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Ion Exchange Resins as Emerging−Submerging Chemical Sensors

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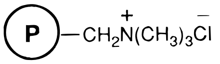
A new concept in chemical sensing has been introduced that uses changes in density of a cross-linked polymer to physically signal changes in solution composition. Prototype systems that have now been developed are based on Amberlite IRA 400 (Cl), where anion exchange provides a driving force for the resin's emergence from, and submergence into, water *due to changes in bead density*. The potential utility of such sensors is briefly described.

Ion-exchange resins are widely used today in laboratory- and industrial-scale purifications and as analytical tools.[1,2] In this paper, we introduce a new concept in chemical sensing that uses changes in density of an ion-exchange resin to *physically signal* changes in solution composition.[3] Specifically, we show that the exchange of anions within Amberlite IRA 400 (Cl) provides a driving force for its emergence from, and submergence into, water *due to changes in resin density* and that such changes signal the presence of a defined anion composition in water.[3,4] We further demonstrate the feasibility of using Amberlite IRA 400 as an "emerging−submerging" (ES) sensor in liquid−liquid phase-transfer catalysis.[5] *The ability of such sensors to operate in the millimolar-to-molar concentration range, together with their high ion specificity and the fact that electrical or optical methods of detection are not required, make them unique as sensing materials. These features could lead to their use as novel sensing materials, especially for industrial-scale synthesis.*

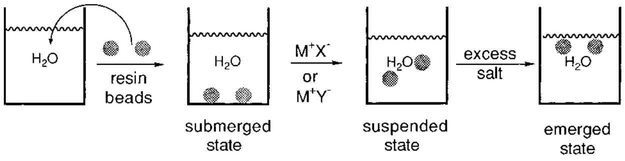


$\text{P}-CH_2\overset{+}{N}(CH_3)_3\overset{-}{Cl}$

Amberlite IRA 400 (Cl)

The basis for our ES sensor concept is illustrated by the following hypothetical example: Introduction of a minimal amount of an anion-exchange resin (X^- form) to water results in swelling of the beads and submergence due to a resin density that exceeds that of water (Scheme 1). If a metal salt of X^- (i.e., M^+X^-) is then added to the aqueous phase, the density of the solution increases. At a sufficiently high concentration of M^+X^-, the density of the solution matches that of the resin and the beads are now transformed into a suspended state. We define this concentration as the *critical solution concentration* with respect to X^- or CSC_x. Any further increase in salt concentration beyond this point drives the beads to the air−water interface (emerged state). A similar experiment that is carried out with this same resin using M^+Y^- also leads to suspended and emerged states. In this case, however, the resin is first converted into its Y^- form via ion exchange, and the critical solution concentration for Y^- is now given as CSC_y. If the density of the Y^- form of the resin is higher than its X^- form, then CSC_y will be greater than CSC_x. Thus, for a solution that is composed of a *mixture* of X^- and Y^-, the observed CSC will depend upon the molar ratio of X^-/Y^- that is present, the equilibrium constant that governs the ion exchange, the contributions that X^- and Y^- make to the density of the resin and to the solution phase, and the contribution that the polymeric counterion itself makes to the density of the resin. In principle, a calibration curve that describes the critical solution concentration as a function of the mole fraction of X^- or Y^- should allow one to identify a defined composition of these two anions by the appearance of a suspended state.

Scheme 1



To establish the ES sensor concept, we first examined the emerging−submerging properties of Amberlite IRA 400 (Cl) in the presence of varying concentrations of hydroxide, chloride, and bromide. Thus, a 45-mL vial was charged with ca. 3.0 mg of the Amberlite resin (16−50 mesh, 0.011 mmol of quaternary ammonium groups, ca. 10 beads) plus 10 mL of a given salt solution that was intially 5.2 mol/kg of water. Gentle swirling of the mixture for 10 min, followed by brief standing (1 min) resulted in emerged states; i.e., in all cases, the beads were floating at the air−water interface. Dilution of each system with water led to suspended states when the concentrations of NaOH, NaCl, and NaBr were 2.21, 3.16, and 3.83 mol/kg of water, respectively. These concentrations correspond to solution densities that are equal to 1.082, 1.109, and 1.264 g/cm^3, respectively.

