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DEVELOPMENT, SYNTHESIS AND CHARACTERIZATION OF NOVEL MULTIFUNCTIONAL POLYMER-SECURED SELF-REGISTERING MOLECULAR ARRAY SYSTEMS

By

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ABSTRACT

DEVELOPMENT, SYNTHESIS AND CHARACTERIZATION OF NOVEL MULTIFUNCTIONAL POLYMER-SECURED SELF-REGISTERING MOLECULAR ARRAY SYSTEMS

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The main objective of this dissertation is to develop novel multifunctional polymer-secured self-registering molecular array systems with potential applications in electronic equipments, magnetic, optical and biomimetic materials development.

In chapter 2, an idealized model with four functional elements was proposed. Based on this model, three systems were developed and described (chapter 3 and 4). System I was a biomimetic material with potential application as bone filler or scaffold of bone tissue engineering. System II and III can be used as templates for extensively ordered nanoparticle structure fabrication. System III also has polydiacetylene function in the electronically and/or optically responsive region, which enables the system to respond to different stimulae, such as temperature, UV light, etc. The synthesis for these systems is very simple and highly efficient. The systems are stable because of the polymerization, and at the same time, very sensitive to the environmental factors that impact on the overall organization. In chapter 5, the three self-registering polymeric systems were evaluated with a variety of methods.

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CHAPTER 1

THE USE OF ORGANIC TEMPLATES FOR THE STRUCTURED AND CONTROLLED ORGANIZATION OF METALS, METAL OXIDES AND SALTS

ABSTRACT

Biomineralization is the facilitated deposition of inorganic substances in organic matrices. Proteins, polysaccharides and lipids frameworks provide the templates for regulated aggregation or nucleation of inorganic minerals in the biological system. This process is used as the guiding principle in the development of new materials. Surfactants, copolymers, dendrimers and in-vitro biological molecules are fabricated into membranes or templates to control nucleation and growth of mineral phases. Salts, metals and metal oxides are incorporated into the organic-inorganic composite system. In this process, the structures of the organic-inorganic composites are highly controlled from atomic to macroscopic levels, resulting in complex architectures that provide multifunctional properties. The composites have found applications in many areas such as electronics, solar cell, magnetic recording, etc.

1.1 Introduction

The goal of this project is to control the deposition of arrays of inorganic materials such as salts, metals and metal oxides on organic templates to form ordered materials. The materials should have extended arrays, periodic structures or very defined local arrays of limited scale in one dimension such as nanosystems. Strategies to accomplish this require the development of advanced organic chemistry based technology and materials to provide the underlying templates to facilitate array formation.

1.2 Biomineralization as a model for templated organization of metal oxides and salts.

The prototypical systems in which soft organic molecules are used as templates to facilitate the arraying of inorganic materials are biological in origin. Examples of these include bone and teeth formation. This entire area is covered under the general theme of mineralization.

Biomineralization is the study of the formation, structure and properties of inorganic solids deposited in biological systems[1]. It is widely seen in nature. Proteins, lipid structures and larger macromolecular frameworks provide the templates to direct the aggregation or nucleation of inorganic minerals. The modulation of the organic components can work through interface interaction or through forming supramolecular organic-inorganic composites. Various interactions such as chemical bonding,

electrostatic attraction or repulsion, mechanical stress, or spatial confinement define the properties of the system[2]. The structures of biocomposites are highly controlled from atomic to macroscopic levels, resulting in complex architectures that provide multifunctional properties.

Inorganic minerals in nature include ion oxides in magnetobacteria, magnesium silicates, calcium carbonates, and calcium phosphates in invertebrate shells and vertebrate skeletons. The most common organic components in organisms include lipids, proteins and polysaccharides[2]. Lipids are water insoluble cellular molecules. These amphiphilic molecules are composed of one or more hydrocarbon (hydrophobic) tails and a polar organic (hydrophilic) head group. The most abundant macromolecules are the proteins. Proteins are polymers of amino acids joined covalently through peptide bonds. Examples of using proteins as templates for biomineralization include collagen as a major component in bones, S-layers in bacteria, and an organic matrix in mollusks or diatom cell walls. The final commonly seen biomolecules used as templates are polysaccharides. Polysaccharides contain more than 20 connected monosaccharides. Important polysaccharides found in nature include cellulose in plants and chitin which is the second most common structural fiber in animals.

1.2.1 Proteins as biomineralization templates:

The organic matrix in situ can control both the morphology and the orientation of

the crystal growth. The matrix in mollusks, for example, is composed of two parts, EDTA (ethylene diamine tetraacetic acid) soluble part and insoluble part. The EDTA soluble part is mainly composed of hydrophilic anionic proteins with functional groups to nucleate the desired mineral and/or interact with the growing crystal faces[3]. The insoluble part is composed of hydrophobic proteins and polysaccharides. It is a scaffold that helps to array the functionalized hydrophilic part. These components work together to form the complex structures found in mollusks.

Similar results were found in the cell walls of diatoms. Diatoms are unicellular algae with cell walls predominantly composed of a biomineral derived from hydrated silica (SiO_2), in association with peptides and polyamines[4]. The silica precipitation mechanism is not very clear, but one hypothesis suggests that the organic matrix in silica deposition vesicles promote and direct the process[5]. Detailed investigations uncover the controlling effects of the organic matrix. Comparison experiments show that the organic matrix helps the process of silica mineralization [6]-- untreated supersaturated silicic acid solution, which can remain stable for several hours, starts to precipitate right after the addition of the organic component separated from diatom cell wall. This demonstrates the nucleate assistant function of the organic component. In addition, the organic components can control the size of the inorganic particles by their molecular weight. The addition of the smallest organic component leads to formation of particles with diameters between 500-700 nm, while the mixture forms particles with the average diameters of < 50 nm.

Bone is one of the most important organic-inorganic biocomposites in higher vertebrates. It is made of an organic matrix that is strengthened by the deposition of an ordered special form of calcium phosphate minerals, hydroxy apatite (HAP). The organic matrix is mainly composed of type I collagen fibers (95 %)[7]. HAP provides bone's hardness, and the organic collagen fibers provide flexibility. The tensile strength of the fiber resists being stretched or torn.

The function of morphology and function of bones are closely connected with the structure of the organic matrix. There are two forms of bones: cancellous (spongy) and cortical (compact). Cancellous bones are made of a loosely packed and disordered porous matrix, and only provide metabolic functions. Cortical bones, however, are composed of organized and densely packed collagen fibers and minerals and provide structural support and protection.

The general importance of proteins and peptides on nucleation and growing stages of minerallization are continuously demonstrated by a variety of in-situ experiments on crystallization of calcium carbonate. For example, chiral crystals of calcite were formed in the presence of pure D-, L-Aspartic acid due to the preferential binding of the amino acid enantiomer to the crystals which provide the best geometrical and chemical match[8]. Homo- or heteropolymers of amino acids also have significant effects on calcium carbonate crystallization[9].

1.2.2 Polysaccharides as biomineralization templates

Chitin is a linear polysaccharide composed of β-(1,4)2-acetamido-2-deoxy-D-glucopyranose residues. It is produced by a variety of animals, insects and fungi[10]. Chitin can be found in one of the three crystalline forms[11]: α-chitin, β-chitin and γ -chitin.

α-Chitin forms the organic matrix of the shell of pink shrimp *Pandalus borealis.* Calcium carbonate associated with the chitin is amorphous, while after continued frozen storage, the amorphous phase crystallizes into two forms—calcite and vaterite. The chitin is an integral part of the crystallized regions and thought to be important in calcium carbonate deposition[12].

The organic matrix found in the internal shell of the cuttlefish (*Sepia officinalis*) is a β-chitin template. Sheets of aragonitic calcium carbonate formed on the template were separated by pillars in a manner similar to a honeycomb[13]. The pillars are sigmoidal in cross section, which provides maximum resistance to crushing with minimum mass of material. β-Chitins also serve as an organic scaffold in the shell of *Lingula unguis* for the apatite crystals to precipitate on. The lamella structure has improved mechanical properties. The fiber axis of β-chitin being parallel to the *c* axis of apatite and the close relationship of unit cell dimensions of chitin and apatite show the orientation effect of β-chitin[14].

Another study determined the modification effect of polysaccharides in the localization

of iron oxyhydroxide mineral precipitation in microorganisms[15]. The iron oxyhydroxide mineral goes through a redox reaction to enhance metabolic energy generation. When compared with representative K-edge X-ray absorption near edge structure (XANES) spectra from various organic polymers, including proteins, lipids, and nucleic acids, the spectrum of nonmineralized fibrils matches best with alginate, an acidic polysaccharide. The author infers that the cells extrude the polysaccharide strands to localize FeOOH precipitate outside the cell membrane to control the proton gradient for energy generation.

1.2.3 Lipids as biomineralization templates:

One common biological strategy employed during the formation of biominerals is controlling the location, size, composition, and shape of mineral crystals by the lipid mesophases[16]. Mesophase materials have domain length scales of the order of a few nanometers to a few hundred nanometers. In aqueous solution, due to the amphiphilic property of lipids, they tend to self assemble into a variety of mesophase structures, including micelles, reverse micelles, hexagonal and inverted hexagonal phases, bilayers and bilayer vesicels (Figure 1.1). The form of the mesophase structures depends on many factors such as the charge capacity of the headgroups, the length and degree of unsaturation of the fatty acid chains, ambient temperature, pH, concentration and the presence of salts and other solutes. A common and biologically important mesophase structure is the

lamellar bilayers. Most of the biological membranes have lipid bilayers as the major building blocks. Together with membrane proteins and cholesterol, lipid bilayers fulfill the functions including maintaining the cellular integrity, communicating with the environment and other cells, storing compounds, cell fusion and metabolic pathways.

Phospholipids are lipids with a phosphate group at the polar end. Phospholipid mediated biomineralization occurs in all different kinds of species and tissues. It controls the nucleation kinetics[17]. The electrostatic, stereochemical and geometric interactions between the phospholipids and the minerals orient the nucleation and growth of the mineral. The phospholipids serve as a molecular blueprint for the conductive formation of the inorganic phase. By changing the shape of the lipid matrix during crystal growth, complex crystal shapes can be formed.

One example is the phospholipids mesophases controlling the formation of coccoliths in the alga *Emiliania Huxleyi*[18]. Alga use coccoliths as an exoskeleton to surround and protect itself. Coccoliths consist of 30-40 oval shaped calcite crystals. During biomineralization, phospholipids self assemble into vesicles followed by the infusion of calcium and carbonate ions. With the help of structural, chiral and chemical complimentarity between the organic matrix and the inorganic minerals, oriented nucleation of calcite crystals occurs. The vesicle compartment shape can be further modified via active cellular cytoskeletal elements, and thereby refine the mineral crystal shape. The phosphorlipid mesophase controlling leads to the highly ordered structures

found in coccoliths and other biominerals.

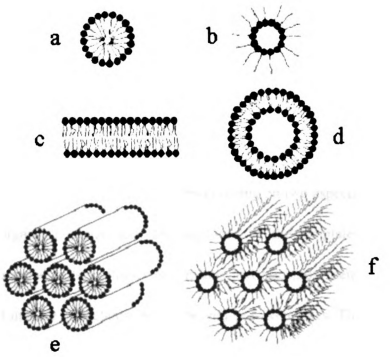

Figure 1.1 Schematic illustration of mesophases formed by lipid self assembly: (a) micelle, (b) reverse micelle, (c) lamellar bilayer, (d) bilayer vesicle, (e) hexagonal, (f) inverted hexagonal. (adapted from reference 16)

Magnetosomes are single crystals of magnetite (Fe_3O_4) or greigite (Fe_3S_4) encapsulated in a bilayer vesicle. It is believed that the long chains of connected magnetosomes with a permanent magnetic dipole that are often seen in the cytoplasm of magetotactic bactia are used to navigate with respect to the earth's magnetic field. This form of magnetosomes shares many features with the coccoliths formation[19]. Magnetosomes are formed in the vesicle compartment, and the formation is controlled by the encapsulation and templating effects from the phospholipid membranes.

Molecular recognition at the inner face is likely to help control the magnetite crystal orientation.

1.3 A view of synthetic templated mineralization systems

Table 1.1 lists recent research in using organic templates to mediate the formation of inorganic layers.

The relevant research has been concentrating on two aspects: the organic template and the inorganic materials that are organized by the template. The inorganic materials include metal salts, metal oxides, metals and transition metals. The organic templates studied include surfactants, polymers, and self-assemblies. These materials are useful in magnetic, optical, electronic, pollution controlling and sensor development. All share the use of an organic template to control and organize the aggregation and orientation of the inorganic material and the organic-inorganic composite has the unique properties that neither the organic nor the inorganic component can provide by itself.

Metal salts mainly include semiconductors and biomimetic materials. Semiconductors such as cadmium selenide, are connected closely with nanotechnology and widely used in electronics, optics and solar cells. With the help of the organic templates, the size of a semiconductor can be brought down to the nanometer range. Properties of these nanomaterials can be tuned by changing the particle size. For example, the band gap of CdSe can be tuned from deep red (1.7 ev) to green (2.4 ev) by reducing the cluster diameter from

200 to 20 angstroms. Size tunable luminescence with efficiency on the order of 10 % was observed for semiconductor nanocrystals at room temperature, which makes it a very good candidate for solar cell materials. Nano-size materials also have unique properties in optics, including non-linear optical properties. These have potential applications in optical instruments, such as optical switches, and other components in all-optical devices. In addition, the extremely small size makes it a good building block for nanoelectronic devices, such as one-electron transistors or nanocapacitors.

Another branch of study is on biomimetics. Biomimetics is defined as microstructural techniques that either mimic or are inspired by biological processes. It includes the study of biological mechanisms and the development of biomimetic materials. The mechanisms of formation of organic-inorganic biocomposites like bones in the human body are not very well understood. Questions such as: 'what controls the initial deposition of mineral crystals?' and 'whether a common mechanism of biomineralization exists?' are still waiting to be answered[20]. Advances in analyzing techniques continue to modify the answers to these questions, and the information obtained can be applied in therapeutics for the treatment of diseases in which mineralization is impaired or excessive, or in the development for artificial tissues.

Metal oxides have many interesting applications in areas such as magnetic, electronics, optoelectronics and solar cells. Ion oxides and titanium oxides are the most studied. Due to the magnetic properties, ion oxides can be applied in security paper, color imaging,

information storage, bioprocessing, magnetic refrigeration, ferrofluids and magnetosomes used in gene therapy. In one of the studies, ferrofluids of iron nanocrystals were processed by thermal decomposition of iron carbonyl in a mixture of decalin with oleic acid as the surfactant. After exposure to air for about one month, a hexagonal close packing of hematite (α -Fe_2O_3) was formed. Block copolymer films were also applied as templates[21]. $[NORCOOH]_{30}[MTD]_{300}$ (NORCOOH = 2-norbornene-5,6-dicarboxylic acid; MTD = methyltetracyclododecene) were synthesized into free-standing nano-composite films, and the iron oxide nanoclusters (γ -Fe_2O_3) were formed in the microdomain of the copolymer.

Titanium oxide, on the other hand, is transparent, which makes it very useful in optoelectronics and solar cell development[22]. In photovoltaic films in solar cell application, except for templating, poly-2-methoxy-5(2-ethyl)hexoxy-phenylenevinylene (MEH-PPV) was used as both the active photgeneration medium and the hole transporter.

Silica, metals and transitional metals are also common inorganic materials studied in inorganic-organic composites. Silica is mainly used in preparation of meso/microporous materials. In the past 60 years, there has been substantial interest in the synthesis of meso/microporous materials in view of their properties and their applications in catalysis, absorption and templates for further modification and reaction[23]. Amines and related compounds (quaternary ammonium cations), linear or cyclic ethers, and coordination compounds (organometallic complexes) have been the most commonly used organic

templates for microporous material preparation. In most cases, an adequate matching exists between the geometries of the organic species and those of the microporous cage or channel network. Therefore, the molecules have template effects, around which the mineral framework is built.

