

# Synthesis and Application of Nano-Size Polymer Colloids

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## ABSTRACT

Over the last 50+ years The Dow Chemical Company has sponsored numerous research programs involving the preparation and use of nano-size colloidal systems. The nano-colloids used range from soft (liquid microemulsions) to solid (polymeric) materials and from organic to inorganic. Application areas include catalysis, polymer latices, delivery systems, consumer and personal care products, reaction media and nanoporous media. In this paper a fundamental study and two related application areas will be reviewed. The first topic covered is fundamentals of microemulsion formulation, followed by their application in the preparation of nano-sized polymer colloids. Also reviewed will be the use of amphipathic block copolymers to form highly stable unilamellar and multilamellar vesicles and their use as delivery systems for sensitive functional ingredients.

**Keywords:** microemulsion, nanoparticle poragen, vesicle, diblock surfactant, encapsulation

## 1 INTRODUCTION

The work described in this paper has its origins in efforts at The Dow Chemical Company to develop a fundamental understanding of the formulation and application of surfactants and microemulsions in a wide variety of applications ranging from cleaning products to reaction media [1]. As part of this work, formulation strategies were developed to form microemulsions which were stable over broad temperature ranges and oil/water volume ratios. Efficient surfactants and cosurfactants were also identified and synthesized. Using this fundamental understanding, microemulsion approaches were utilized for the synthesis of nano-sized polymer colloids as small as 5 nm. These colloids were subsequently dispersed in a polymer films for the preparation of nanoporous films for use in microelectronic devices. Studies designed to identify more efficient surfactants led to the development of ethylene oxide/butylene oxide block copolymers. In addition to their utility for the preparation of microemulsions, we have found that these block copolymers form highly stable vesicles. These vesicles have shown promise in the stabilization and delivery of actives in a number of applications.

## 2 MICROEMULSION FORMULATION

Microemulsions have been used in a broad range of applications ranging from drug delivery to enhanced oil recovery. Work has focused on the development of stable

microemulsion formulations requiring the minimum amount of surfactant while maintaining phase stability under use conditions. In order to study the efficiency of surfactants for the preparation of microemulsions we characterized the efficiency of surfactant systems in bicontinuous (Type III) microemulsions for equal volumes of water and oil. This characterization can typically be done through the generation of “fish” diagrams such as that shown in Figure 1 [2, 3]. The surfactant efficiency is defined by the minimum surfactant concentration at which a single phase microemulsion is obtained.

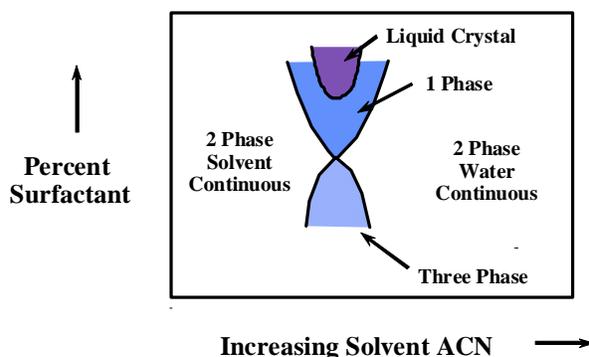


Figure 1: “Fish” diagram used for determining surfactant efficiency.

Fish diagrams can also be used to study the effect of oil structure, oil/water ratio, electrolyte content, temperature and other factors on phase behavior. An example of one such diagram is shown in Figure 2. In this study it was shown that it is possible to produce microemulsions using as little as 0.5wt% surfactant at equal volumes of oil and water.