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(1) Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962.

(2) *Handbook of Ion Exchange Resins: Their Application To Inorganic Analytical Chemistry*; Korkisch, J., Ed.; CRC Press: Boca Raton, FL, 1989.

(3) For reviews of sensors, see: Hughes, R. C.; Ricco, A. J.; Butler, M. A.; Martin, S. J. *Science* **1991**, *254*, 74. Janata, J.; Josowicz, M.; DeVaney, D. M. *Anal. Chem.* **1994**, *66*, 207R.

(4) Amberlite IRA 400 is a strongly basic anion-exchange resin that has a porous gel structure, which is based on a styrene/divinylbenzenze copolymeric framework.

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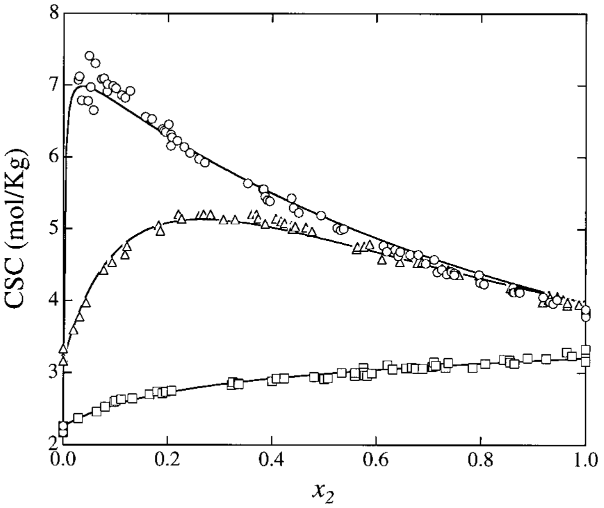

Figure 1. Plot of CSC for Amberlite IRA 400 as a function of mole fraction of (○) NaBr in NaOH/NaBr; (△) NaBr in NaCl/NaBr; (□) NaCl in NaOH/NaCl in solution. The solid lines represent curves that are based on eq 6.

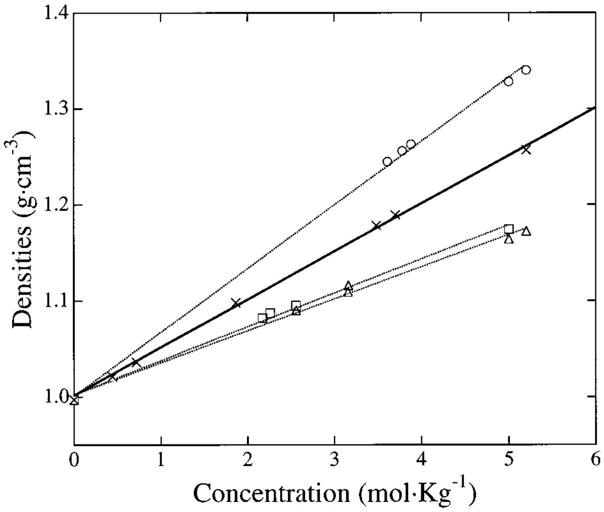

Figure 2. Plot of solution density as a function of salt concentration: (○) NaBr; (×) 50 mol % NaCl in NaCl/NaBr; (□) NaOH; (△) NaCl.

Isolation of the resin by filtration, followed by washing with deionized water, drying under reduced pressure, and combustion analysis confirmed that ion exchange was essentially complete.

To demonstrate the feasibility of using Amberlite IRA 400 as an ion sensor, critical solution concentrations were then determined as a function of the mole fraction of hydroxide that was present in varying mixtures of sodium hydroxide and sodium chloride. Specifically, dilution of mixed salt solutions, followed by gentle swirling and settling of the beads, yielded CSC values that are shown in Figure 1. Analogous experiments that were carried out using mixtures of sodium chloride/sodium bromide and sodium hydroxide/sodium bromide yielded calibration curves that are also shown in this figure.