The dimensions and accessibility of pores in the microporous structured hybrid materials (with pore diameter below 2 nm) were restrained to the sub-nanometer scale. This limited its application to small molecules. In order to overcome the limitation, molecular sieves with larger pore size assemblies (micellar aggregates rather than molecular species) were used as templates to make mesoporous silica and aluminosilicate compounds (with pore diameters between 2 nm to 50 nm). The M41S family developed by a research group at Mobil Oil is the most widely studied[24].

Metals can be prepared into different shapes and morphologies by using different templates. By the addition of a colloidal or dispersed solid to an about-to-gel silica solution, followed by supercritically drying, can form composite aerogels in which nanoscopic surface and bulk properties of each component are retained in the solid composite. The volume fraction of the second solid can be varied above or below a percolation threshold to tune the transport properties and thereby design nanoscale materials for chemical, electronic, and optical applications. The composite aerogel is widely used as the template for making three- dimensional metal nanostructures.

Metal nanowires have potential applications in microelectronic devices, magnetic

records et. al. DNA templates, mesoporous silica matrices[25], and copolymers such as polystyrene-polymethylmethacrylate (PS-PMMA) have been used to make metal nanowires. Another commonly seen structure is a nanotube such as a peptide functionalized nanotube. Surfactants have been reported as the templates for making nanotubes.

1.4 Biomineralization mimetic systems using synthetic organic molecular or biomolecular assemblies as templates

The underlying molecular mechanism of biomineralization has lead to the idea of using organic compounds as templates to generate ordered inorganic structures and materials. Inorganic materials have all different morphologies and crystal structures, but the varieties are very limited compared to the structures of supermolecules and other organic compounds. Both natural bioorganic and synthetic organic templates have been applied in these systems[26]. Transferring the structures from organic templates to the inorganic minerals allows molding of the inorganic structures on a microscopic level. This method provides a new way to form materials with complex inorganic structures.

Table 1.1 Use of organic templates to mediate and control the formation of inorganic systems

Materials	Application	Template	Details	Ref
metal salts	Electronics	Inorganic	CdSe:Si, one electron transistor, microelectronic architecture	[72,73]
		cP	Nanocapacitors and nanotransistors	[74]
		S	CdS:polyethylene oxide; SnS_2: CTAB	[75,76]
	Biomineralization	P	$CaCO_3$, Calcium phosphate, repairing bones or teeth	[77,78]
	Opitcs	P	CdSe:PPV,LED, optical switch	
		P	CdSe, CdS	[79]
	Solar Cell	P	CdSe:MEH-PPV; photovoltaic films used in photo-Voltaic and photosynthetic systems	[80,81]
metal oxides	Magnetic	cP	Fe_2O_3: $[NORCOOH]_3[MTD]_{300}$, security paper,color imaging, information storage,bioprocessing,magnetic refrigeration, ferrofluids ,megnetosomes used in gene therapy	[82-89]
	electronics	S	Fe_2O_3: Triol surfactant	[90]
	Optoelectronics	S	SnO_2 mesoporous structure	[91]
		P	TiO_2, waveguide	[92]
	Solar Cell	P	TiO_2 : MEH-PPV	[93]
metals	Enviromental Engineering	P	heavy metal: Mercaptopropylsilane	[94]
	catalyst/molecular sieves	S	Ti:silica; tubule Pd: M41S; hollow tubules, Al	[95-97]
	Optical	S	Au:silica aerogel	[97]
	electronics	SA	Pt:peptide functionized nanotube; Cu	[98,99]
		DNA	Ag nanowire	[100]
	Magnetic	cP	Co or Cu: PS-PMMA, magnetic nanowire array as ultrahigh-density Recording media	[101]
Transition Metal	membrane separation	S	mesoporous Si, biomolecular Si as catalyst and molecular sieves	[102]
	sensor	S	$[Re(CO)_3(L)]_4$(L-pyradine, 4,4'-bipiridine)] for VOC* sensor	[103]

VOC: volatile organic compound

P: polymer

S: surfactant

SA: self-assembly

CP: copolymer

Generally, synthesis of these materials includes two steps[27]. First the organic template with preformed functional groups or self-assembled entities is brought into contact with the inorganic precursor or small particles of the inorganic minerals. This procedure will form organic-inorganic hybrid materials with the inorganic material deposited on the surface of the organic templates. The following step involves removing the organic template. This step is optional. The removing methods include heat treatment[28], microwave irradiation[29] or washing with organic solvents[30]. After the organic template is removed, the isolated inorganic material with a morphology directly related with its organic template is formed. It can be further modified with other organic compounds to be functionalized. If the organic template is not removed, the organic-inorganic hybrid material has proved to have many interesting applications as well.

1.4.1 Surfactant molecular assemblies as templates:

The idea of synthesizing mesoporous solids in the presence of surfactant solutions was proposed by Beck et al. in 1992[31]. In the light of the rich variety of elaborate inorganic structures derived from closed-packed arrays of large vesicles in nature, Walsh and Mann have synthesized networks of porous calcium carbonate from microemulsions of didodecyldimethyl ammonium bromide (DDAB), tetradecane and aqueous calcium bicarbonate solutions. Adding polystyrene spheres in the mixture gives rise to structures that resemble the coccospheres of certain marine algae[32]. Singh and Kosuge form hollow

spherical silica with alkaline hydrolysis of tetraethylorthosilicate(TEOS), octylamine and aqueous HCl. The Coulombic interactions between the protonated amines in acidic condition result in the spherical shape of the octylamine aggregates[33]. Gemini-type surfactants such as $RNH(CH_2)_2NH_2$ or $NH_2(CH_2)_nNH_2$ were used to form highly stable vesicular porous silica sturcures with very thin, robust shells with the potential application as molecular sieves[34].

Unilamellar vesicles have recently been reported as templates to transport morphology into silica by German and coworkers[35]. Through controlling the rate of acidification of a solution of sodium silicate, butanol and myristyltrimetrylammonium bromide (C14TMAB), pillar-like structures containing silica spheres were obtained[36]. Spherical aluminum phosphate was made with vesicle templates of alkylammonium dihydrogen phosphate aggregates when pseudoboehmite was added. The procedure shows strong similarity to the formation of rediolaria and diatom skeletons[37].

With the exception of spherical structures, surfactant systems can form tubular and wirelike structures as well. Baral and Schoen coated phospholipid tubules with silica by sol-gel methods[38] to form tubule shaped silica. Single silica nanotubes, as well as bundles of tubes, have also been prepared by using the sol-gel method with TEOS and a template based on laurylamine hydrochloride[39]. In a similar experiment, magnetic and nonmagnetic iron oxide tube-like structures were formed by using mixtures of a sugar-based lipid and its anionic sulfated derivative as templates[40]. The mineralization

starts at the anionic sites followed by the formation of organic-inorganic composites. However, dense and uniform coatings cannot be formed.

It has been reported that $BaCO_3$ nanowires were prepared through reaction of barium and carbonate ions in the cores of nonionic reverse micelles[41]. The preferential orientation of surfactant molecules along the surface planes parallel to one crystal axis after nucleation is assumed to lead the wirelike crystal growth.

1.4.2 Synthetic polymers as templates

Many synthetic polymers have been used as templates, most of them are polystyrene-based. The inorganic minerals and preparation procedures vary. Hollow ZnS shells were prepared through sonicating carboxy-modified polystyrene particles with zinc acetate and thioacetamide, followed by calcinating the polymer[42]. This method is also extended to other materials such as PbS and different morphologies of TiO_2. Another preparation method use miniemulsions which consist of small oil or water droplets 30-300 nm in diameter[43]. The miniemulsions containing styrene or other easily polymerizable monomers are used as templates. After polymerization, the latexes are covered with clay sheets, which react then with tetramethylorthosilane through a polycondensation reaction to form nanocapsules with thicknesses of about 1.5 nm.

Other polymer templates explored include poly(L-lactide) fibers[44]. Greiner and coworkers processed the fiber by coating it with aluminum through physical vapor

deposition. Stiff single-walled aluminum tubes were formed after thermal degradation of the polymer templates. Poly(L-lysine)-amine aggregates were also used to form hollow silica spheres by the sol-gel transcription method[45]. Its successful transcription into silica depends on the hydrogen-bond donating ability of the amine.

Cha et. al. tried to control the formation of ordered silica morphologies through changing the degree of oxidation of the poly-L-cysteine domains of cysteine-lysine block copolypeptide aggregates[46]. Under a nitrogen atmosphere, in its reduced form, spherical silica was formed. When the reaction was performed in air in which the sulphydryl groups of the copolypeptide were partially converted into disulfides, ordered columnar silica was formed.

Amphiphilic block copolymers have been employed as templates. Compared with surfactants, block copolymer templates are more stable against phase transition due to the longer relaxation time.New developments in this field include growth of nanoparticles in double-hydrophilic block copolymers[47]. Double-hydrophilic block copolymers consisting of a solvating poly(ethylene glycol) (PEG) block and a poly(ethylene imine) (PEI) binding block were used to make monodisperse CdS nanoparticles with controllable size and stability against oxidation for months due to its polymer shell.

Selectivity was achieved through preferential wetting of one of the copolymer blocks by a metal in the system with the polystyrene-block-poly(methylmethacrylate) (PS-b-PMMA) diblock copolymer as the template[48]. The parallel cylindrical domains of

PMMA with a repeat spacing of 50 nm was surrounded by PS. The selectivity of the two copolymer domains is very apparent immediately after metal deposition for a wide range of metals and small deposited amounts. The behavior of Au, Ag, In, Pb, Sn and Bi was observed with Au and Ag preferring the PS domain, and In, Pb, Sn and Bi the PMMA domain. In each of these cases, the preferred domain becomes the scaffold.

Methods based on polymer-assisted layer-by-layer assembly[49] is applied to assemble metal-based magnetic nanoparticles[50]. The idea is to exchange the stabilizers bound to the particles with multifunctional polymers that attach to a substrate to control the assembly of magnetic nanoparticles. The assembling process involves exchanging oleic acid/oleyl amine around each magnetic nanoparticle with a functional polymer such as poly(ethylenimine) (PEI). The PEI/FePt multilayer assembly that has been formed was proven to be ferromagnetic. Such an assembly might be suitable for future ultrahigh-density data storage media.

The exchanging method is also used to develop a general method to make a controlled self-assembly of nanoparticles, which is also called the ' bricks and mortar' approach[51]. In this method, colloidal gold particles functionalized with recognition elements were glued with polymers bearing complementary functionality. Diaminotriazine-functionalized polystyrene was employed as the polymer template, and gold particles were covered with an octanethiol self-assembled monolayer followed by thiol place-exchange with a thymine-functionalized alkanethiol to form

thymine-functionalized colloids. Diaminotriazine-thymine three-point hydrogen bonding interactions were used as the complement. The conformational flexibility of the polymer compensates for irregularities in the size and shape of the aggregate structure, allowing the efficient propagation of order during the self-assembly process.

Dendritic polymers represent an additional and unique well-defined polymer template for nanoparticle growth[52] and encapsulation[53]. Compared with other organic templates, dendrimer structures have unique aspects in the chemistry of the terminal groups, the generation-dependent size, the three-dimensional structure, the radial distribution function of polymer density, and the presence of endoreceptors within the dendrimer.

Dendrimers were used to stabilize and control the growth of nanoparticles by forming interdendrimer complexes. With this approach, Murphy and co-workers prepared agglomerates of CdS and dendrimers[54]. Crooks and co-workers have prepared related materials consisting of Au and dendrimers[55], and Esumi and co-workers have prepared Pt, Au, and Ag nanoparticles stabilized by dendrimers absorbed to their exterior[56]. New results indicate that even semiconductor quantum dots (CdS) are accessible by this synthetic route[57], and Amis et. al. have further expanded the scope of dendrimer-encapsulated nanoparticles by preparing them within monolithic dendrimer-containing polymer composites[58].

1.4.3 In-vitro biological molecules as templates

In-vitro biological systems use nature's biomaterials (macromolecules such as proteins, glycoproteins, and polysaccharides) to control nucleation and growth of mineral phases and thus manipulate the microstructure and physical properties of the system.

In general, biomolecules can self-assemble into a wide range of structures. Proteins in particular can form intricate structures that can be readily manipulated and functionalized because their synthesis is genetically directed. Natural materials such as bacterial surface layer proteins[59], virus capsids[60] and phage[61] have also been used as templates and in other nanoscale applications.

A study on cyanobacterial S layer in 1992 demonstrated that a crystalline surface layer can function as a template for fine grain mineralization[62]. Later studies show that surface protein monolayers on substrates and sheet-like self-assembly products in suspension promote the precipitation of monodisperse cadmium sulfide[63] and gold nanoparticles[64].

Virus protein cages (capsids) exist as well defined large individual molecules instead of aggregate ensembles, such as lipid vesicles, and thus can be used as templates for nano-engineering of materials with precise and controllable morphologies. A range of polyoxometalate species such as vanadate, molybdate and tungstate spatial-selectively crystallize within the cowpea chlorotic mottle virus capsid. The same mineralization reaction with tungstate is also possible with Norwalk Virus[65]. Douglas et. al. believed that

the crystallization is electrostatically induced at the basic interior surface of the protein. The negatively charged polyoxometalate ions (such as $H_2W_{12}O_{42}^{10-}$) aggregate at this interface facilitating crystal nucleation. Thus, the author suggested that the protein shell acts both as a nucleation catalyst and a size and shape constrained reaction vessel.

Monodisperse biomaterials with anisotropic shape are promising components as well-ordered structures. A recent study involves genetically engineered M13 bacteriophage, viruses with monodisperse size and shape, and ZnS precursor solutions to self-assemble highly oriented, self-supporting films[66]. In this system, both the length of bacteriophage and the type of inorganic materials can be easily modulated through genetic modification and selection. The resulting quantum dot (QD) hybrid film material was ordered at the nanoscale and at the micrometer scale into 72-μm domains. These domains repeated continuously over a centimeter length scale. Moreover, viral suspensions containing ZnS QDs were prepared in which the liquid crystalline phase behaviors of the hybrid material was controlled by solvent concentration and by the use of an applied magnetic field.

Polysaccharide dextran is used to prepare self-supporting macroporous frameworks of silver, gold and copper oxide, as well as composites of silver/copper oxide or silver/titanium[67]. Magnetic sponges can be similarly prepared by replacing the metal salt precursor with preformed magnetite nanoparticles. The use of dextran as a soft sacrificial template for the fabrication of metal and metal oxide sponges should have

significant benefits over existing technologies because the method is easy, inexpensive, environmentally benign, and amenable to scale-up and processing.

Lamellar DNA-cationic membrane complexes, originally studied for gene therapy, are a new class of hierarchically organized nanoporous biopolymer- membrane system. DNA has a diameter of only 2 nm and micrometer-long distribution of well-defined sequenced DNA bases.

Braun and coworkers made a DNA-template-based silver nanowire around 100 nm thick and 15 nm long[68]. The metallization was performed in three steps. First, the DNA was fixed between two gold electrodes. The sodium was then exchanged with a solution containing silver ions, which bind to the DNA bases. In the third step the DNA was metallized with silver using a standard photographic enhancement technique. The nanowires made this way showed a resistance of several mega-ohms as a result of the coagulation of silver, which leads to clusters with a diameter of 50 nm. Pladium clusters with a diameter range from 3 nm to 20 nm controlled by different length of reduction time was reported in another work by Schackert and coworkers[69].

