and lateral diffusion rates, have emerged as attractive complementary models for mechanistic use.[3,7] In principle, the preparation of a polymeric phospholipid membrane via assembly of a preformed polymer has one important advantage over polymerization of preassembled lipids: membrane components are not subjected to a polymerization reaction. At present, however, only a few phospholipid polymers have been used for such purposes.[8] In these cases, the lipid head groups were covalently linked to a polymethacrylate backbone through a hydrophilic spacer, resulting in an unnatural membrane exterior; the spacer moiety provides a means for decoupling the motion of the lipid bilayer from that of the polymer main chain.[9] In this paper we show that *spacers are not essential for preserving "monomer-like" packing behavior of a polymeric surfactant and that **2** represents the closest structural and functional polymeric analogue of any phospholipid reported to date.*

By use of procedures similar to those previously described,[3] 26 mg of **1** was dispersed in 5 mL of water via vortex mixing and oxidized with 20 equiv of hydrogen peroxide (40 °C, 5 h). Subsequent dialysis (200 mL of water, 18 h) and freeze drying afforded 24 mg of **2**. End group analysis[3] (thiol content) indicated a maximum number average degree of polymerization of ca. 33.[10]

Surface pressure–area isotherms and temperature–area isobars observed for **1** and **2** revealed a striking similarity. Monolayers of **1** and **2** were spread from 9:1 hexane–ethanol (v/v) solutions (0.3 mg/mL) onto a pure water subphase of a computerized MGW Lauda film balance and were compressed at a rate of 29.3 cm^2/min. Surface pressure–area isotherms obtained for both lipids at 25 °C were *identical*, within experimental error (Figure 1); similar results were obtained at 15 °C. Collisional areas for **1** and **2** were calculated from data obtained between 0.0–9.0 dyn/cm (six isotherms, 15 °C), using the *semiempirical* two-dimensional Langmuir "duplex layer" equation $(\pi - \pi_0)(A - nA_0) = inRT$, which describes a liquid-expanded monolayer state.[11] These collisional areas were 50.1 ± 2.4 and 50.6 ± 4.0 Å^2/lipid for **1** and **2**, respectively.[11] Isobars measured for monolayers of **1** and **2** at 30 dyn/cm revealed a phase transition at ca. 16 °C and were characterized by an increase in area of ca. 5 Å^2/lipid. To the best of our knowledge, lipids **1** and **2** exhibit the smallest difference in packing behavior of any surfactant monomer/polymer pair reported thus far.

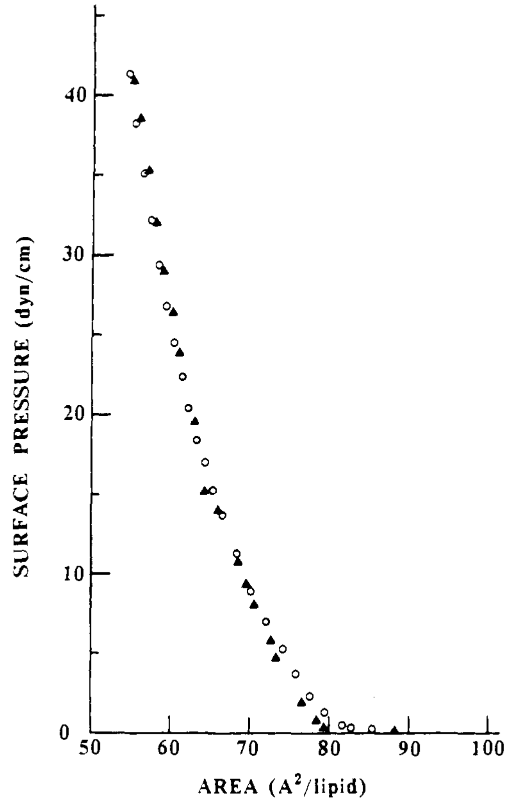

Figure 1. Surface pressure–area diagram (25 °C) for **1** (○) and **2** (▲).

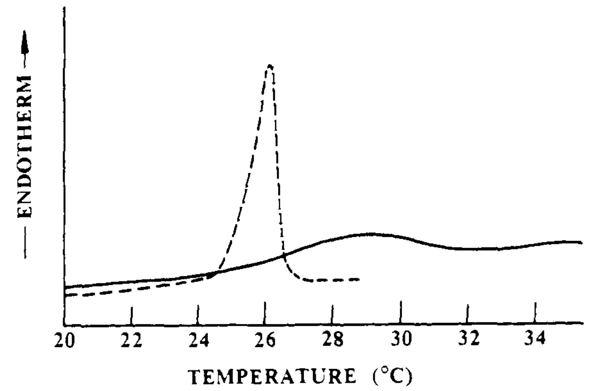

Figure 2. DSC scans of **1** (---) and **2** (—), recorded on a Microcal MC-1 scanning calorimeter using a heating rate of 0.25 °C/min.

Transfer of compressed monolayers (20 dyn/cm, 18 °C) to glass slides by single passage from water into air (0.5 cm/min) resulted in transfer ratios of 1.08 and 1.06 for **1** and **2**, respectively.[12] While attempted transfer of a second layer of **1** (air into water, 13 cm/min) resulted in net loss of lipid from the slide (transfer ratio = −0.50), transfer of a second layer of **2**, under identical conditions, yielded a transfer ratio of +0.60.[13] Similar results

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(13) Prior to the second transfer (air into water), samples were allowed to remain in air for exactly 5 min.

were obtained at 10 °C with use of a constant surface pressure of 25 dyn/cm. The improved transferability of **2** is presumed to reflect a stronger interlipid association in the polymeric state.