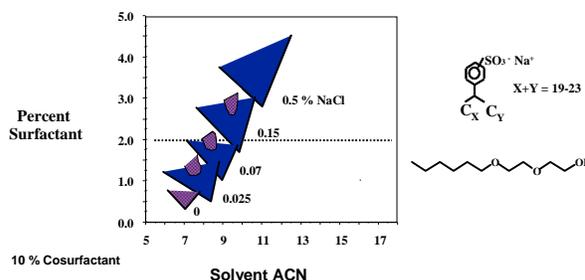


Figure 2: “Fish” diagram (top portion) used for model system prepared using 10% diethylene glycol hexyl ether. Numbers in chart represent percent NaCl present

Using the “fish” diagram approach, numerous surfactants have been characterized for their efficiency in forming microemulsions. In addition to commercially

available surfactants experimental surfactants such as ethylene oxide/butylene oxide (EO/BO) block copolymers have also been characterized. Figure 3 shows surfactant efficiency for a series of EO/BO copolymers with equivalent EO content in a water-hydrocarbon system. In this series, surfactant efficiency increases with molecular weight up to a total polymer molecular weight of ~4500. Presumably this increase in efficiency is due to an increasing tendency of the polymers of higher polymer MW's to reside at the oil-water rather than the air-water interface.

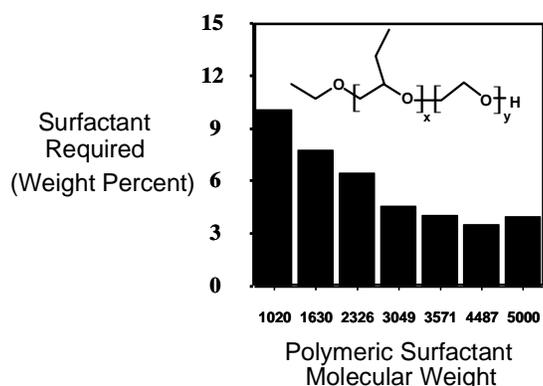


Figure 3: Efficiency vs. MW (EO/BO Polymeric Surfactants).

This fundamental understanding of surfactants and microemulsion phase behavior was used to develop polymerization conditions for the preparation of polymer nanoparticles such as those described in the Section 3. In addition the understanding of the relationship between surfactant structure and interfacial activity has led to the development of surfactants for other colloidal systems such as the EO/BO block copolymer vesicles described in Section 4.

### 3 POLYMER NANOPARTICLE TEMPLATES FOR POROUS FILMS

A continuing need in the microelectronics industry is, as interconnect linewidths decrease, for better interlayer insulating materials with ever lower dielectric constant  $\kappa$  to enable increased device densities and faster processing. SiLK<sup>TM</sup>, a polyarylene interlayer dielectric developed by Dow, has dielectric constant  $\kappa=2.65$ ; efforts to develop lower  $\kappa$  polyarylene materials have focused on decreasing  $\kappa$  by introducing porosity. This section will overview a key approach taken in these laboratories to develop the desired porosity [4, 5, 6].

Requirements for the porosity include: uniformly small pore size and pore distribution, closed porosity, and the porous material must exhibit good fracture toughness and a high pore yield.

A variety of attempts were made to introduce porosity by including a polymeric poragen with the matrix monomer, B-staging, spin coating, and heating to cure and devolatilize the poragen. Linear and star-shaped polymers with ethynyl functionality, as well as densely side-chain functionalized polyacrylates were employed to this end [4,7].

A key issue with these poragens is that pore generation is highly process sensitive; the result is that pore size, shape and density are highly dependent on the cure temperature profile. In retrospect, this is not surprising as pore formation depends on self-assembly of the poragen in a polymer matrix in which it may not have been fully soluble.

It was hypothesized that an approach employing a pre-organized spherical poragen, in which one poragen would template one pore, would allow good control of pore shape, size, and size distribution, with low process sensitivity.

A microemulsion polymerization approach [8, 9, 10] was employed to prepare the desired poragens [11, 12, 13]. Key poragen requirements include ionic and elemental purity (C, H, O only), a low volume swell factor (VSF) to avoid particle-particle overlap, ability to yield spherical pores, robustness to thermal processing, with low residue yield and volume (~weight) average diameter ( $D_v$ ) controllable from 5-20 nm. These requirements pointed to the use of styrene-based poragens made with non-ionic components only.

The microemulsion polymerization method also offered a great deal of synthetic flexibility in terms of allowing flexibility of monomer content, surface functionality, etc. This would allow tuning of properties such as the thermal devolatilization profile, and minimization of devolatilization residue.