In recent research, the synthetic biomolecular templates consist of periodic structures with parallel anionic DNA chains confined between stacked two-dimensional cationic lipid sheets. DNA and cationic lipids self-assemble into multilamellar nanoporous complexes in which a one dimensional DNA lattice is intercalated between lipid membranes. Divalent counter ions can be organized into the inter-helical DNA pores, and

the resultant arrays of ionic precursors can be used to grow inorganic crystals. CdS was used in a model system. Cd^{2+} ions were organized within the interhelical pores between DNA strands. Subsequent H_2S treatment forms CdS nanorods with controllable widths and crystallographic orientation[70] aligned parallel to the negatively charged sugar-phosphate DNA backbone due to the strong electrostatic interactions. A similar sandwich structure is reported elsewhere with tubule networks[71].

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CHAPTER 2

A MULTIFUNCTIONAL POLYMER-SECURED SELF- REGISTERING MOLECULAR ARRAY SYSTEM

ABSTRACT

An idealized model which combines the idea of self assembly and polymer architecture is proposed. The template is composed of polymer-secured self-registering molecular arrays. It is robust due to the polymerization, and at the same time, very sensitive to the environmental factors that impact on the overall organization. The system has four major elements: the polar recognition and chemo-responsive region, the hydrophobic alkyl chain spacer region, the electronically and/or optically responsive region and functionalized anchor region for attachment to the substrates. All the regions can be functionalized or modified for different purpose. The polar region is hydrophilic, which can incorporate chirality, polymerization moieties, biological recognition elements and chemical functionalities for inorganic phases binding. The hydrophobic alkyl chain region gives stability and order to structure, and separate different regions as a spacer. The electronically and/or optically responsive region can have groups such as polyphenylene, diacetylene, diphenyl or phenyl acetylene which response to different electronical or optical signals.

2.1 A Polymer-secured self-registered molecular arrays system

There are two ways to make functional systems composed of many molecular units. There are cases where these units are not covalently connected, but they are connected through electrostatic forces, Van der waals interactions, π -stacking or hydrogen bonds. This is referred to as self-assembly. In the other instance, the units are connected covalently. These systems are referred to as polymers. Because of their architecture, self-assembled systems are very sensitive to outside stimulae, such as pH and temperature. Their properties are also very dependent on concentration, etc. On the other hand, polymers tend to be more insensitive to these factors. Polymers have more mechanical strength compared to self-assembled systems. They can be processed to make stable rugged devices. The ideal system would have both the sensitivity of self-assembled systems to environmental stimulae and the stability and ruggedness of polymers. The design and fabrication of such systems is the objective of this work. To this end, we have developed a lamellar chiral polymer-secured self-registering template capable of being functionalized at a variety of levels. Such systems will be powerful materials for producing functional materials.

This approach enables the possibility to construct hierarchically structured materials with order at different scale lengths. There are two general approaches in making ordered structures at different scale lengths—top-down and bottom-up approaches. The top-down

approach carves out or adds molecules to surfaces using such methods of soft lithography or dip-pen lithography. The bottom-up approach, on the other hand, assembles molecules into structures. Compared with the traditional top-down approach, bottom-up fabrication provides numerous advantages, such as the possibility of three-dimensional assembly, the likelihood of inexpensive mass fabrication and the attainment of nanosized material[1]. For example, due to the resolution limit of optical photolithography, it has to be replaced by e-beam or x-ray lithographies for continued miniaturization according to Moore's Law. This exponentially raises the cost of microfabrication below the 0.1 μm scale. The bottom-up approach does not have the above limitation down to the 10 Å scale, but at the same time it lacks high yields and uniformity.

Self-assembly is one of the few practical strategies to arrive at the ordered structure based on this bottom-up approach. The self-assembly process is defined as the spontaneous organization of components into structurally well-defined aggregates joined by noncovalent bonds[2]. The organization or the assembly forms the desired structures through naturally intended phenomena, either through physical or chemical processes or assisted by biomolecules to promote molecular selectivity and specificity. It also rejects defects energetically, and therefore the degree of perfection is relatively high[3]. Molecules and nanoclusters can be assembled through electrostatic and surface forces, hydrogen bonds, hydrophobic and hydrophilic interactions[4].

The strategy we used can be called polymer-secured self-registering molecular arrays manufacturing. It borrows the self-arrangement idea from the self-assembling methods. The amphiphilic molecules self register through hydrophobic and hydrophilic interactions. Amphiphiles are 'dual character' molecules with two moieties at the ends having quite opposite properties[5]. One moiety is hydrophilic which is polar and 'water loving', while the other end is hydrophobic which is nonpolar and 'water hating'. The most well known class of amphiphiles is surfactants, which are widely used in the detergent, cosmetic, pharmaceutical and food industries. In addition, biological amphiphiles such as phospholipids serve as building blocks of cell membranes.

The amphiphilic molecules can be regarded as building blocks for larger superstructures such as structures with cubic or hexagonal symmetry or extended and flat lamellar structures. In aqueous solutions, amphiphiles tend to self-register into aggregates, with the hydrophilic moiety pointing outward to water and their hydrophobic moiety pointing inward or interacting with other hydrocarbon groups. The solubilized aggregates can be spherical or lamellar in shape. In our case, it has lamellar structure. The lamellar structure has several advantages. It has biological analog models in living systems. Therefore it is possible to make biomimetic systems to be used as sensors for signal tranductions across a membrane, to study interactions between cells, or to detect living cells and components. These systems can serve as models for cellular processes of important biological events such as photosynthetic systems and vascular systems where

lamellar structures provide compartments. Due to its flatness, the lamellar structures can be stacked to make a multilayer structure with long range order. The lamellar structure can be easily applied to modify or functionalize surfaces. Since the reaction sites are exposed in the lamellar structure, it is easy to characterize or modify the system. For example, we can add polymerizable moieties in the head groups, or functionalized groups in the nonpolar phase which bring high UV, fluorescence, nonlinear optical property, semiconductor or conductor behaviors into the system.

The properties of the amphiphilic molecule and the higher level superstructures are tightly linked. External parameters such as temperature or concentration can also lead to extensive rearrangements and structural changes on several scale lengths, in other words the system is very sensitive to environmental stimuli. Elucidating the correlations between molecular structures, external stimuli and macroscopic properties of these materials is a major scientific challenge, and has potential applications in sensor development.

Self-registering systems form well-ordered systems at the nanometer scale. Through entropy minimalization, the whole process is spontaneous Therefore the process is cost-effective, versatile and facile. However, self-registering systems have an inherent shortcoming due to the non-covalent interactions. These systems are weakly connected and not robust enough for practical applications. A good strategy is to combine self-registering systems with the covalent polymerization systems.

Covalent polymerization is the most important strategy for preparing molecules with high molecular weights[6]. In covalent polymerization, a relatively simple, reactive low molecular weight substance (a monomer) reacts with itself to produce a molecule comprising many covalently connected monomers (a polymer). The molecular weight of synthetic polymers can be high and easily prepared. However, the molecular structure is simple and repetitive, and the polymerization process only provides limited opportunity for controlled variation in the structure or for control of its three-dimensional shape[2]. For example polymers donot usually form bilayer systems such as the system that we developed. Also, polymers are not very sensitive to environmental stimuli. Therefore their applications as sensors are limited, and the structures cannot be fine tuned by altering conditions.

The combination of covalent polymerization and self-registering could make a system with ordered structures through relatively simple synthesis with high sensitivity. In this project, we are designing and synthesizing systems with the combined advantages of self-assembly and covalently linked polymers, and yet avoid all the disadvantages.

2.2 Multifunctional system

As mentioned above, the properties of the amphiphilic molecules and the higher level superstructures are tightly linked. The macroscopic properties of the material can be modified through introducing functionalized elements to the amphiphilic molecules

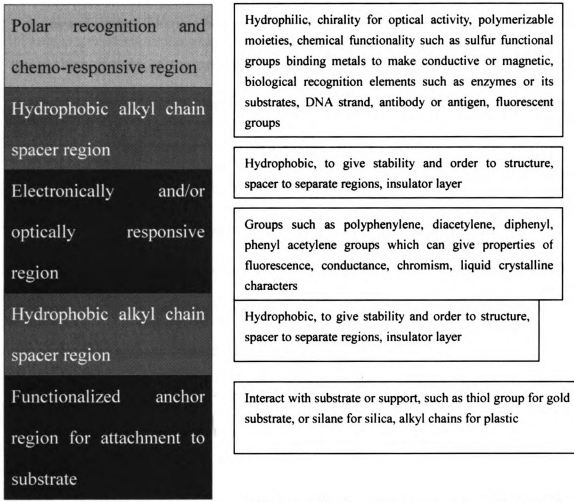

Figure 2.1 Overview of the multifunctionalized polymer-secured self-registering molecular array system

2.2.1 Polar region modification

Into the polar region, we can introduce chirality, polymerizable moieties, chemical functionalities that are derivable, inorganic phases, biological recognition elements or inorganic phases or fluorescent groups. Polar regions provide the site to secure the side chains and control the space between the side chains at the same time. They also dictate the packing pattern of the system. The polymerizable moieties of the polar region

chains and control the space between the side chains at the same time. They also dictate the packing pattern of the system. The polymerizable moieties of the polar region stabilize the whole system through covalent bonds. The chirality makes the system optical active. When light passes through a polar layer with chirality, circular dichroism and optical rotary dispersion will happen. The polarization state of light is affected, and the reflectivity is different for the left hand circular and right hand circular light.

In our system, the head groups in the molecules are covalently connected and the elongated lipid chains sticking to the head groups pack in a parallel pattern. Therefore this system has a chiral smectic liquid crystal phase, which has found an application in rapidly switching electrooptic shutters with response times within the microsecond range[7] due to their ferroelectric properties. This system also has potential applications in many other areas.

The structure can be made more complex by mixing the organic membrane with inorganic additives. The synthesis of semiconductor nanoclusters and the exploration of their nonlinear optical, electrical, photochemical, spectroscopic properties have attracted a lot of interest lately due to their possible applications in solar cells, chemical and biological sensors, and telecommunications. The crucial step towards their application is the formation of nanocomponents into functional and desired nanostructures without aggregation. The membrane we developed serves as a good template for nanocluster deposition. With sulfur function groups, for example, certain metal ions can be combined,

and template control on nucleation and growth of metal ions can be achieved. The same controlling effect can be achieved on calcium carbonate or calcium phosphate deposition on membranes with phosphate groups or other biomineralization analog cases. The morphology and chemical properties of the inorganic phase can be controlled through pH, charge distribution, and lattice size and shape that can be adjusted by template design. Chemical functionalities other than phosphate or sulfur function groups (such as carboxylic acid, hydroxyl group, etc.) can be added to the polar region to introduce metal affinity. Except for the nanoclusters mentioned above, metals also can be deposited to the organic membrane to adjust the conductivity (such as Ag or Cu) or magnetic properties (such as Co or Ni) of the system and improve the response of the system to outside electrical or magnetic fields effects.

Biological recognization elements can also be added as customizable moieties. This modification makes the system a potential biosensor with a specific biological element that creates a recognition event and a physical element that transduces the recognition event. Biological elements such as enzymes or their substrates, DNA strands, antibodies or antigens are used as the analyzing sector. They distribute on the top membrane of the system, and therefore have good exposure to the environment. They can recognize and selectively combine the complementary component from the environment, and give responsive signals. The responses of these recognization elements can be expressed through structural changes and transported through the elongated chains connected to the

detector where it can be recorded and measured. Due to the multiple properties of the system that we developed, different measurement parameters can be used such as current, potential, conductivity, dielectric constants or the changes in the characters of light. If fluorescent groups (such as cascade blue or aminometylecoumarin) are added to the polar region, the molecular structure changes from specific binding can be identified directly through fluorescence microscopy.

2.2.2 Non-polar region modification

The nonpolar portion includes the hydrophobic alkyl chain region, the electronically and/or optically responsive region and the functionalized anchor region for attachment to a substrate. The functionalized anchor is used to interact with a substrate or support. For example, a thiol group can be added to the end of the alkyl chain so that the system can be anchored on a gold surface. Thereby, the gold surface can be modified using the system that we developed, and at the same time, this solid surface can help to further stabilize the whole system. There are other substrates on which the systems can be adhered using different functionalized anchors, such as silane for silica or alkyl chains for plastic substrates.

The alkyl chains are the main component of the hydrophobic part. The alkyl chains give order and control to the system through hydrophobic properties and the alkyl chain-alkyl chain interactions. Due to their hydrophobic character, the alkyl chains pack in a parallel

pattern and self register at the polar-nonpolar interfaces to form the lamellar structure. The hydrophobic alkyl chain region provides spacers for the different regions. The polar groups, electronically and/or optically responsive regions and the functionalized anchors are separated from each other by the alkyl chain regions. In addition, alkyl chains are not conductive, therefore this layer can be the insulator layer between the polar region (which can behave as conductors or semiconductors depending on the chemical functionalities and the inorganic phases incorporated), and the electronically and/or optically responsive region, which can be conductive due to its high conjugation. This complex structure can be very useful in signal transduction in electronic equipment, and would be hard to produce through other methods.

2.2.3 electronically and/or optically responsive region

The electronically and/or optically responsive region can provide the system properties of fluorescence, conductance, chromism or liquid crystalline character. The electronically and/or optically responsive region can be composed of the groups shown in figure 2.2. The insertion of groups such as pyrene, diphenyl, diacetylene or phenylacetylene makes an electronically and/or optically active region. These groups have a common feature of high conjugation, which makes them very conductive. This feature can be controlled by changing the geometry of the chains, as Π-conjugation depends on the relative orientation of the functional groups, and thus gives rise to a molecular switch and other applications in electronics. Also, the conjugated system forms

excimers which brings a red shift through charge separation by intra-chain movement of the photogenerated charge carriers. This system has the potential application in long-wavelength laser production.

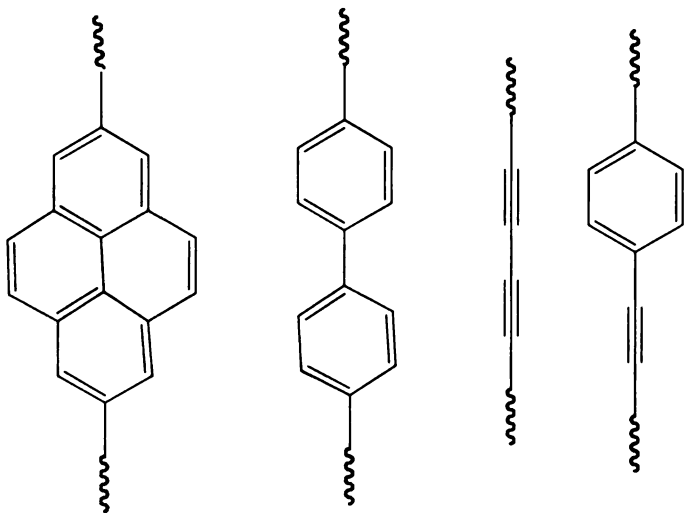

Figure 2.2 Electronically and/or optically responsive groups A) pyrene B) diphenyl C) diacetylene, D) phenylacetylene

Rigid polycyclic aromatic hydrocarbons that do not incorporate oxygen or nitrogen atoms generally have large quantum yields of fluorescence. The hydrophobic pyrene fluorophore is readily accommodated within the hydrophobic region. The pyrenebutaboic acid conjugates have been reported to have exceptionally long excited-state lifetimes (t > 100 nanoseconds), and are consequently useful for time-resolved fluorescence immunoassays and nucleic acid detection[8]. The excimer-forming process of pyrene can be used to characterize membrane structural domains and their dependence on temperature and other external disturbances.

