

and isolated as a crystalline product as evidenced by single-crystal X-ray analysis and ^{31}P NMR.¹⁸ Thus, as originally anticipated, from inspection of molecular models, easier access by the bulky base to the *pro-R* hydrogen in the *R,R* reagent, for example, leads to a carbanion that shows high diastereofacial bias.¹⁹

Reagents of the type described in this work are unique because of their inherent topology, chirality, and symmetry elements, which are *integral parts of the molecules*, and they differ from other types of phosphorus reagents where asymmetric induction in olefination has been reported.³⁻⁵ The synthesis of optically enriched (alkylcyclohexylidene)ethanes²⁰ and alkylphosphonamides such as demonstrated in the present study may find applications in the synthesis of vitamins,²⁰ pheromones,²¹ etc. as well as in the design of novel chiral catalysts.²²

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Supplementary Material Available: Analytical data, experimental procedure, and a perspective view of the product from **1**, R = Me (9 pages). Ordering information is given on any current masthead page.

(18) For R = Me, mp 96–96.5 °C; $[\alpha]_{\text{D}} -81.5^\circ$ (CHCl_3), R = Ph, mp 95–97 °C, $[\alpha]_{\text{D}} -34.6^\circ$. The allyl derivative from the *S,S* reagent showed mp 87–89 °C, $[\alpha]_{\text{D}} +92.8^\circ$.

(19) When the anion was quenched with deuteriomethanol and the resulting deuterated phosphonamide (54% deuterium content) was treated sequentially with KDA then benzyl bromide (THF, –78 °C), the diastereomerically pure *R*-benzylated product contained only 14% deuterium, indicating a higher proportion of *pro-R* deuterio species in the deuterated phosphonamide and reflecting on the substantial “*pro-R*” bias of the anion.

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Ghost Vesicles¹

Steven L. Regen* and Jae-Sup Shin

*Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233*

James F. Hainfeld and Joseph S. Wall

*Department of Biology
Brookhaven National Laboratory
Upton, New York 11973*

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In this communication we describe the use of surfactant vesicles as templates for the synthesis of ultrathin spherical polymer membranes. Microspheres that are produced *upon removal of the lipid bilayer* are termed “ghost vesicles”.

We have previously reported the synthesis of a new class of polymerized vesicles in which a lipid bilayer is encased within concentric polymeric counterions.² Recently it occurred to us that by forming cross-linked analogues, it might be possible to extract the surfactant bilayer and to leave behind extremely thin

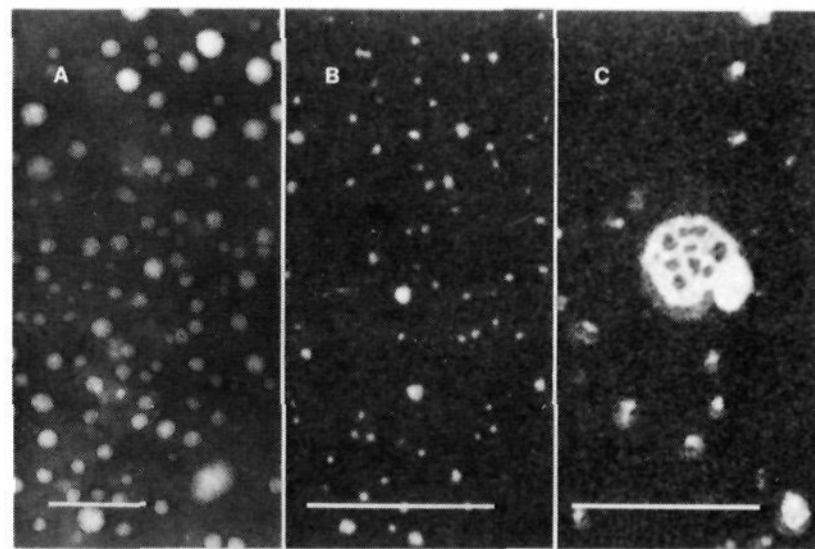


Figure 1. Electron micrographs of **3**: (A) 2% uranyl acetate stain (bar represents 3000 Å); (B) STEM (bar represents 5200 Å); (C) STEM (bar represents 2600 Å).

polymeric spheres. We further reasoned that such “ghost vesicles” would not only be unique in structure, but that they also could be of considerable practical value. They could, for example, serve as attractive packaging material for the encapsulation of metal colloids, enzymes, and other catalysts.³ Because of their thinness, the barrier toward mass transport of reactants into and products out of the carrier should be minimal. In addition, ultrathin membranous compartments might constitute an ideal medium for separating donor and acceptor species over *short* distances, making highly efficient energy- or electron-transfer processes possible.⁴ With these ideas in mind, we have begun to focus on the feasibility of preparing such polymers. In this report we now describe the synthesis and preliminary characterization of the first example of a ghost vesicle, derived from polymerized vesicles of diallyl-ammonium dihexadecylphosphate (**1**) plus sodium dihexadecylphosphate (**2**).