A typical polymerization [11] was conducted in semi-continuous mode as follows: a styrene-divinylbenzene plus a functional monomer mix was continuously fed into an aqueous solution of a nonionic surfactant at 30 °C. The redox initiator (hydrogen peroxide/ascorbic acid) was co fed. The product was precipitated with an equal volume of methyl ethyl ketone followed by centrifugation. The resulting solid was resuspended and washed repeatedly. The total residual metal content was 1.3 ppm and the residue on thermal treatment at 500 °C under N<sub>2</sub> was 0.37 wt%.

The nanoparticles were characterized by size exclusion chromatography (SEC) using viscometric detection [11]. The retention volume at each time increment was related to a  $\text{Log}(IV \cdot M)$  using the universal calibration [14]; M could then be calculated at each retention volume from the measured intrinsic viscosity (IV). The VSF was also be determined from these data. From the polymer density  $\rho$ , weight average molecular weight M, and Avogadro's number L,  $D_v$  was calculated as follows:

$$D_v = 2 * \left( \frac{0.75M}{\pi L \rho} \right)^{1/3}$$

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The Mark-Houwink plot had slope  $\alpha \sim 0$  across the molecular weight distribution, showing that the suspended polymer nanoparticles are spherical (Figure 4) [15].

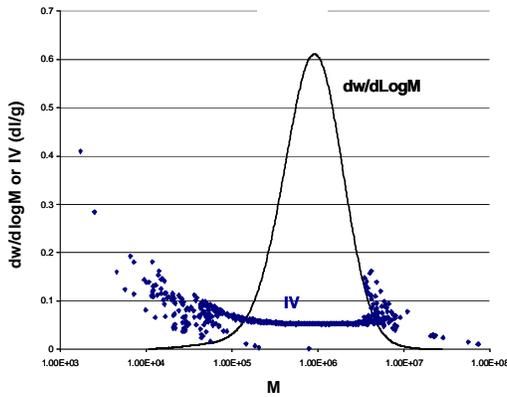


Figure 4. Molecular weight distribution and Mark-Houwink plot for a 15.4 nm diameter polymer nanoparticle.

By this method, the particles have a “collapsed” (unswollen)  $D_v = 15.4$  nm. Dynamic light scattering in THF shows a mean particle diameter, after correcting for solvent swelling ( $VSF = 2.10$ ) and the  $M_z/M_w$  ratio, of 17.5 nm. SEC using MALLS detection yielded a collapsed particle diameter of 16.6 nm. The particle sizes determined by these different methods are in very good agreement. Results using these methods typically also correlate well with hydrodynamic chromatography and TEM results.

The isolated dry particles form a dusty solid that may be swollen and dispersed in appropriate solvents. The proton NMR spectrum shows signals typical for a crosslinked styrenic polymer; a resonance typical of poly(ethylene oxide) is present also. This resonance did not disappear on repeated re-precipitation, suggesting that a small amount of the nonionic surfactant grafts to the particle surface during nanoparticle formation.

Typically, the poragens are B-staged with arylene monomers in solution to yield a prepolymer containing the poragen [11, 13]. The resulting solution is diluted and spin coated on a silicon wafer, then cured to 430 °C resulting in a nanoporous film (Figure 5) with approximately spherical pores 8~10 nm diameter, in high yield.

Porous films made using 12 and 7 nm poragens exhibited successively smaller pore diameters of 8-10 and 5-6 nm respectively on film formation, as shown by SAXS. Pore morphology was relatively insensitive to the cure profile.

Spherical polymer particles as small as 4.9 nm ( $M_w = 28,500$ ) have been made by this method. The synthetic process has been successfully scaled from a lab scale of a few grams to multiple kilograms in a pilot plant.