The biphenyl group has the structure of two benzene rings joined by a carbon-carbon

bond. Energy changes in the system such as UV light excitation, or thermal energy exchange will cause conformational changes of the biphenyl group, which will lead to packing density and pattern adjustments of the alkyl chains. The torsion angle (Ψ) is connected with the energy in the system. The energy curve reaches its minimum at $\Psi=45^{\circ}$ and its maxima with 7 kJ above the minimum at $\Psi=90^{\circ}$ and $\Psi=0^{\circ}$ (figure 2.3). The biphenyl group has a strong absorption in the UV range but weak fluorescence. π -electron delocalization reaches its maximum when the two phenyls are in a coplanar arrangement, and the delocalization leads to a bathochromic shift in the absorption spectra. Thus the biphenyl groups respond to optical stimuli differently, and give information about their conformation structure.

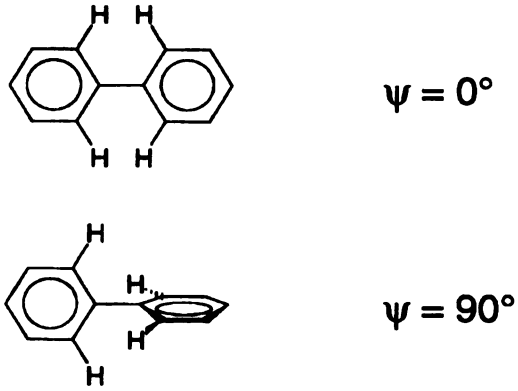

Figure 2.3 Biphenyl conformation (adapted from reference 9)

The diaceylene group is not polycyclic, however, due to the high conjugation of the repeating double and triple bonded alternating structure it forms after polymerization. The diacetylene introduction can bring several unique properties into the system. First,

Polydiacetylene compounds have very unique chromatic properties. Polydiacetylene compounds demonstrate color changes between blue forms and red forms with exciton absorption peaks at 640 nm and 560 nm under environmental perturbations such as solvent, pH, mechanical and temperature changes. Second, Polydiacetylene (PDA) has a high nonlinear optical (NLO) coefficient. When the intense light goes through a material with diacetylene moieties, significant non-linear effects such as second harmonic generation, four-wave mixing and frequency doubling appear. These effects can be applied to a lot of different non-linear optical devices. Thirdly, PDA is photo-linkable material. Under the irradiation of heat or UV light, PDA is very easy to polymerize and forms another polymerized layer to make a two dimensional system with additional stability. Last, due to its highly conjugated system PDA has high electronic conductivity. The polydiacetylene chain is the primary candidate for molecular wires for integrated nano-sized electronic circuits.

Phenyl acetylene is another possible functionalized group that can be inserted in the non-polar part of the system. It is commonly used as a precursor for the synthesis of the polymer polyphenylacetylene. Polyphenylacetylene has non-linear optical properties, and has potential use in semiconductors, electrophotographic photoreceptors and chemical sensor devices[10]. polyphenylacetylene can be viewed as a combination of multiple bonds and aromatic rings. Therefore polyphenylacetylene has optical responses through configuration changes between the *cis* and *trans* forms of double bonds and the

orientation change of the phenyl ring. The polymerization also brings additional stability.

The multifunctional polymer-secured self-registering molecular arrays system includes four different parts—the polar recognition and chemo-responsive region, the hydrophobic alkyl chain spacer region, the electronically and/or optically responsive region and the functionalized anchor region. All these different parts were connected together to form self-registering polymerized structures with functionalized multiple-layers. This system has potential applications in many important areas such as biosensors, electronic or magnetic equipments and optical communications.

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CHAPTER 3

DESIGN OF THREE POLYMER-SECURED SELF-REGISTERING MOLECULAR ARRAYS SYSTEMS

ABSTRACT

Three systems have been developed based on an idealized model for systems composed of polymer-secured self-registering molecular arrays with four components: the polar recognition and chemo-responsive region, the hydrophobic alkyl chain spacer region, the electronically and/or optically responsive region and functionalized anchor region for attachment to the substrates. In system 1, there is negatively charged phosphoric acid in the polar region for template-regulated calcium phosphate deposition to make a biomimetic material with potential application as bone filler or scaffold of bone tissue engineering. Both systems 2 and system 3 have sulfur function in the polar region for extensively ordered nanoparticle structure fabrication using soft cations such as cadmium and zinc. In system 3, the electronically and optically responsive region contains diacetylene groups which have unique chromatic properties that include optical and electronic responses once polymerized. Photopolymerization of the diacetylene groups also gives the system additional stability. Potential uses include the fabrication of sensors, detectors, electronic components, bioreactor compartments, etc.

Here we describe the preparation and characterization of the organic structures that serve as templates for the directed deposition of inorganic systems. As explained previously, our ideal target system has a polar recognition and chemo-responsive region, hydrophobic alkyl chain spacer regions, an electronically and/or optically responsive region and a functionalized anchor region for attachment to a substrate. The electronically and/or optically responsive region and the functionalized anchor region are important for transducing signals and the fabrication of hybrid materials.

The organic templates we designed are polymer-secured self-registering molecular arrays. Each unit is amphiphilic with polar heads and nonpolar alky chains. The polar heads are connected and interact with more polar solvents and the chains in the nonpolar regions assemble to form regular arrays. This self- registering method originates from nature. It uses entropy as its driving force for orientation and saves a lot of endeavors. Three different systems were designed and prepared based on this general architecture.

3.1 Polymer-secured self-registering molecular arrays system with phosphoric acid group in the polar region and saturated hydrocarbon chains (system I)

Polymer-secured self-registering molecular arrays system with phosphoric acid groups in the polar region and saturated hydrocarbon chains has two structural and functional regions (Figure 3.1).

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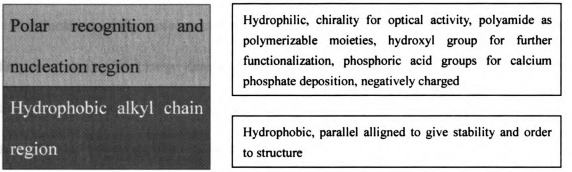

Figure 3.1 Table illustration of system I

System I has the phosphoric acid groups introduced into the polar region. This results in a biomimetic material with potential application as bone filler or scaffold of bone tissue engineering. The amphiphilic molecules self-orient at the interface of polar and nonpolar solvents. With the additional stabilization of polymerization, it forms a robust two dimensional template resembling collagen templates in bones.

The phosphoric acid group is negatively charged, and therefore it combines metal ions such as calcium through ionic interactions. Calcium phosphate has been used extensively for bone replacement due to its similarity to the mineral component of bone[1]. Thus calcium phosphate was chosen as the inorganic phase for our system. It makes the surface of the template biocompatible and bioactive so that the material can be integrated into the tissue by the same processes of healthy bone remodeling. The main draw back of bulk calcium phosphate is its brittle nature and poor mechanical properties, which can be greatly reduced by the self-assembled polymerized templates[2].

The structure of this hierarchical system can be controlled in a lot of different ways.

The thickness of the template can be chemically tailored by changing the length of the fatty acid chain. The charge density and the morphology of the inorganic phase can be controlled by conditions such as the concentration of the polymer, the pH of the solution and the temperature. The chemical structure of polymer-secured self-registering molecular arrays with phosphoric acid groups in the polar region and saturated hydrocarbon chains is shown in figure 3.2.

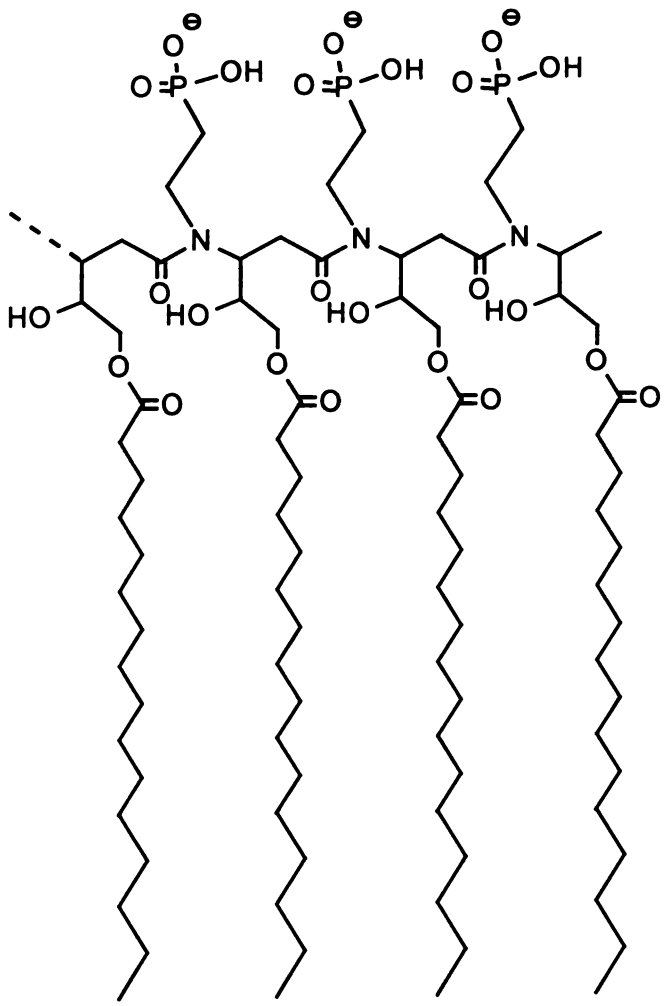

Figure 3.2 Polymer-secured self-registering molecular arrays with phosphoric acid groups in the polar region

3.2 Polymer-secured self-registering molecular arrays with thio-ether groups in the polar region and saturated hydrocarbon chains in the nonpolar region (system II)

The second system we have developed featured two regions, the polar recognition and chemo-responsive region and a hydrophobic alkyl chain region (figure 3.3). This system has polyamides as polymer linkages in the polar region. As a result, the polar region is hydrophilic with strong dipoles. Hydrocarbon chains connected to the polymer backbone are in parallel arrays, therefore the system has smectic liquid crystal properties.

Sulfur functional groups in the polar region have a high affinity towards metals such as gold or mercury[3]. Therefore, systems like this can modify the metal surface by changing the conductivity, morphology and polarity. They have potential applications in electrode modification in electrochemistry, corrosion protection and new material manufacturing.

Polar recognition and chemo-responsive region	Hydrophilic, neutral, chirality for optical activity, polyamide as polymerizable moieties, thio-ether group binding metals to make conductive or magnetic, hydroxyl group for further functionalization
Hydrophobic alkyl chain region	Hydrophobic, 15 methylene groups, parallel alignment gives stability and order to structure, insulator, affinity for the plastic surface

Figure 3.3 Table illustration of system II

The hydrophobic alkyl chain region can also serve as anchoring group. The hydrocarbon chains are hydrophobic, therefore can be attached to the plastic surface. The nonconductive plastic surface can now be made conductive and be used in electronic

elements by combining metal ions to the sulfur function groups in the polar region with following reduction or counterion combining. Electronic conducting components with plastic substrates can be manufactured using this method.

The saturated fatty acid chain is straight comparing with the unsaturated ones. Consequently, the chains are packed more tightly and induce different properties in the system, e.g. the crystal lattice, the melting point, etc. The structure of the polymer-secured self-registering molecular arrays with thio-ether groups in the polar region and saturated hydrocarbon chains in the nonpolar region is shown in figure 3.4.

3.3 Polymer-secured self-registering molecular arrays with thio-ether groups in the polar region and diacetylene moieties in the nonpolar region (system III)

System III has polymer-secured self-registering molecular arrays with thio-ether groups in the polar region and diacetylene moieties in the nonpolar region as illustrated in figure 3.5. It features four major structural and functional regions and can be developed into a variety of sensors or electronic devices[4].

3.3.1 Polar region of system III

Unlike self-assembled systems, where the units connect with each other through electrostatic forces, Van der waals interactions, π -stacking or hydrogen bonds and the systems are too delicate for practical applications, this strategy of connecting the units

with covalent bonds gives these systems more stability and mechanical strength. The polyamide moieties are biological analogues of polypeptides and should consequently be biocompatible with cells and biomolecular systems. The electrons from the double bond in the carbonyl group migrate to the bond between the C and the N producing partial positive and negative charges on the N and O. This dipole makes the polymer very polar and hydrophilic. The regular repeating unit helps to space and align the side chains. The distance between the monomeric units is close due to the short covalent bond length. This polymerized system is much more stable and densely packed than the traditional self-assembled system.

System III has two chiral centers in each unit in the polar region. The chirality makes the system optically active. It can rotate the polarized light, and cause circular dichroism and birefringence. As most important biological molecules are chiral, the stereochemical sites of system III can selectively bind the biomolecules according to their chirality and then be used for biomolecular detection and purification. Chirality can also bring biological activity to these systems.

In system III, the elongated side chains lie in parallel alignments and orient perpendicular to the chiral polymeric polar region. Therefore our system is a liquid crystalline material with stabilized chiral smectic C phases. Liquid crystals have an orientational order and in some cases a weak positional order, and they also flow like liquids[5]. They are called soft materials because of their combination of orientation and

fluidity. Since the orientation and hence anisotropic properties are carried by liquid, liquid crystals can be manipulated very easily by changing electrical, magnetic or optical fields. This gives them big electro-optical, magneto-optical and opto-optical effects. The electro-optical effects of liquid crystals have already been widely used in the display industry. The magneto-optical effects of the liquid crystals can be used in recording media, and the strong opto-optical effects can be used in non-linear optics, which is important for all-optical switching and other devices in future optical information technologies.

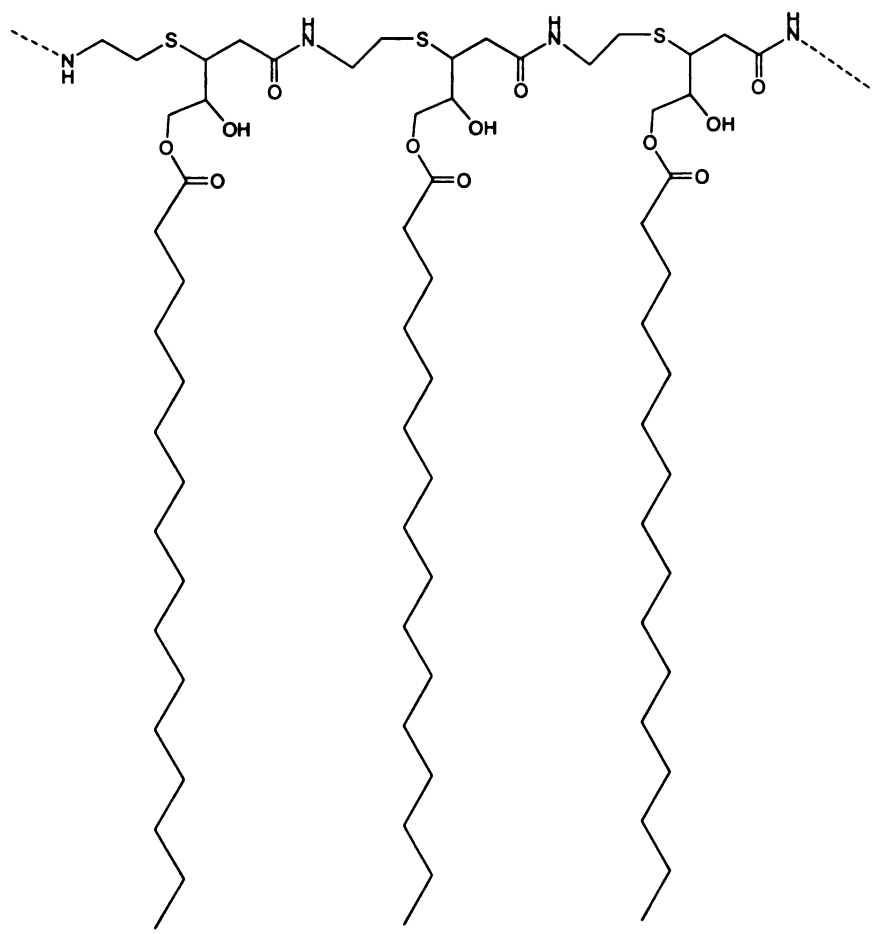

Figure 3.4 Self-registering polymeric system with sulfur functions in the polar region

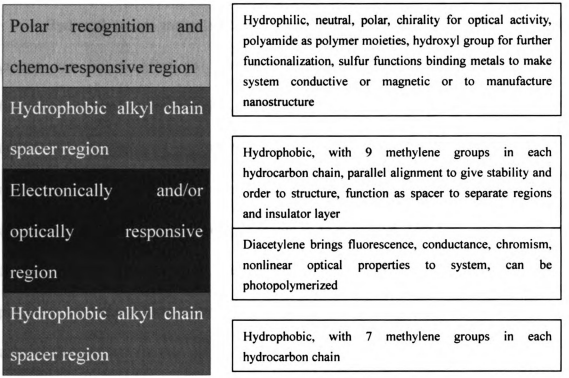

Figure 3.5 Table illustration of system III

The liquid crystal is classified by the orientation of its axis and molecular order. Among all these different species, the smectic phase is the most ordered mesophase. This phase has not only orientational order, but also to some extent positional order. The smectic C phase has the elongated side chains tilted with respect to the perpendicular axis of the main chain. This gives the smectic C phase an optically biaxial property. Chiral smectic C (smectic C*) phases have the same structure as smectic C phases except for their chirality. Materials with smectic C* phases can be used in rapidly switching electrooptic shutters with response times within the microsecond range[6] because of their ferroelectric properties.