The complex nature of these calibration curves can be readily understood, qualitatively, if one takes into account the ion selectivity that is characteristic of strongly basic anion-exchange resins such as Amberlite IRA 400 (i.e., $Br^- > Cl^- > HO^-$), and the densities of the corresponding salt solutions. Specifically, the appearance of a CSC maximum for the NaOH/NaBr curve reflects the fact that the resin has a preference for binding bromide ion over hydroxide ion and that the density that is associated with NaBr solutions is much greater than that of NaOH solutions at comparable concentrations. Thus, as the mole fraction of bromide that is present in solution increases, the mole fraction of bromide within the resin increases to a greater extent. Since the bromide form of the resin has a higher density than that of its hydroxide form and since NaOH solutions are lower in density, high concentrations of mixed salt solutions are needed to produce a suspended state at relatively high NaOH/NaBr ratios; i.e., the CSC values increase. When the bromide content within the resin is sufficiently high, however, further increases in bromide ion concentration in solution result in minimal changes in resin density. At this point, the CSC values begin to decrease since lower concentrations of the salt solution that now become richer in NaBr are needed to match the density of the resin. Under these conditions, the resin begins to act more as a *densitometer*. In essence, to the "left" of the CSC maximum, the resin functions as an ES sensor for HO^-/Br^- ratios; to the "right" of the maximum, it acts more as a densitometer. Qualitatively, similar behavior can be seen for the NaCl/NaBr system. In this case, however, the ES sensor range is extended (the maximum shifts to the right) as a result of reduced ion selectivity.

The calibration curve that is associated with NaOH/NaCl differs significantly from each of the others within this series. Here, the CSC values *continue to increase* on going from pure NaOH to pure NaCl solutions. The reason for this difference lies in the fact that the solution density profile for NaOH and NaCl are essentially the same (Figure 2). Specifically, while chloride ions contribute more to the density of Amberlite IRA 400 than do hydroxide ions, both ions contribute similarly to the density of aqueous solutions; i.e., at similar concentrations, the density of aqueous NaOH and NaCl solutions are nearly identical. As a consequence, CSC values are found to increase, monotonically. Similar to the NaOH/NaBr and NaCl/NaBr systems, the curvature that is apparent in this plot reflects ion selectivity, i.e., the resin favors the binding of chloride ions over hydroxide ions.

From an operational standpoint, the appearance of a suspended state in solutions made from mixtures of NaOH and NaCl reveals *one* specific anion ratio. In contrast, the formation of a suspended state in each of the NaCl/NaBr and NaOH/NaBr systems can signal the presence of two distinct anion ratios in solution—a consequence of having a CSC maximum. Thus, depending upon whether an experiment is begun to the "left" or to the "right" of this maximum, and also depending upon which direction one is going, experimentally, either one of these ratios can be identified. It is particularly noteworthy that while densitometry could, in principle, be used as an alternate analytical tool for the NaCl/NaBr and NaOH/NaBr systems, it would not be applicable in the case of NaOH/NaCl, since solution densities are essentially independent of HO^-/Cl^- ratios.

A quantitive description of these calibration curves can be obtained, if one considers both the ion-exchange equilibrium that exists and also the changes in density within the resin and within the solution phase that accompany changes in salt concentration. Thus, if we let K represent the equilibrium constant that governs the ion exchange and if we express the concentration of the soluble and resin-bound ions in terms of mole fractions, then this equilibrium can be described by eq 1, where y_2 is the mole fraction of the Y^- form of the

$$\mathrm{resin{\cdot}X} + \mathrm{Y}^- \rightleftharpoons \mathrm{resin{\cdot}Y} + \mathrm{X}^-$$

$$K = \frac{[\mathrm{resin{\cdot}Y}]\cdot[\mathrm{X}^-]}{[\mathrm{resin{\cdot}X}]\cdot[\mathrm{Y}^-]} = \frac{y_2}{1 - y_2}\,\frac{1 - x_2}{x_2} \qquad (1)$$

resin, and x_2 is the mole fraction of M^+Y^- in the total salts that are present in solution.[6] Rearrangement of this equation then allows y_2 to be defined in terms of K and x_2 (eq 2). If it is assumed that the contributions

$$y_2 = \frac{Kx_2}{1 + (K - 1)x_2} \qquad (2)$$

that X^- and Y^- make to the density of the resin are additive, then the resin density can be defined by eq 3,

$$\rho_{\mathrm{resin}} = (1 - y_2)\rho_{\mathrm{resin},1} + y_2\rho_{\mathrm{resin},2} = \frac{(1 - x_2)\rho_{\mathrm{resin},1} + Kx_2\rho_{\mathrm{resin},2}}{1 + (K - 1)x_2} \qquad (3)$$

where $\rho_{\mathrm{resin},1}$ and $\rho_{\mathrm{resin},2}$ represent the individual densities of the resin in their X^- and Y^- forms, respectively. Substitution for y_2 in this equation then yields a rearranged form that expresses the resin density in terms of x_2.