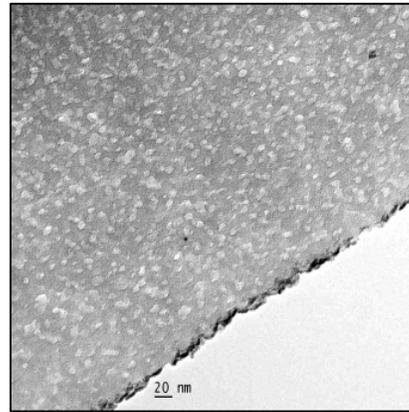


Figure 5. Porous polyarylene film prepared using a 12 nm poragen.  $\kappa = 2.1-2.2$ .

#### 4 EO/BO BLOCK COPOLYMER VESICLES

Surfactant materials can self-assemble into a wide variety of meso-scale structures depending on surfactant composition, extent of hydration and aqueous environment [16]. One such structure is a vesicle; a hollow, spherical nano-particle composed of a bilayer surfactant wall and an aqueous core. These structures are naturally produced from phospholipids and are the basic template of biological cells. However, formation of vesicles from phospholipids can be a laborious and complicated process [17]. Work was initiated in the 1970's to explore whether or not these structures could be useful for encapsulation of actives, but they proved to be too fragile for most commercial applications [18].

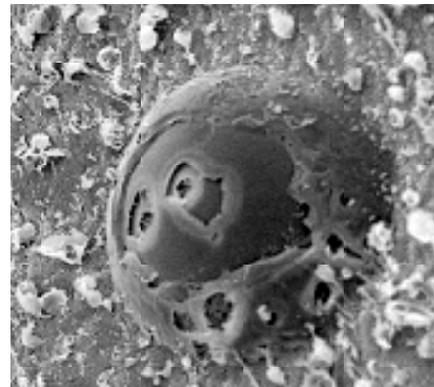


Figure 6. Cryo-SEM micrograph of  $BO_{12}EO_{12}$  MLV in 1.0 wt % aqueous solution taken 10 weeks after formation. The particle is  $\sim 7$   $\mu m$  in diameter.

Surfactants prepared from ethylene oxide/ butylene oxide diblock copolymers have been shown to spontaneously produce vesicles on hydration [19]. Proper selection of block lengths ensures vesicle formation, while the hydration regime can produce vesicles that range from

~80 nm to 1 mm in diameter from the same copolymer composition [20]. Vesicles may be multi-lamellar (MLV) or uni-lamellar (ULV) structures depending on synthesis conditions. Like phospholipid-based structures, post-structure formation processing can be used to convert MLV's into ULV's.

Research on the potential of these materials for actives encapsulation has shown that both hydrophilic and hydrophobic materials can be sequestered [21]. These structures are particularly robust, easy to load and easy to process, thus offering significant potential for use in many encapsulation applications. Work done by Jordan *et al.* show that the materials can encapsulate, protect and deliver vitamin A and other selected organic acids [22].

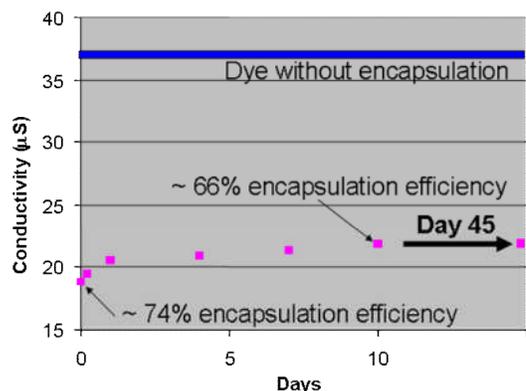


Figure 7: Release profile of an ionic dye in  $\text{BO}_{12}\text{EO}_{12}$  MLV in 1.0 wt % aqueous solution as measured by conductivity.

## 5 CONCLUSIONS

Fundamental work done over a number of years in the areas of microemulsion phase behavior and surfactant structure activity relationships has been applied to a number of technology areas of interest to The Dow Chemical Company. Nanoparticle poragens made by microemulsion polymerization have found application in low  $\kappa$  dielectric film formation, and vesicles composed of novel block copolymer surfactants can be formed spontaneously, and have utility in personal care applications.

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