γ- Hydroxyl groups makes system III more hydrophilic and polar. The hydroxyl groups can be modified to form ethers or esters, which allows for further functionalization of the polar region. Another modification that can be done to the polar region of the system is to incorporate inorganic phases. Functional groups in the polar region provide sites for ordered deposition of ions and crystal growth. For instance, certain cations can be bound in the polar region in an induced pattern and then reduced or combined with anions to form salts. The inorganic phase might import different properties such as conductance or semi-conductance, magnetism (in the case of nickel or cobalt), fluorescence (in the case of cadmium sulfide or selenide) and nonlinear optical properties to the system. In addition, labeled or unlabeled ligands, enzymes, antibodies, antigens, receptors, nucleic acids, oligonucleotides or other biomolecules can be incorporated and used to measure, monitor or study biologically important processes. With different functional groups and conditions such as pH, temperature and concentration, the physical and chemical properties of the inorganic phases can be adjusted.

In system III, thio-ether groups in the polar region have a high affinity for certain metal elements. The polymer-secured self-registering molecular arrays closely pack at the interface to provide the template for the deposition of these metal ions and for nanostructures and other ordered arrays to grow.

3.3.2 Hydrophobic alkyl chain spacer region of system III

The alkyl chain is the main component in the nonpolar region. The alkyl chains are connected to the polar region through ester bonds. Under multiple effects such as head group arrangement, hydrophobic interactions and interactions between the chains, they align in parallel arrays to give stability and order to the structure. The alkyl chains are hydrophobic and insulating. The alkyl chain region can be viewed horizontally as spacers between the polar region and the electronically and/or optically responsive region, which we will introduce later. The thickness of the layer can be tailored by changing the number of ethylene groups. In system III, there are nine ethylene groups in the first hydrophobic alkyl chain region and seven ethylene groups in the second. The hydrophobic chains also prevent polar molecules, ions, etc. from diffusing across the membrane, and therefore help to stablize the inorganic phase.

3.3.3 Electronic and/or optically responsive region of system III

The electronically and/or optically responsive region of system III has the diacetylene groups. The diacetylene moiety raises many research interests due to its ability to form conjugated double-triple alternating bonds under heat or UV-light irradiation, the quasi-one-dimensional highly conjugated system which gives it high electrical conductivity, fluorescence, high third-order nonlinear optical coefficiency, and chromatic properties. These special properties enable it to be used in a variety of applications in

electronics and optics. Generally, when the adjacent diacetylene residues in a crystal lattice are stacked parallel at a distance of about 5 Å and the angle between monomers with stacking axis is about 45°, diacetylene moieties can be polymerized (figure 3.6) [7]. Therefore in order for the diacetylene to photopolymerize, the hydrocarbon chains have to be well parallel ordered. In the system III that we have currently developed, the long fatty acid chains with diacetylene residues automatically arrange in parallel order and the polymer backbone connects the hydrocarbon chains within a polymerizable distance. The diacetylene moiety is in the middle of the polar region and the fatty acid chain, this location helps protect the diacetylene part from oxidative degradation and improves its processability. After photopolymerization, a system with two folds of linked layers is formed. The crosslinking of diacetylene improves the mechanical properties of the system.

Our system III has potential applications as elements in electronic devices in which the conductive diacetylene layer is separated from the conductive or semi-conductive layer with inorganic phases by an insulating alkyl layer. The thickness of this insulating layer can be controlled by the length of the intervening alkyl chains. Environmental stimuli can cause packing pattern alterations in the polar region. The signal will be transferred along the side chains and be detected at the responsive region with the diacetylene moieties through color, fluorescent or conductance changes.

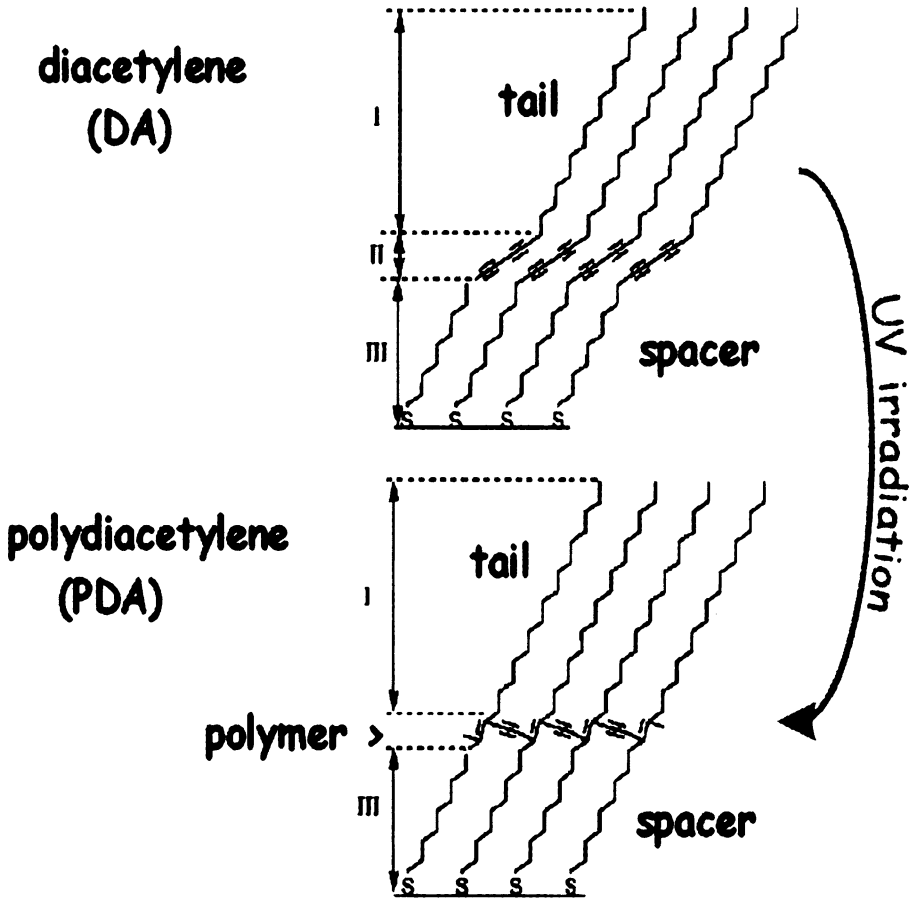

Figure 3.6 The polymerization of diacetylene (adapted from reference 7)

Another important potential application of this system is its use as masks in photolithographic methods, which are widely used in integrated microelectronic circuit printing[8]. The diacetylene groups crosslink under the irradiation of lasers, and therefore protect the regions that are covered by the material. After the laser treatment and removal of the protecting material, the desired pattern can be achieved. The chemical structure of

the polymer-secured self-registering molecular arrays with thio-ether groups in the polar region and diacetylene moieties in the nonpolar region is shown in figure 3.7.

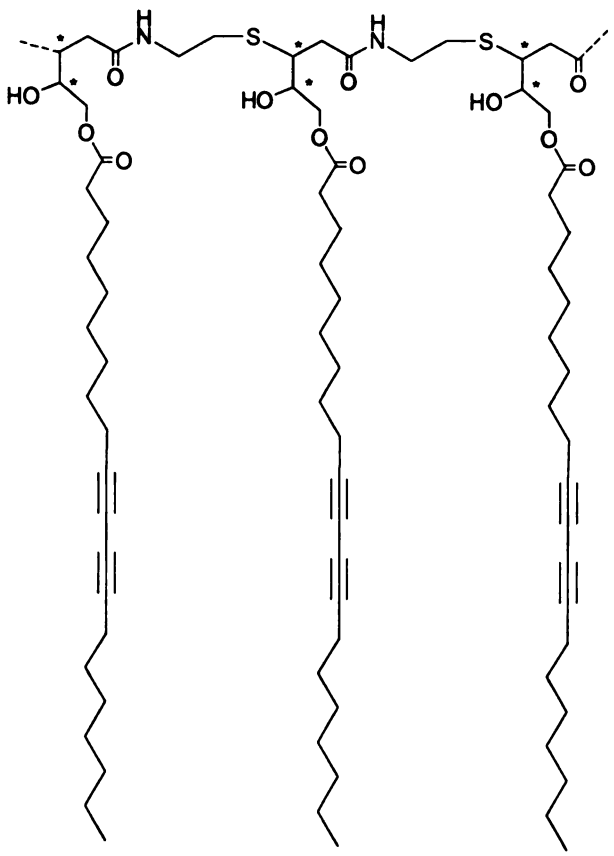

Figure 3.7 Polymer-secured self-registering molecular arrays with thio-ether group in the polar region and diacetylene moieties in the nonpolar region

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CHAPTER 4

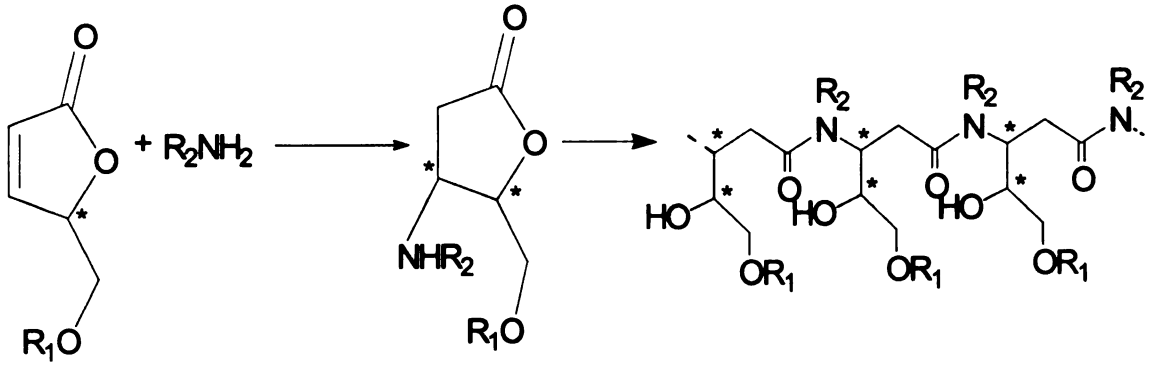
PREPARATION AND CHARACTERIZATION OF THE THREE POLYMER-SECURED SELF-REGISTERING MOLECULAR ARRAY SYSTEMS

ABSTRACT

The strategies for making the polymer-secured self-registering molecular arrays are discussed. There are 2 such strategies. In the first one a suitably functionalized primary amine is added to a 5-substituted-2(5H)-furanone to form an intermediate 3-amino- γ -lactone which is then polymerize to form substituted β -polyamino acid. In the second strategy an aminothiol is reacted with the furanone to form an intermediate (2-aminoethyl)thio-substituted γ-lactone which is then polymerized to form a scaffold containing alternative thio-ether and amide linkages. Four systems using one or the other of these strategies were prepared. System I which was prepared with strategy 1 mimics phospholipid biomembranes. System II and III which were prepared with strategy 2 served as scaffold for forming extensively ordered nanoparticale arrays using metal salts such as CdSe, CdS, ZnSe and ZnS. System III has diacetylene groups incorporated in the long fatty acid chain. Polymerization of these allow them to be used as electronically and optically responsive systems. The high long range order of polymer IV was explored with X-ray diffraction method.

4.1 General strategies for polymer-secured self-registering molecular array system preparation

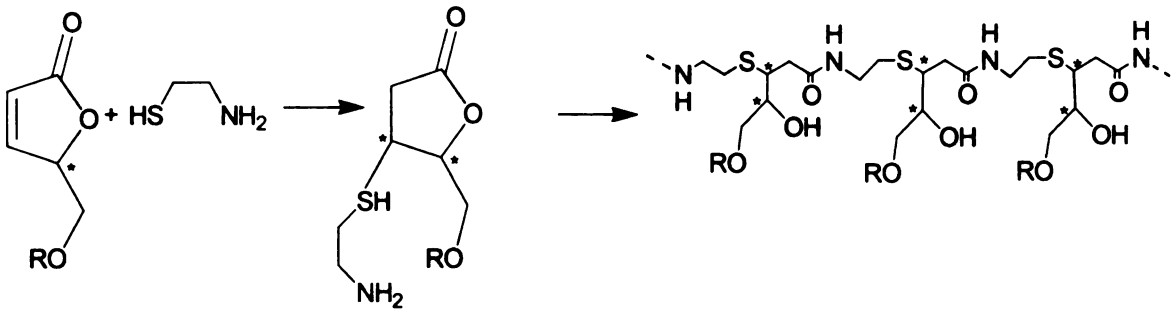
There are two general strategies for preparing polymer systems as the backbone of the polymer-secured self-registering molecular arrays. In the first strategy, a suitably functionalized primary amine was added to a 5-substituted-2(5H)-furanone to form an intermediate 3-amino- γ -lactone which is then polymerize to form substituted β -polyamino acid. This strategy is illustrated in scheme 4.1.



Scheme 4.1 General strategy 1

In the second strategy an aminothiol is reacted with the furanone to form an intermediate (2-aminoethyl)thio-substituted γ-lactone, which was then polymerized to form a scaffold containing alternative thio-ether and amide linkages (scheme 4.2). In both cases, a choice of the substitutents on the furanone allows the incorporation of critical elements of the design such as the functionality in the electronically and optically responsive region, the type of anchor group, and the separation of these elements by the hydrophobic regions. The choice of the amine allows the incorporation of critical

elements at the polar interface region.

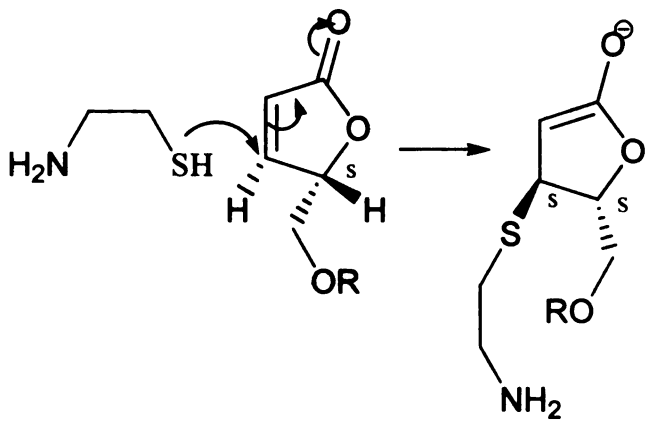


Scheme 4.2 General strategy 2

In both strategies, a substituted 2(5H)-furanone was used as the Michael acceptor in the preparation of the polymer-secured self-registering systems. Generally, an equimolar amount of a primary amine or aminothiol was added to the suitably derivatized furanone under mild conditions to form the intermediate 3-substituted γ-lactone, and the temperature was then raised to effect polymerization.