Dihexadecylphosphoric acid was converted into **1** by treatment with diallylamine in ethanol/water (6/4); the resulting surfactant was recrystallized from ethyl acetate and gave the expected ^1H NMR spectrum. Dispersal of 118 mg (0.18 mmol) of **1** plus 104 mg (0.18 mmol) of **2** in 100 mL of water, via vortex mixing and sonication at 80 °C (to constant turbidity), afforded a stable vesicle dispersion. Thin-layer chromatography indicated that no lipid decomposition occurred during sonication [silica gel, 1:1 $\text{CHCl}_3/\text{CH}_3\text{OH}$, $R_f(\mathbf{1})$ 0.75; $R_f(\mathbf{2})$ 0.70]. Vesicle polymerization was carried out by direct UV irradiation at 254 nm (12 h) under a nitrogen atmosphere using procedures similar to those previously described.⁵ Thin-layer chromatography indicated the disappearance of **1**, retention of **2**, and a product remaining at the origin. Temperature-dependent turbidity measurements (400 nm) confirmed the presence of bilayers, before and after photopolymerization; both exhibited a well-defined phase transition in the expected range of 63–66 °C.⁶ The resulting dispersion was (a) treated with 20 mL of 1.0 M HCl and stirred at room temperature for 6 h, (b) dialyzed twice against 2 L of water for 24 h, and (c) freeze-dried. After the successive and dropwise addition of chloroform (10 mL) and ether (10 mL), the mixture was allowed to stand for 6 h. The vesicular ghost was then collected by filtration and dried [24 h, 25 °C (0.05 mm)], yielding 15.3 mg (62%) of **3**. Anal. Calcd for a polymer having a repeating unit consisting of $\text{C}_6\text{H}_{12}\text{NCl}^{1/4}\text{H}_2\text{O}$: C, 52.17; H, 9.12; Cl, 25.67; N, 10.14; P, 0.00. Found: C, 52.18; H, 9.00; Cl, 25.57; N, 9.88; P, 0.05. The IR spectrum of **3** showed nearly complete disappearance of the olefinic absorption band $\nu_{\text{C}=\text{C}}$ 1635 cm^{-1} , indicating that the extent of polymerization is high.

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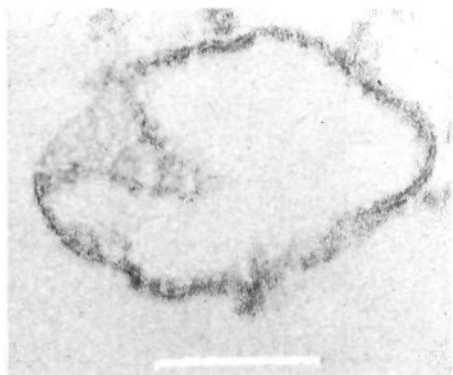
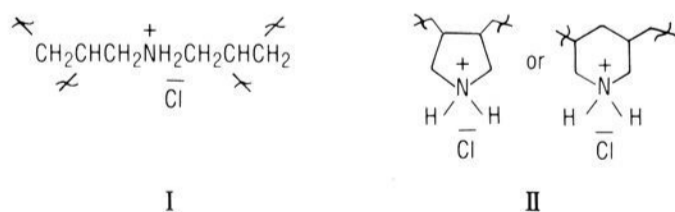


Figure 2. Electron micrograph of a stained (uranyl acetate) thin section of **3** (bar represents 2000 Å).

Redispersal of **3** (0.5 mg) was readily achieved by simple vortex mixing in distilled water (2.0 mL) at 60 °C. Passage of this dispersion through a Sephadex G-50 column afforded an 84% recovery of the polymer in the void volume of the column (nitrogen analysis).⁷ Electron microscopic examination (negative staining) confirmed the presence of closed spheres having diameters ranging between ca. 200 and 2000 Å (Figure 1A). Incubation of the dispersion with an aqueous solution containing (¹⁴C)sucrose for 100 h at room temperature, followed by gel filtration (Sephadex G-50), resulted in negligible entrapment of the marker.⁵ The inability of these ghosts to retain low molecular weight species is presumed to be due to the absence of a continuous lipid layer.

Examination of an *unstained* dispersion by scanning transmission electron microscopy (STEM) at low magnification revealed a size distribution similar to that found by negative staining (Figure 1B).^{8,9} A plot of the measured mass for a representative sample of ghosts (46 particles having diameters ranging from 100 to 520 Å) as a function of particle radius gave a best fit to a hollow sphere model with a membrane thickness of 14 Å (assuming a density for the bulk polymer of 0.92).¹⁰ Virtually none of the data fell within a solid sphere model. Some of the membranes of the larger ghosts appeared to be torn (Figure 1C). Analysis of such vesicles (600–2300 Å diameter) indicated an apparent quantization in membrane thickness; i.e., the thinnest layers observed were 14 Å; most other thicknesses measured were ca. 28, 42, or 56 Å. We presume that the larger thicknesses observed are due to vesicle aggregation.