If it is further assumed that the contributions that X^- and Y^- make to the *solution* densities are additive (eq 4, where ρ_{sol} is the density of the solution and $\rho_{\mathrm{sol},1}$

$$\rho_{\mathrm{sol}} = (1 - x_2)\rho_{\mathrm{sol},1} + x_2\rho_{\mathrm{sol},2} \qquad (4)$$

$$\rho_{\mathrm{sol},i} = k_iC_i + b_i \qquad (i = 1, 2) \qquad (5)$$

$$\mathrm{CSC} = \frac{\dfrac{(1 - x_2)\rho_{\mathrm{resin},1} + Kx_2\rho_{\mathrm{resin},2}}{1 + (K - 1)x_2} - [b_1(1 - x_2) + b_2x_2]}{k_1(1 - x_2) + k_2x_2} \qquad (6)$$

and $\rho_{\mathrm{sol},2}$ are the individual densities of the single component solutions containing X^- and Y^-, respectively) and that the solution density is directly proportional to the salt concentration, C (eq 5, where k_i is the proportionality constant and b is the density of the solution in the absence of the salt), then under conditions in which the resin is in the suspended state (when the density of the resin, ρ_{resin}, equals the density of the solution, ρ_{sol}), it can be shown that the critical solution concentration is given by eq 6. The facts that the solution density of a 1/1 molar mixture of NaCl/NaBr is directly proportional to its concentration and that its proportionality constant lies midway between that found for NaCl and NaBr solutions verify our assumptions concerning the additivity rule in solution (Figure 2).

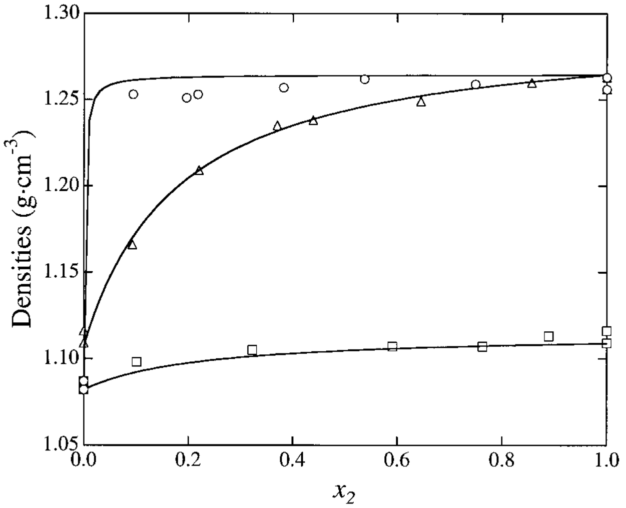

Figure 3. Plot of resin density (determined by measuring the solution density at the CSC) as a function of mole fraction, x_2, of (○) NaBr in NaOH/NaBr, (△) NaBr in NaCl/NaBr, and (□) NaCl in NaOH/NaCl in solution. The solid lines represent theoretical curves based on eq 3; values for $\rho_{\mathrm{resin},1}$, $\rho_{\mathrm{resin},2}$ and K were obtained by curve fitting of the data shown in Figure 1.