The three critical elements in the real designs of these systems are:

(1) The furanone – (S)-5-hydroxymethyl-2(5H)-furanone, which is optically active. Michael addition to the furanone is generally stereospecific[1] and another chiral center is therefore introduced. Due to the stereohindrance of hydroxymethyl groups, the addition takes place on the opposite face to that containing the hydroxymethyl groups. Take strategy 2 for example, as described in scheme 3, the chiral center in furanone has the S configuration. In the expected scenario for the addition of an aminothiol the newly introduced chiral center would have the absolute configuration of S.



Scheme 4.3 Mechanism of Michael addition of an aminothiol to the furanone

(2) The hydrophobic alkyl chain region (usually as an acid chloride) that incorporates the reporter elements, such as the diacetylene group, and anchoring functionalities.

(3) The headgroups/interface component which is a primary amine or an aminothiol. These may contain additional functionalities such as charged groups.

System I was prepared using strategy 1 and system II and III were prepared using strategy 2.

4.2 Preparation of a stabilized phospholipid biomembrane monolayer mimetics (system I)

Phospholipid biomembrane mimetics have been widely studied and have many significant scientific and technological applications. They are used as interfaces between living systems and man-made materials. Desirable properties of biomembrane mimetics

include the ability to inhibit the denaturation, degradation or precipitation of proteins, and the prevention of cell transformation on contact with nonbiological materials. Biomembrane mimetics should also display hemocompatibility, that is the ability to stop blood cells from depositing, lysing or clotting on contact with foreign surfaces. Other applications include making biocompatible implants or artificial tissues. Biomembrane mimetics are also important for the fabrication of sensors for biological or biochemical application where cells, antibodies, antigens, receptors and enzymes must be presented in a context that resembles the surface chemistry of a living cell. Biomembrane mimetics can be used to coat surfaces in the fabrication of bioreactors in which the living cells anchor to a support where in-vivo conditions were imitated.

We designed a polymer system which has the surface properties of a phosphatydic acid monolayer system in which the noncovalently associated glycerol components are replaced by a polyamide chain (figure 4.1). There are several advantages to the design of this system:

1 The functionality in the head groups of our system is the same as in phospholipids and proteins (should result in biocompatibility).

2 The covalent connection of the headgroups gives the system a stability and robustness that cannot be matched by ones based on noncovalent interactions. Many applications that require conditions where the phospholipids are not stable can now be explored.

3 Flexibility: The alkyl chain and head group regions can be incorporated without

2
20

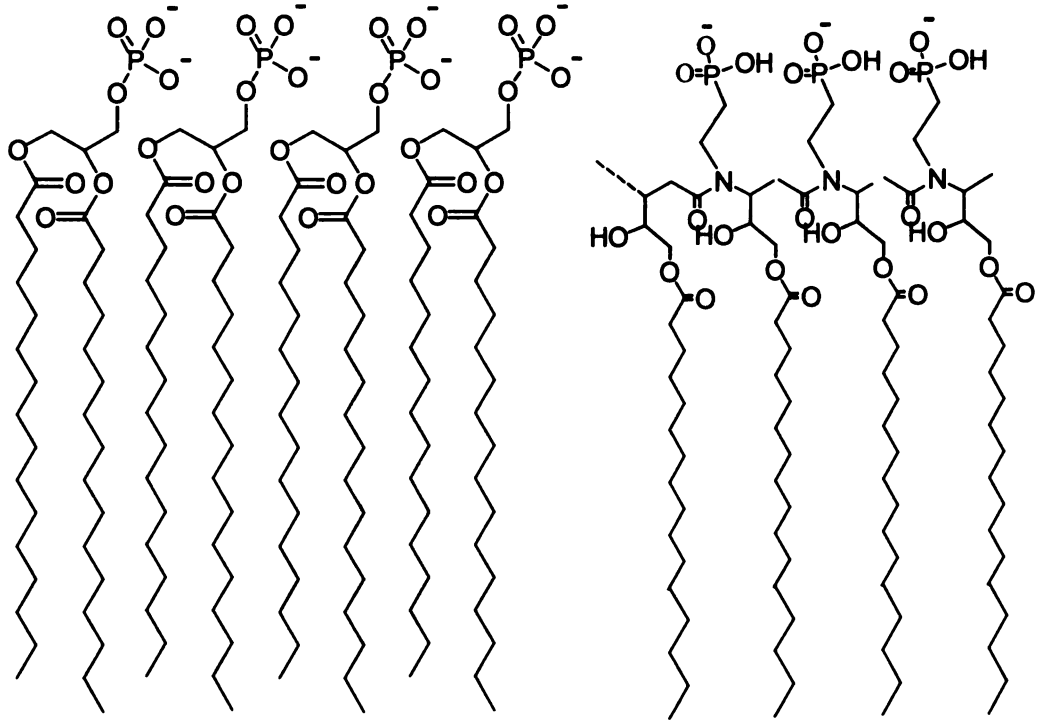
difficulty.

4 General utility: The head groups can be modified chemically or biologically.

5 Robustness: The system is easy to process as self-standing films or as supported layers without risk of breaking.

6 Higher structural integrity than phospholipids where fatty acid chains can be heterogeneous

7 Chirality in the polar head group region enabling the use of polarization techniques and allowing enantioselective discrimination

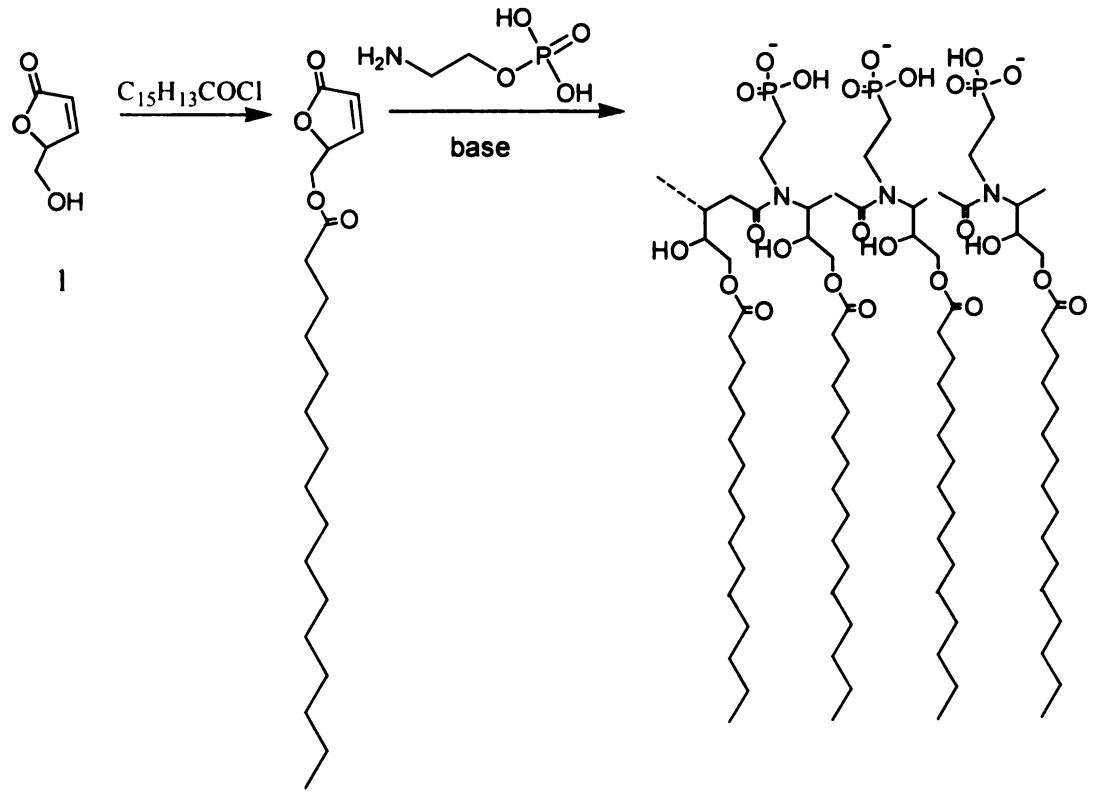


I

Figure 4.1 Comparison of a natural phosphatidic acid self-assembled system (left) and the stabilized phospholipid biomembrane monolayer mimetic I (right)

In addition to the attributes described above, the biomembrane mimetic system we

designed has added advantages of simplicity of preparation and ease of purification. The synthetic strategy to prepare the biomembrane mimetic system (system I) is illustrated in scheme 4.4.



Scheme 4.4 Synthesis of system I

In the synthesis of system I, (S)-(-)-5-(hydroxymethyl)-2(5H)-furanone (**1**) is reacting with hexadecanoyl chloride to form the intermediate Michael acceptor (**2**), which is then reacted with 2-aminoethyl dihydrogen-phosphate to eventually form the desired polymer system I— the phosphatidic acid mimetic.

The potential applications for phosphatidic acid mimetics are many, such as making man-made materials (i.e. plastic or metals) biocompatible for use in clinical applications, serving as elements or matrices in biosensors, or as coatings for bioreactors as mentioned above. Here we explored the utility of the phosphatidic acid mimetics I as a primary foundation or template for the ordered deposition of calcium phosphate to model bone formation. This process is illustrated in figure 4.2. One common biological strategy employed in biomineralization is controlling the location, size, composition, and shape of mineral crystals by the lipid mesophases[2]. Generally the process begins with the capture of calcium ions by the negatively charged phospholipid layer, followed by subsequent capture of phosphate ions, layer upon layer, as illustrated in figure 4.2. Because of its similarity to phospholipid membrane systems, the synthetic stabilized phospholipid membrane mimetic I should serve as an efficient template for the promotion of calcium phosphate deposition.

Polyethylene was used as a substrate on which the polymer system I was coated. On contact of an aqueous solution of I with polyethylene, the fatty acid chains (being hydrophobic) will attach to polyethylene with the polar surface facing outward toward the aqueous medium. The coated plastic was then exposed to calcium and phosphate ions under equilibrium conditions for 7 to 35 days. The experimental conditions were arranged so that the modified plastic surface was never contacted by preformed calcium phosphate particles. This was accomplished by separating the treated plastic from calcium

phosphate with a membrane. Thus, the properties of the inorganic phase (calcium phosphate in this case) such as density, morphology, growth orientation etc. will be controlled by the template made from the phosphatidic acid mimetics.

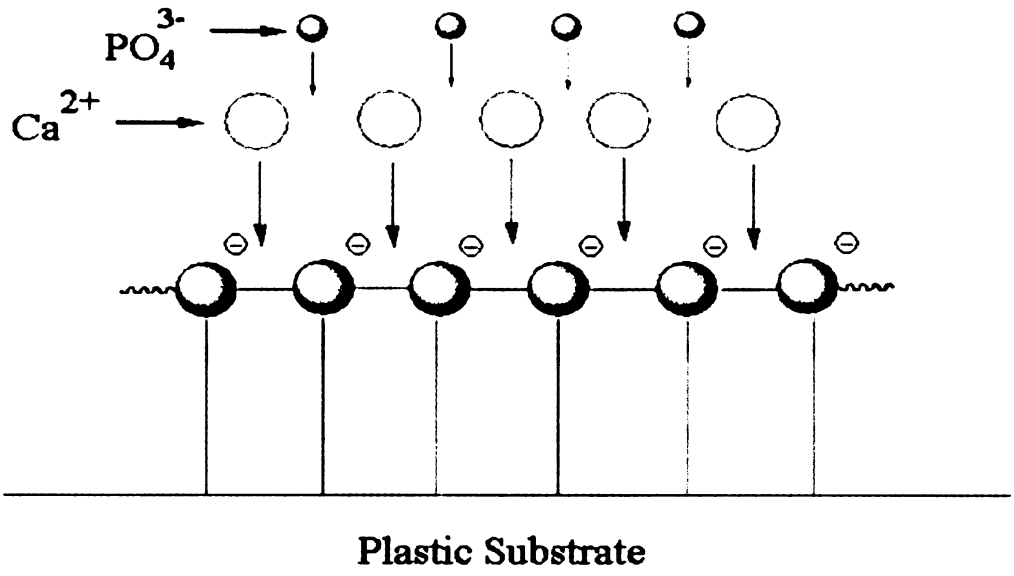


Figure 4.2 Illustration of the phosphatidic acid mimetics' template control over calcification

4.3 Preparation of nanoparticle arrays on self-standing and unsupported two-dimensional self-registering polymeric systems (system II and III)

Nanoparticles are microscopic particles with all three dimensions being within the nanometer scale (i.e. between 1 to 100 nm). On this scale, since the size of the nanoparticles is smaller than the Bohr radius of an electron-hole pair, quantum confinement effects come into play. The most desirable types of nanoparticles include cadmium and zinc salts because they are semiconductors. Their nonlinear optical,

electrical, photochemical and spectroscopic properties have attracted much interest due to the possible applications in solar cells, chemical and biological sensors and telecommunication.

Nanoclusters have very high surface areas. This feature gives them attractive properties, such as high activity, with potential applications in catalysis and chemo-responsive sensors, but at the same time it also makes them aggregate very easily and lose their activity. Processing of nanoparticles is very problematic and challenging because of their poor mechanical strength and stability. Dispersion of nanoparticles in polymers has solved the problem to some extent. The two most common approaches include blending and *in situ* polymerization[3]. Direct blending mainly uses the shear force between the particle and polymer melt or solution. This method is relatively easy, but often unsuccessful in achieving efficient nanoparticle dispersion. *In situ* polymerization methods were adopted because nanoparticles are more easily dispersed in the monomer solution which can be polymerized afterwards. However, this method is restricted to certain polymerization procedures due to the particular requirement of this approach.

4.3.1 A two dimensional self-registering polymeric system without an electronically and optically responsive region (system II)

The first of the sulfur functionalized self-registering polymers we designed as a template for the controlled deposition of inorganic nanoparticles is shown in figure 4.3.

The polymer can form a two dimensional stabilized membrane with specific orientation that could be used to incorporate the zero-dimensional nanoparticles in ordered arrays on the hydrophilic surface and efficiently protect them from aggregating and precipitating (figure 4.4).