Dispersal of **1** in pure water (1.0 mg/mL) via vortex mixing produced a multilamellar dispersion exhibiting a main-phase transition (DSC) at ca. 26 °C (Figure 2), in agreement with temperature-dependent turbidity measurements.[3] The melting endotherm had a peak width at half-height of ca. 0.8 °C with $\Delta H = 5.1 \pm 1.2$ kcal mol^{-1} (four scans). In contrast, **2** exhibited a substantially broadened endotherm at 29 °C with a peak width of 5 °C and a ΔH of ca. 1.7 ± 0.5 kcal (lipid-mol)$^{-1}$ (three scans). The lower ΔH value of **2** appears to be compensated by a smaller ΔS, resulting in an overall increase in the transition temperature. Smaller values of ΔH and ΔS for **2** are a likely consequence of limited fluidity in the "liquid-crystalline" state and/or increased disorder in the gel state, due to the presence of the polydisulfide backbone. Bath sonication of these dispersions produced small vesicles having diameters ranging between 200 and 1000 Å (electron microscopy); dynamic light scattering revealed a similar size distribution.[3] Thin-layer chromatography confirmed the retention of the monomeric and polymeric states of **1** and **2**, respectively.

Space-filling models (CPK) of **2** suggest that the disulfide moiety, positioned α to the carbonyl groups, introduces a minimal perturbation in the packing behavior of the aliphatic chains. Results presented herein confirm this prediction and clearly demonstrate that spacer groups are not a prerequisite for forming tightly packed membranes from preformed polymers. This finding should stimulate further efforts in the design of new polymerizable surfactants. From the standpoint of membrane modeling, the feasibility of preparing polymeric phospholipid monolayers and bilayers directly from **2** should provide new opportunities for constructing unique "biological-like" membranes bearing highly sensitive components. Studies now in progress are aimed at exploring and exploiting these possibilities.

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Electron-Transfer Photochemistry of α-Silylamine-Cyclohexenone Systems. Medium Effects on Reaction Pathways Followed

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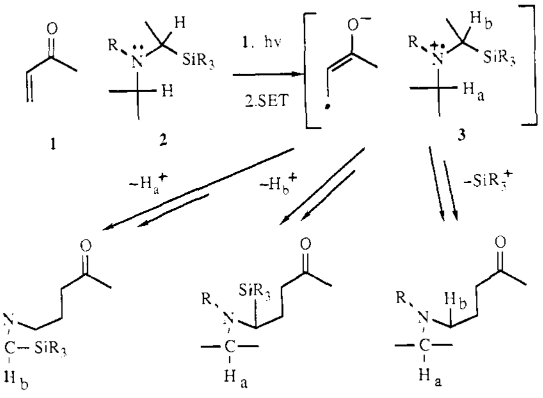
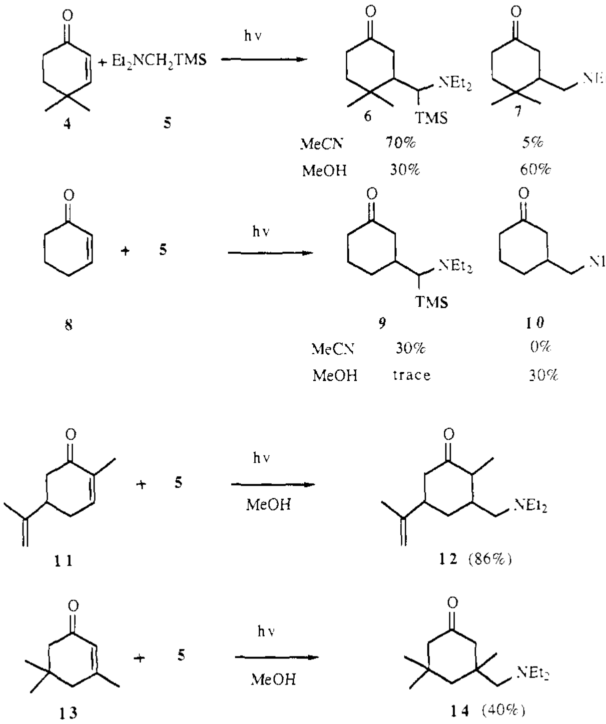
Previously, we demonstrated how photostimulated electron-transfer (SET) processes of α-trialkylsilyl-substituted electron donors can be employed to generate free radical systems.[1] Initial efforts focused on SET processes of iminium salts. Recently, we expanded this methodology to include arenecarbonitriles.[2] In this communication we report on the SET photochemistry of α,β-unsaturated cyclohexenones with an α-silyl tertiary amine donor. Earlier studies have shown that cation radicals derived from tertiary amines react via α-deprotonation and α-C-C bond cleavage,[3] and that α-silylamine cation radicals undergo α-C-Si bond rupture to produce α-amino radicals.[2] Also, tertiary amines are known to serve as electron donors to the triplet states of conjugated cyclohexenones. This process produces amine cation radicals[4] in pathways leading to adduct formation.[5]

Scheme I



Scheme II



These observations suggest that α,β-unsaturated ketones **1** and tertiary α-silylamines **2** could participate in electron-transfer-induced photoaddition reactions as outlined in Scheme I. Pathways

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