Included in Figure 1 are curves that have been obtained by fitting the CSC data as a function of x_2 by use of eq 6; specific values of b_1, b_2, k_1, and k_2 that were used were experimentally determined. As is readily apparent, the fit in each case is excellent. On the basis of such analysis, specific values of $\rho_{\mathrm{resin},1}$ (or $\rho_{\mathrm{resin},2}$) are estimated to be $\rho_{\mathrm{resin,OH}} = 1.082$, $\rho_{\mathrm{resin,Cl}} = 1.109$, and $\rho_{\mathrm{resin,Br}} = 1.264$, which are in excellent agreement with those obtained by direct measurement (vide ante). In addition, the ion selectivity of the resin showed the expected ordering ($Br^- > Cl^- > OH^-$); specific values for K were $K_{\mathrm{Cl/OH}} = 5.5$, $K_{\mathrm{Br/OH}} = 590$, $K_{\mathrm{Br/Cl}} = 6.5$.[7] Finally, plots of resin density as a function of x_2, which have been calculated using eq 3, were in excellent agreement with experimental values that were obtained by measuring the solution density at the appropriate CSC (Figure 3). This agreement lends strong support for our assumption concerning the additivity of the resin-bound anions, with respect to their contributions to the overall density of the resin.

In principle, one would expect that the dynamic range of an ES sensor should be extended to lower ion concentrations if changes in the buoyancy of the resin were determined more by changes in resin composition and less by changes in solution density, which result from changes in ion concentrations in solution. Two

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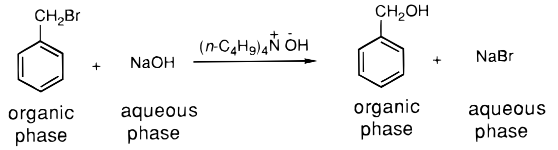
(5) *Phase-Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives*; Starks, C. M., Liotta, C., Eds.; Chapman and Hall: New York, 1994.

(6) The equilibrium constant that is defined in eq 1 is the same as the ion-exchange selectivity coefficient when the ion content of the resin is negligible with respect to the total ion content of the solution. It should be noted that selectivity coefficients depend upon the degree of cross-linking of the resin, the degree of substitution within the ion-exchange sites, the concentration of salts in the external solution, the temperature, and other experimental factors.[1,2]

(7) As mentioned in footnote 6, selectivity coefficients are highly dependent upon the specific experimental conditions used. For this reason, no quantitative comparisons have been made with other literature data.

experimental approaches that can be taken in order to create such a situation are as follows: (i) to synthesize resins that have densities that match that of the aqueous solutions (in the absence of the ions that are to be detected) and (ii) to use an inert solute for adjusting the density of the solution. For feasibility studies, we have chosen the latter approach. Specifically, we have found that Amberlite IRA 400 favors an emerged state in the presence of sucrose (1.09 mol/kg of water) that contains 0.017 M NaCl. When 17 mol % of the NaCl is substituted by NaBr, however, a suspended state is favored; at higher levels of substitution, a submerged state was observed. At these concentrations, no significant change in solution density was observed on going from NaCl to NaBr.

In preliminary experiments, we have found that Amberlite IRA 400 (Cl) can be used as an ES sensor in liquid−liquid phase-transfer catalysis. Thus, introduction of 4 mg of the resin to 3 mL of a 5.0 M solution of NaOH, which was placed over 3 mL of a 0.3 M benzyl bromide solution in CH_2Cl_2, resulted in an emerged state. After addition of 0.3 mmol of a phase transfer catalyst (tetra-*n*-butylammonium hydroxide) and moderate stirring at room temperature, the beads began to "drop" to the aqueous/organic interface after 2 h.[8] Analysis of the organic phase by gas chromatography showed the appearance of an 82% yield of benzyl alcohol.[9] Although we have not constructed a calibration curve for aqueous NaOH/NaBr, when in contact with dichloromethane, we have found that the presence of dichloromethane increases the CSC for aqueous NaOH from 2.21 to 3.00 mol/kg of water. Thus, caution should be used in applying this technique to each new system of interest.