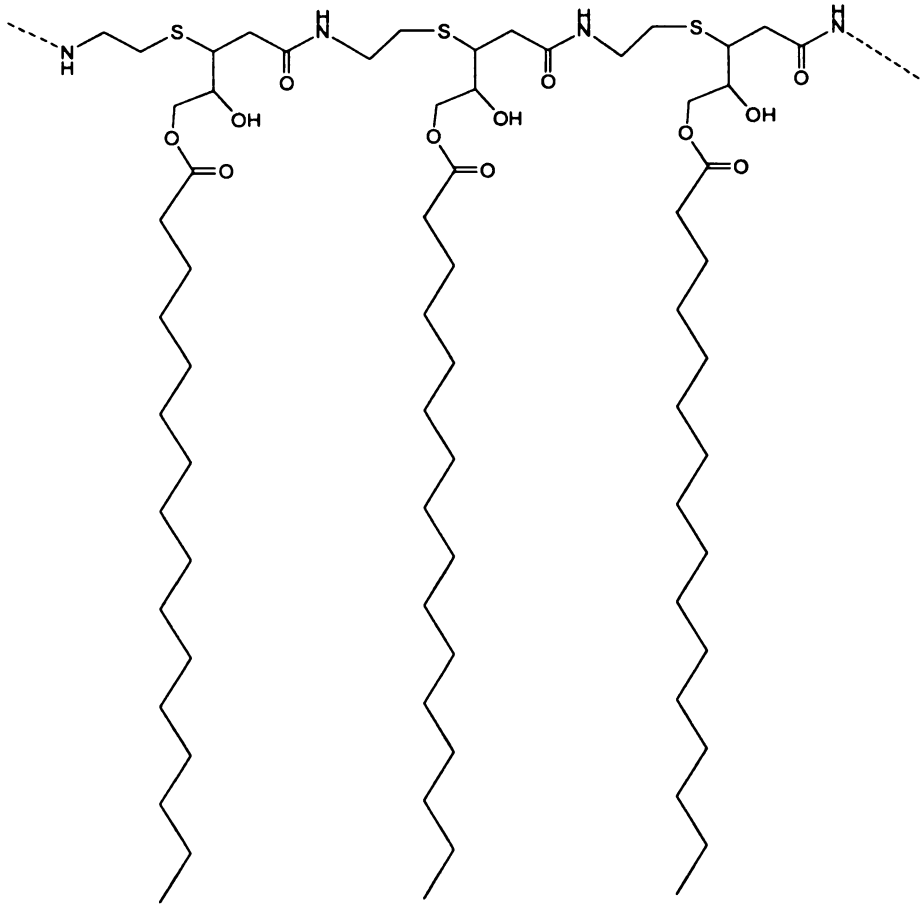


Figure 4.3 Polymer-secured self-registering molecular arrays with thio-ether group in the polar region (system II)

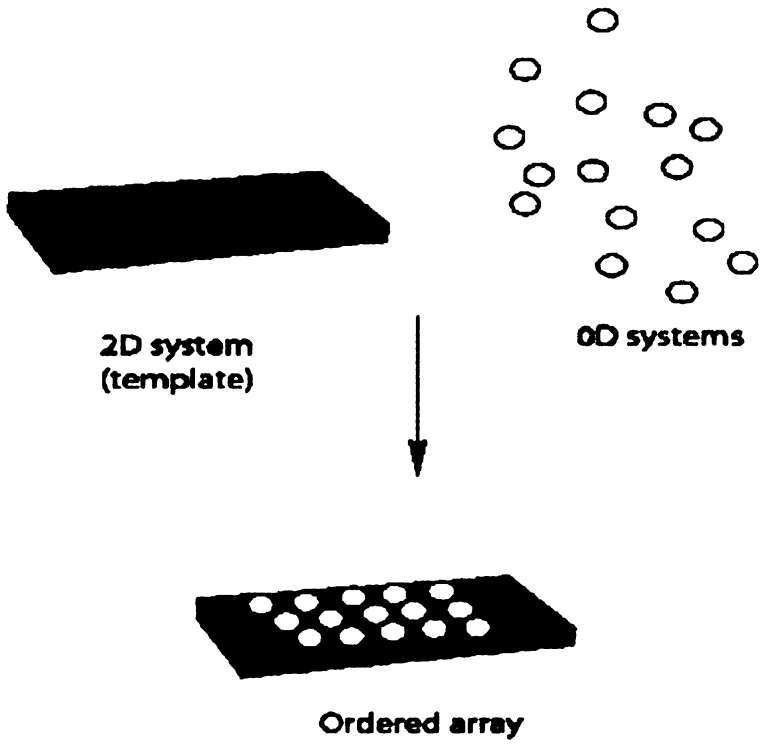
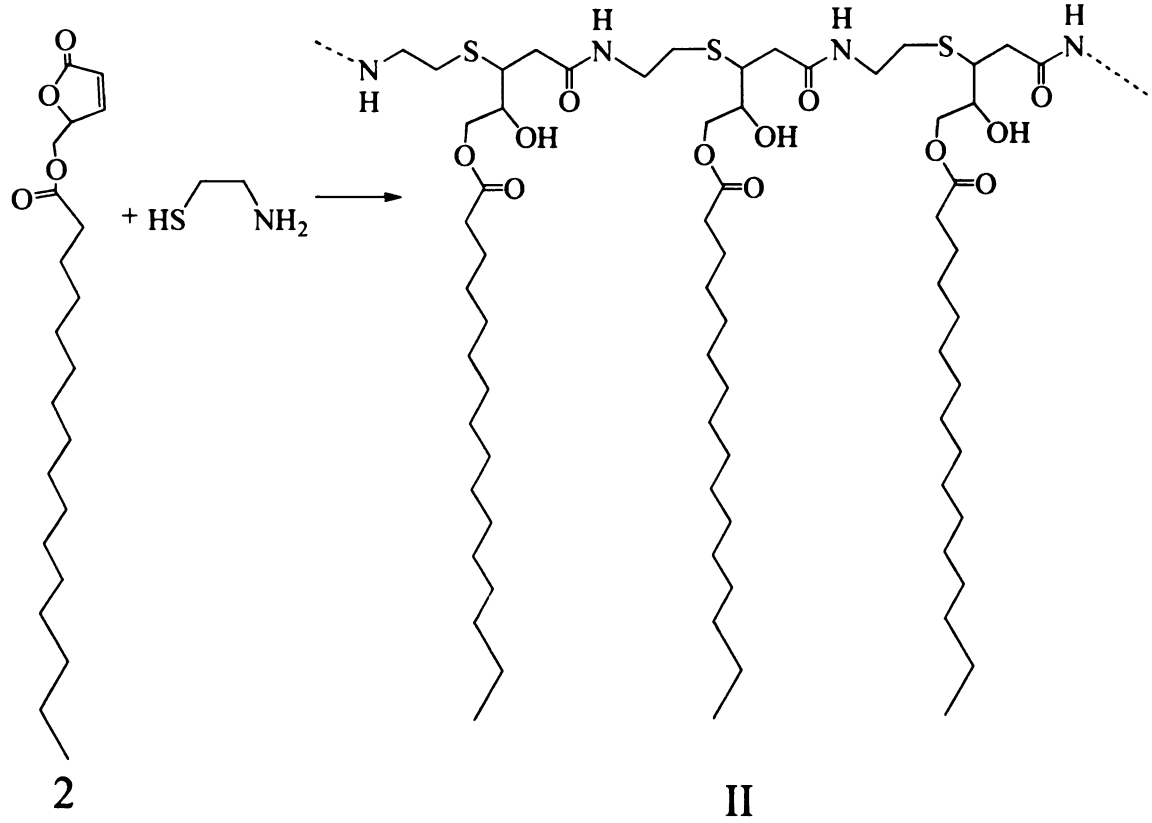


Figure 4.4 Ordering effects of the two dimensional template on nanoparticles

System II has sulfur functional groups which have strong affinities for certain metals such as cadmium and zinc in its repeat unit. Individual sulfur atoms can be sequestered at regular points on this 2-dimensioanl system and each can serve as the nucleus for the slow, directed and controlled growth of individual nanoparticles. The specific arrangement of sulfur functional groups in the template is transferred to the nanoparticle, and organized arrays of the nanoparticles will be formed. This method is more efficient compared to the blending method, which only uses the shear force between the particles and the solution. The template is very accessible by a concise synthetic scheme. It can

be prepared as a free-standing system or as a supported layer. As a consequence, a two-dimensional nanoparticle array on a processable membrane system is formed.

The self-registering polymer with saturated alkyl chains and sulfur functions in the polar region (system II) was formed through the condensation of the Michael acceptor **2** and 2-mercaptoethylamine shown in scheme 4.5.



Scheme 4.5 Synthesis of sulfur functionalized self-registering polymer II

4.3.1.1 An unsupported membrane made from polymer II

The preparation of calcium selenide arrays on the polymer template II is illustrated in figure 4.5. The solution of II was deposited on top of the cadmium perchlorate aqueous

solution. After the solvent evaporated, the polymer formed a membrane floating on top of the aqueous solution. The hydrophilic head groups or the polar region of the polymer were immersed in the semiconductor solution, and the hydrophobic alkyl chains pointed to the air in parallel arrays. After incubation, ordered arrays of cadmium perchlorate nanoparticles with wurzite structure were formed on the hydrophilic polar surface of II under the control of the sulfur groups. The stabilized two-dimensional membrane with cadmium perchlorate as the inorganic phase modification was formed on top of the water. In step 1 indicated in figure 4.5, perchlorate ions were replaced by selenide in sodium selenide solution. In the second step the membrane was removed from water to form the unsupported membrane with ordered arrays of cadmium selenide nanoparticles incorporated in the polar region. The cadmium/zinc chacogenide nanoparticles can all be deposited on the unsupported membrane made from polymer II using this method.

The cadmium/zinc chalcogenide crystals are semiconducting. They are anchored on the polar region of the polymer, which has the long insulating hydrocarbon chain. Therefore, the hierarchical structure is electronically dipolar. In addition, the quantum dots formed with cadmium/zinc chalcogenide have optical properties such as nonlinear optical effects and fluorescence. The head groups are covalently linked by polyamide bonds, so the membrane formed is robust and can be easily removed from the top of water and used in different ways, such as surface coating, conductance converters and optical devices.

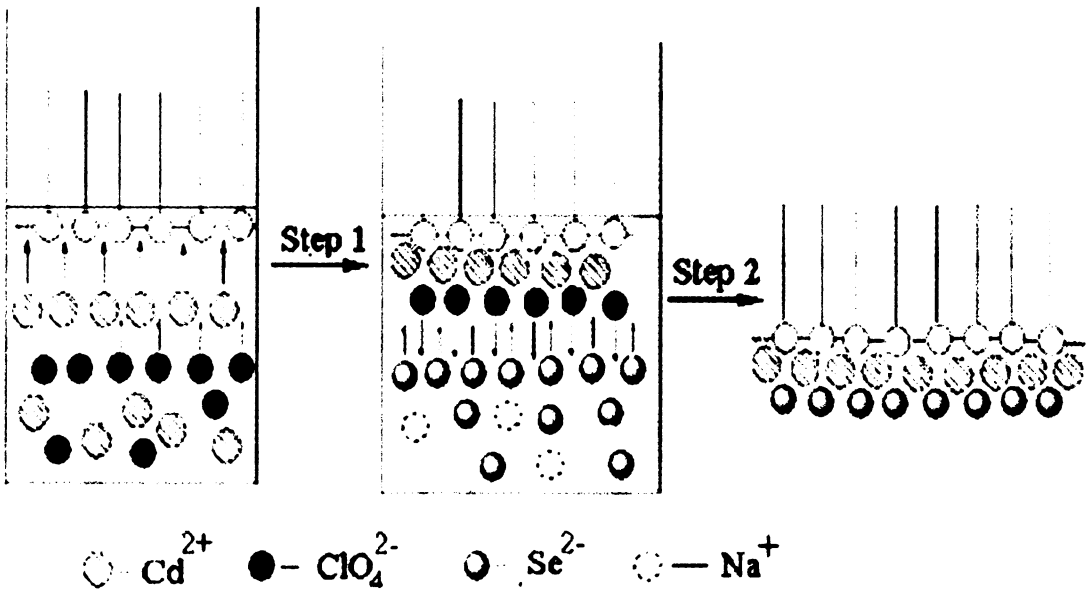


Figure 4.5 Preparation of an unsupported membrane made from polymer II

4.3.1.2 A freestanding film made from the sulfur functionalized self- registering polymer II

A freestanding film of the sulfur functinalized self-registering polymer has also been prepared as illustrated in figure 6. The standard procedure for preparing freestanding lipid membranes was adopted. In this method, a concentrated solution of the polymer was cast across a fine metal wire loop with diameter of 1 mm. After the solvent evaporated, the metal loop with the polymer membrane was placed in water overnight. In the presence of water, the amphiphilic molecules in the membrane should rearrange to form a bilayer arrangement with the polar heads pointing toward the aqueous phase and the hydrophobic hydrocarbon chains oriented inwards between the layers to interact with each other.

Self-assembled lipid freestanding membranes derived from phospholipids can normally only be 0.1 mm^2 in area at the maximum. They are fragile and the lifetime is normally no more than 24 hours. The membrane system we prepared with polymer II has a much larger area and a much longer lifetime (7 days at least) due to the stablization of polyamide linkages in the polymer.

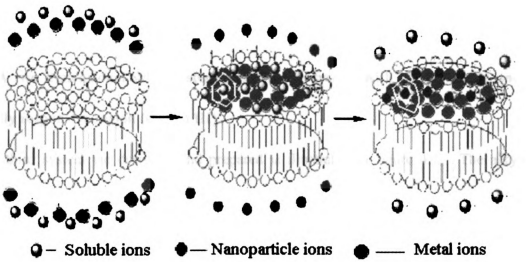


Figure 4.6 Preparation of freestanding membranes made from II

Cadmium or zinc chalcogenide particles were then deposited on the membrane in ordered arrays. The metal ions attached to the top of the membrane to form crystals, which by virtue of their optical properties had the wurzite structure.

This method of freestanding membrane preparation is straightforward, easy, flexible, cost-saving and fast. This is in contrast to the Langmuir-Blodgett method, which is necessary for the preparation of films from typical self-assembled systems. The

self-registering polymeric membrane preapared from polymer II is robust, well ordered and very amenable to inorganic mineral modifications.

A similar method was adopted to make pinhole supported self-standing membranes. In this method, suspension of polymer II was painted across a pinhole in a polyethylene sheet. After the solvent was evaporated, the membrane was put in water to form a bilayer. The membrane can then be modified with inorganic phases by dipping into solutions.

4.3.2 A two dimensional self-registering polymeric system with electronically and optically responsive region (system III)

The third system we designed and prepared is illustrated in figure 4.7. The alkyl chain in this system incorporates a polydiacetylene functionality. This self-registering polymer shares the same backbone with the first sulfur functionalized self-registering polymer II described in the previous section. The diacetylene functional groups can polymerize by irradiation with heat or UV radiation. This will further stablize the system and greatly modify the properties of the system at the same time.

Polydiacetylene compounds have very unique chromatic properties. They have two distinct spectroscopic phases, blue forms and red forms with exciton absorption peaks at 640 nm and 560 nm. Under environmental perturbations such as structural changes in the polar region, solvent, pH, mechanical and temperature changes, polydiacetylene functionalities can demonstrate color changes from blue to red. This property can be used in the investigation of membrane interactions in biological studies and sensors for

different chemicals. Polydiacetylene has high nonlinear optical (NLO) effects which will further modify the properties of the light beam passing through the material including the phase, frequency and state of polarization after nanoparticle modification in the polar region. In addition, with doping, polydiacetylene can be very conductive. This will enable the fabrication of electronic devices with multiple layers of different conductivity.

To make the polymers, 10,12-docosadiynedioic acid (scheme 4.6) or 10,12-tricosadiynedioic acid (scheme 4.7) was transferred into the corresponding acid chloride through reaction with oxalyl chloride. The acid chloride reacts with (S)-(-)-5-(hydroxymethyl)-2(5H)-furanone to form the Michael acceptor monomer. The monomer was then mixed with 2-aminoethanethiol and primarily polymerized.