In principle, every surfactant bilayer containing **1** should be capable of generating two concentric polymeric spheres. Electron micrographs of stained thin sections of **3** (ca. 900 Å) not only confirm their hollow nature but also reveal regions where two distinct membranes can be identified (Figure 2). Whether or not portions of these membranes have joined together during the polymerization remains to be established. Polymerization of **1** in the highly condensed vesicular state is expected to result in substantial cross-linking and the formation of a porous network,^{11,12} i.e., the generation of type I monomer units. The observed



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 (10) Ultracentrifugation (100 000 rpm, 30 min) of an aqueous dispersion of **3** in pure water indicated a very slow rate of flotation. Taking 1.00 g/cm³ as an upper limit for the density of the bulk polymer, and 0.85 g/cm³ (density of polypropyleneimine) as an estimate for the lower limit, the density of **3** is estimated to be ca. 0.92 g/cm³; within a density range 0.75–1.00 g/cm³ the calculated membrane thickness varied by less than 25%.
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retention of the spherical state of **3** in water provides very strong indirect evidence for the existence of such cross-linking. The extent to which competing cyclopolymerization occurs (yielding 5- or 6-membered rings II in each of the monolayers), however, is less certain.

Experiments now in progress are aimed at defining and controlling the porosity of **3**, further characterizing its membrane structure, and extending this methodology to the synthesis of related polymer colloids. The results of these studies will be reported in due course.

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Registry No. Diallylammonium dihexadecylphosphate (homopolymer), 91550-89-9; sodium dihexadecylphosphate, 60285-46-3.

Metal-Promoted Insertion of an Activated Alkene into a B–H Bond of an Exopolyhedral *nido*-Rhodacarborane: Rhodium-Catalyzed Hydroboration

John D. Hewes, Charles W. Kreimendahl, Todd B. Marder, and M. Frederick Hawthorne*

Department of Chemistry
 University of California at Los Angeles
 Los Angeles, California 90024

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In conjunction with our mechanistic studies of the catalytic hydrogenation of alkenes using *exo-nido*-[(PPh₃)₂Rh][7,8-μ-(CH₂)₃-7,8-C₂B₉H₁₀] (I),¹⁻³ we have observed the metal-promoted insertion of an activated alkene into a terminal B–H bond of the carborane ligand of I. We report here the synthesis⁴ and X-ray crystallographic structure determination⁵ of the product of this reaction, *exo-nido*-[(PPh₃)₂Rh][7,8-μ-(CH₂)₃-10-[(CH₂)₂C(O)-O(CH₂)₃CH₃]-7,8-C₂B₉H₉] (II), and propose a mechanism for its formation from I.

The molecular structure of II (Figure 1) consists of a rhodium(I) bis(triphenylphosphine) moiety attached to a *nido* C₂B₉ icosahedral fragment through a pair of three-center, two-electron Rh–H–B bonds. The unique BH at vertex 10 in I has been transformed into B(CH₂)₂CO₂(1-C₄H₉) in II by formal hydroboration of the acrylate ester.

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(4) A 10 mL of THF solution containing 0.50 g (0.57 mmol) of I, 4.0 mL (28 mmol) of 1-butyl acrylate, and a trace of hydroquinone was stirred at 40 °C for 5 days in a sealed Pyrex tube. Concentration of the solution in vacuo and addition of heptane produced dark red crystals of II in 69% yield. Anal. Calcd for C₄₈H₅₈B₉P₂O₂Ph: C, 62.04; H, 6.29; B, 10.47; Rh, 11.08; P, 6.67. Found: C, 62.22; H, 6.58; B, 10.14; Rh, 10.66; P, 6.73. Results from spectroscopic analysis were consistent with the observed structure and with previously reported structures.^{1,2}

(5) Crystal data for II: A red, thin, irregularly shaped parallelepiped crystal suitable for X-ray analysis was grown from pentane/CH₂Cl₂ by vapor diffusion under N₂. Triclinic, *P1*; *a* = 12.404 (3) Å, *b* = 13.826 (4) Å, *c* = 14.941 (4) Å, α = 95.58 (2)°, β = 101.92(2)°, γ = 109.35(2)°; *V* = 2327 (4) Å³; *Z* = 2; *d*_{calcd} = 1.326 g/cm³; μ(Mo Kα) = 4.68 cm⁻¹. An automated diffractometer (Syntex P1) was used to gather 6220 reflections with *I* > 3(*I*), corrected for absorption, with the crystal at 133 K. The structure was solved by using standard Patterson, Fourier, and least-squares techniques and refined to residuals of *R* = 0.053 and *R*_w = 0.064 with a "goodness-of-fit" index of 1.66. *R* = Σ(|*F*_o| - |*F*_c|)/Σ|*F*_o|; *R*_w = [Σw(|*F*_o| - |*F*_c|)²]/Σ(w|*F*_o|²)]^{1/2} where *w* = [1/Σ|*F*_o|²]; "goodness-of-fit" = [Σw(|*F*_o| - |*F*_c|)²/(*N*_{obsd} - *N*_{parameters})]^{1/2}.