The ability of an ion-exchange resin to act as an ES sensor relies upon its ability to undergo a change in overall density as a result of ion exchange. These changes depend not only upon the specific ions and counterions involved, their concentrations in solution and within the polymer, the equilibrium constant that governs the ion exchange, the degree of swelling, and the hydration state of the resin but also the structure of the polymer itself, i.e., the structure and composition of the polymer backbone and pendent groups and the concentration of the cross-link units and pendent groups that are present. One would expect, therefore, that some degree of control over the emerging/submerging properties of a resin should be possible by chemical design. The fact that *physical movement of an ES sensor is directly coupled to an ion-exchange process* raises the intriguing possibility that such sensors could have practical utility as chemically responsive switches or check valves for flow reactors, where steady-state concentrations of ions are sought.[10] Moreover, the facts that ES sensors do not require any electrical or optical input for detection and that they are capable of operating at high ion concentrations should make them attractive analytical alternatives, especially for industrial-scale synthesis, e.g., as "stand-alone" sensors for on-line applications. Finally, it should be noted that the emerging/submerging characteristics of an ES sensor should be well-suited for practical development by use of combinatorial strategies, where desirable combinations of polymeric hosts and guests can be rapidly identified.[11] Efforts aimed at expanding the ES sensor concept, with a view toward cations, other anions, and neutral solutes are continuing in our laboratories.

Experimental Section

Materials. Amberlite IRA 400 (Cl) and all of the salts used in this work were obtained from Aldrich Chemical Co. and used without further purification. House-deionized water was purified using a Millipore Milli-Q-filtering system containing one carbon and two ion-exchange stages. Borosilicate glass vials (28 × 108 mm, 11 dram), equipped with polyvinyl-faced/pulp-lined caps, and disposable transfer pipets (polyethylene, fine tip, 5.0 mL), which were used for all dilutions, were purchased from VWR Scientific Products.

General Method for Determining Critical Solution Concentrations. In a typical experiment, a 45-mL vial was charged with 3.0 mg of the Amberlite resin (16−50 mesh, 0.011 mmol of quaternary ammonium groups, ca. 10 beads) plus 4.94 g of an aqueous NaOH solution (5.2 mol/kg of water) and 3.70 g of an aqueous sodium chloride solution (5.2 mol/kg of water). After the mixture was gently swirled for 10 min at ambient temperature, all of the resin appeared at the air−water interface. Water was then added, incrementally (3−4 drops, 0.06−0.08 mL), and was followed by gentle swirling (30 s). The contents were then allowed to stand for ca. 2 min in order to determine whether the beads were in the emerged, suspended, or submerged state. If they remained in the emerged state, further dilution with water was carried out using this same procedure. The suspended state was evident when the beads maintained a random distribution throughout the aqueous phase for more than 5 min. If the beads appeared to become submerged, the entire experiment was repeated. In this experiment, a total volume of 5.41 mL of water was required in order to reach the suspended state, which corresponds to a CSC of 2.92 mol/kg of water and a mole fraction of NaCl of 0.41. For the NaOH/NaCl and NaOH/NaBr mixtures, the beads were randomly distributed throughout the aqueous phase. In the case of the NaCl/NaBr mixtures, only a fraction of the beads became suspended; emerged and submerged beads were also observed.

Acknowledgment. This research was based, in large part, on studies that were carried out as part of

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(8) In this experiment, the reaction mixture was vigorous stirred and stopped, intermittently, to identify the location of the beads. Here, "flotation" effects were evident. Thus, with only *mild* stirring, the beads were "held" at the air−water inteface due to surface tension effects. It should be noted that flotation methods (widely used for the separation and purification of metals and polymers) are based on forces that are fundamentally different than those of ES sensing. Specifically, while flotation relies upon surface tension effects, ES sensing relies upon changes in *bead density and gravitational forces*. For a more complete discription of flotation methods, see: *Physico-chemical Elementary Processes In Flotation*; Schulze, E. J., Ed.; Elsevier: New York, 1984. An alternate way of eliminating surface tension for ES sensing would be to place the beads in a "cage" that is submerged in order to avoid contact with the air−water interface. Under such conditions, the suspended state within the cage would be evident; emerged and submerged states would correspond to intimate contact with the upper and lower portion of the cage, respectively.

(9) Tridecane was used an internal standard for quantitative analysis.

(10) *Perry's Chemical Engineers' Handbook*, 6th ed.; Perry, R. H., Green, D., Eds.; McGraw-Hill Book Co.: New York, 1984.

(11) For recent reviews describing the combinatorial method, see: (a) Czarnik, A. W., Ellman, J. A., Eds. *Acc. Chem. Res.* **1996**, *29*, 112. (b) Szostak, J. W. *Chem. Rev.* **1997**, *97*, 347 and other papers in this special issue.

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