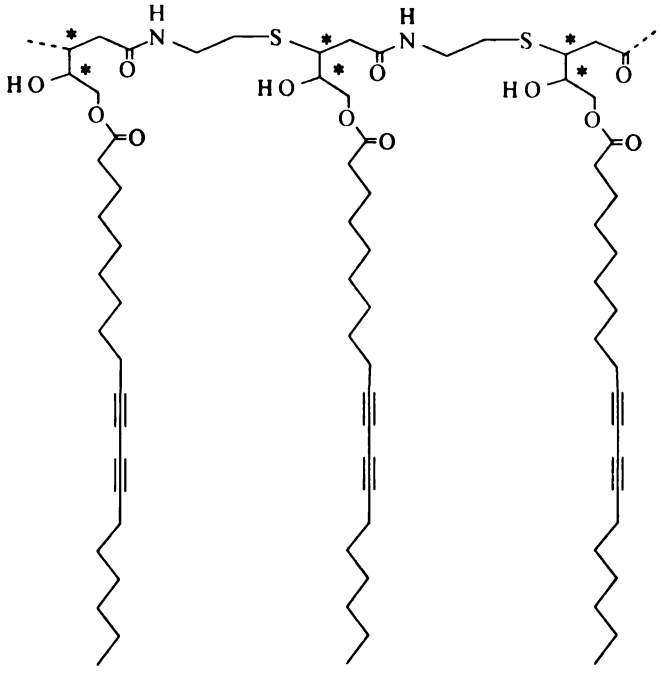
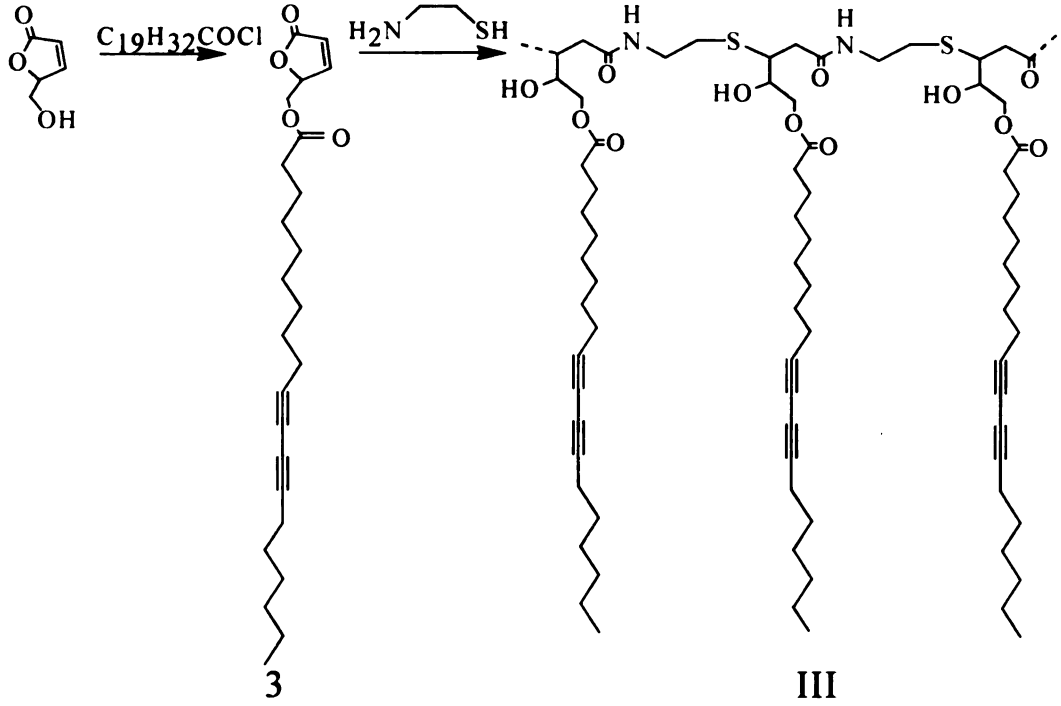
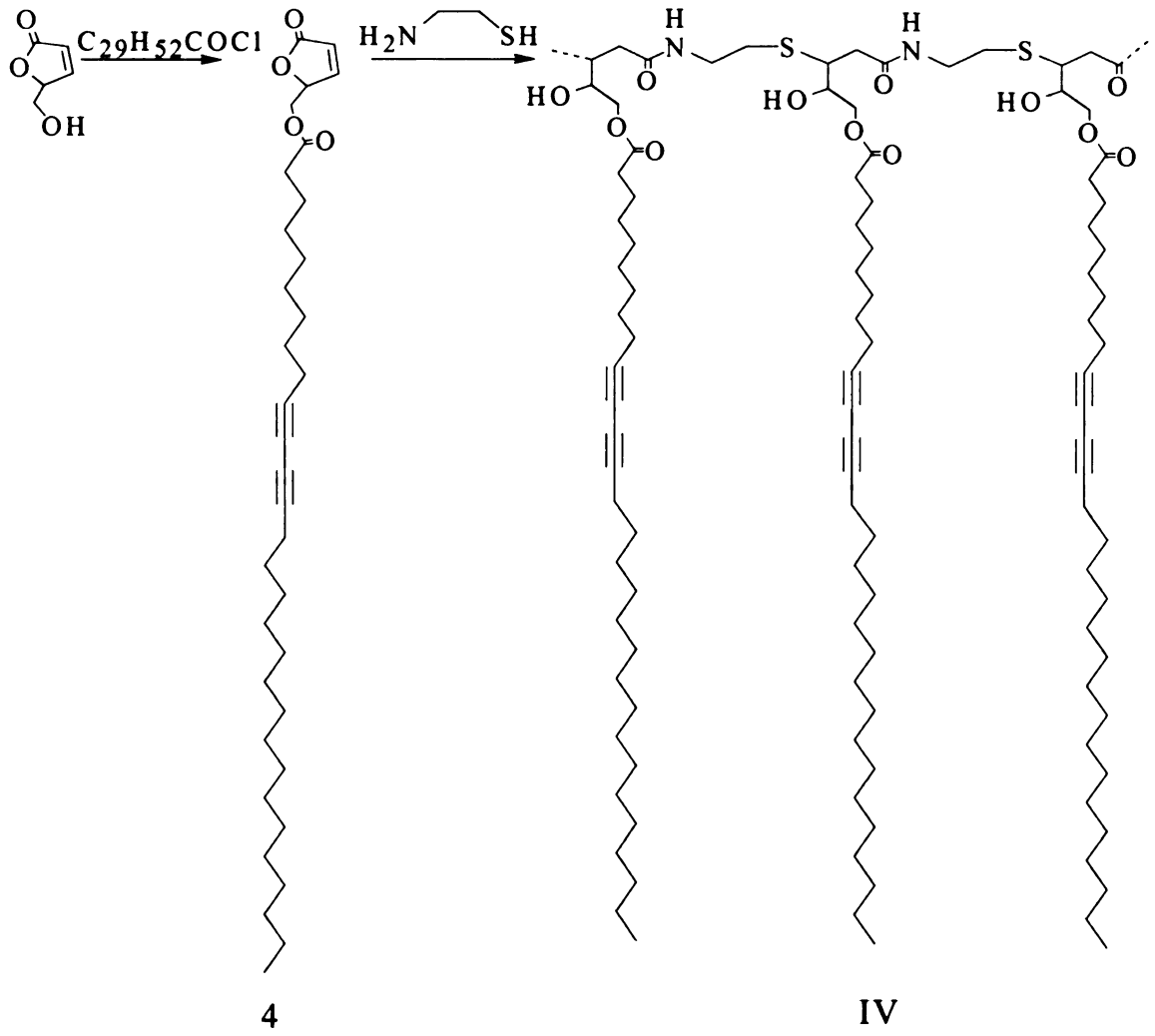


Figure 4.7 Diacetylene functionality incorporated self-registering polymer III



3 III

Scheme 4.6 Synthesis of a 20C-self-registering polymer incorporating diacetylene (polymer III)



Scheme 4.7 Synthesis of a 30C-self-registering polymer incorporating diacetylene (polymer IV)

After the formation of the polymer, the diacetylene residues can be further polymerized to form the two dimensional polymer-secured self-registering structure under UV irradiation (figure 4.8). There are two kinds of films-- free-standing films and unsupported films prepared with the diacetylene incorporated polymers, which will be further discussed.

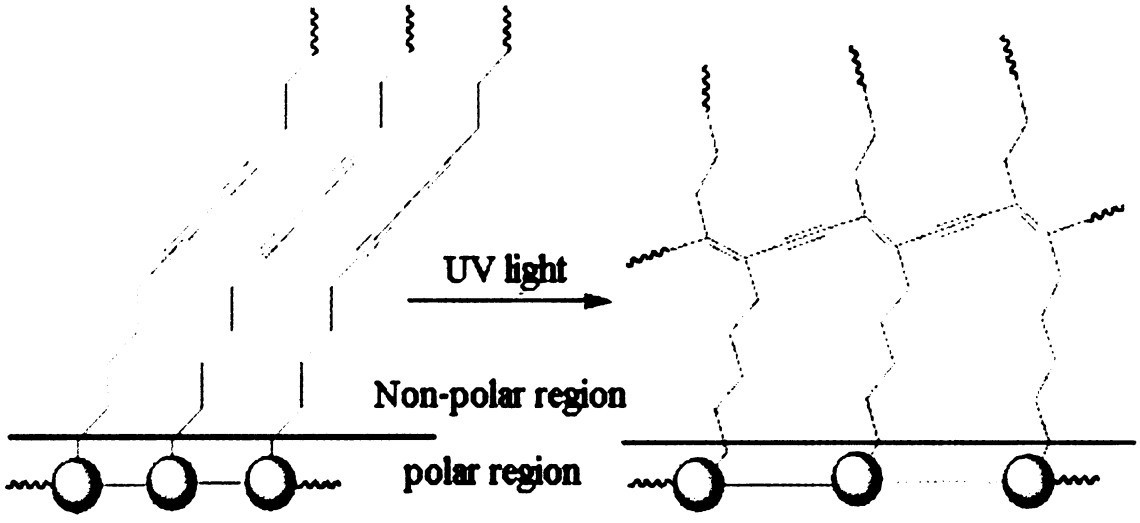


Figure 4.8 Secondary polymerization of organic template formed with diacetylene incorporated self-registering polymer

4.3.2.1 Preparation of freestanding films made from the diacetylene incorporated self-registering polymers

Freestanding films made from diacetylene incorporated self-registering polymers were made into a very concentrated solution. The solution was then cast across a fine metal wire loop. After the film was air dried, it was put in water overnight to enable the self-registering process. After the rearrangement, the freestanding film attached to the metal loop was formed. Further inorganic phase modification was achieved through dipping the metal loop into the semiconductor solution.

The membrane was further polymerized with irradiation by UV light to crosslink the diacetylene moieties as shown in figure 4.8. After the diacetylene moieties crosslink, a

layer made of alternating double-triple bonds was formed. This system can correspond to environmental changes (such as molecules combing at the polar region, temperature, light or current) with signals that can be detected--including color changes. In addition, photopolymerization of the diacetylene groups further stablizes the system and makes it more rigid.

4.3.2.2 Preparation of unsupported film made from the diacetylene incorporated self-registering polymer:

A primarily polymerized diacetylene incorporated self-registering polymer solution was cast on top of water. After the solvent was evaporated, a water-supported self-registering polymer membrane was formed at the interface of water and air. To modify it with inorganic elements, semiconductor metal salts were dissolved in the water subphase. After overnight incubation, the hierarchical material was subjected to UV irradiation to crosslink the diacetylene moieties. Fendler and co-workers[4] prepared sufficiently small metal sulfide particles to realize nanosize quantum effects by infusion of H_2S from the air-water interface. This method was also used here to make semiconductor sulfide nanoparticles. Under treatment of H_2S gas, small semiconductor particles with nanoscale sizes were formed and stabilized on the membrane formed from the polymer.

The systems we prepared with the diacetylene incorporated self-registering polymers have inorganic phases with nanosized particles (which can also be called quantum dots)

in the polar region separated by the diacetylene groups in the electronically and/or optically responsive region by the hydrophobic, insulating hydrocarbon chains. This gives the structure multi-functionalized-layer properties. Once it is coated to the substrate, the system brings all these unique properties to the surface, and makes it highly applicable in areas such as device fabrication.

4.4 Experimental Section:

Preparation of compound 1: Hexadecanoyl chloride in 10 ml dichloromethane was put in a dropping funnel. (S)-(-)-5-(hydroxymethyl)-2(5H)-furanone 2.28 g was dissolved in 40 ml dichloromethane and 5 ml pyridine, and was then mixed and stirred in a 100 ml round bottom flask in an ice bath. The funnel was connected to the flask and the acid chloride was added to the mixture drop by drop. After all of the acid chloride was added, the reaction was incubated for 2 hous in an ice bath and 2 hours at room temperature. Dichloromethane 50 ml and a hydrochloric acid solution (5 ml HCl in 25 ml ice water) was added to the product. After washing, the aqueous portion was discarded. The product was washed again with 30 ml of water, then 30 ml of a sodium bicarbonate solution. Sodium sulfate was added to the product to absorb excess water. The liquid was drained into another flask. The solvent was evaporated and compound 1 was achieved. ^{1}H NMR (300 MHz, $CDCl_3$), 7.55 (t, 1H), 6.28 (d, 1H), 5.34 (q, 1H), 4.42 (d, 2H), 2.40 (m, 2H), 1.40 (m, 23H)

Preparation of Polymer I: 2-Aminoethyl dihydrogen phosphate 0.5592g and 1.65 ml TEA was mixed in a flask. Water was added dropwise untill the solid dissolved, and the reaction proceeded for 5 minutes before removing the water by evaporation. The mixture was added to compound 1 and 60ml solvent of 1:1 dichloromethane : tetrahydrofurane. This reaction was incubated then for 2 hours in an ice bath, 2 hours at room temperature and 4 hours between 50 to 60 °C. The solvent was evaporated and the mixture was heated at 100 °C for three hours to obtain polymer I. ^{1}H NMR (300 MHz, $CDCl_3$), 5.65 (broad), 5.18, 3.6, 3.18, 2.2, 0.81-1.68 (m). ^{13}C NMR (300 MHz, $CDCl_3$), 13.85, 19.64, 22.03, 29.82, 58.95. ^{35}P NMR (300 MHz, $CDCl_3$), 2.2. IR ($CHCl_3$, NaCl), 3377, 2961, 2926, 2874, 2851, 2166, 1743, 1464, 1381, 1172, 1068, 929, 887, 729.

Synthesis of polymer II: 2-Mercaptoethylamine 0.2669g was dissolved in 10 ml methanol, and then poured into a dropping funnel. The 2-mercaptoethylamine was added dropwise to a 100ml round bottom flask placed in an ice bath with 1.2180 g of compound 1 dissolved in 50 ml dichloromethane. The reaction proceeded for 2 hours on an ice bath, 2 hours at 50 °C. After the removal of all the solvent, the mixture was heated at 100 °C overnight to obtain polymer II. ^{1}H NMR (300 MHz, $CDCl_3$), 2.39(t), 1.53, 1.24, 0.89. ^{13}C NMR (300 MHz, $CDCl_3$), 73.6, 64.2, 58.8, 40.5, 37.4, 34.6, 31.1, 30.8, 29.6, 28.1, 25.2, 18.9. IR ($CHCl_3$, NaCl), 3351, 2919, 2851, 1701, 1558, 1541, 1466, 1178, 1068,

939

Preparation of compound 3: Docosadiynedionic 476mg acid was mixed with 5 ml oxalyl chloride in dichloromethane 5 ml, and reacted at 70°C for 10 hours with refluxing. The excess oxalyl chloride and toluene were removed quickly under low pressure by rotoevaporation. Toluene 10 ml was added to the product and evaporated immediately to make mixture 1. (S)-(-)-5- (hydroxymethyl)-2(5H)-furanone 150 mg, 1 ml pyridine and 0.5 g potassium carbonate were mixed in 5 ml anhydrous dichloromethane to make mixture 2. Mixture 2 was poured into mixture 1 and reacted at room temperature overnight. The final product, compound 3, was purified with a silica column. ^{1}H NMR (300 MHz, $CDCl_3$), 6.00 (d, 1H), 5.12 (q, 1H), 4.18 (d, 2H), 2.40 (m, 6H), 1.40 (m, 24H). ^{13}C NMR (300 MHz, $CDCl_3$), 19.9, 24.6, 28.4, 33.8, 62.2, 81.7, 123.8, 152.2.

Synthesis of polymer III: 2-Aminoethanethiol 0.023 g was prepared into 10 ml methanol solution with a 10 ml volumetric flask. The methanol solution 2 ml was combined with 0.117g compound 3. Tetrahydrofuran 10 ml was added to the mixture and the reaction proceeded for 5 hrs. The mixture was then heated at 70 °C for another 3 hours with refluxing and polymer III was formed. ^{1}H NMR (300 MHz, $CDCl_3$), 2.35, 2.25, 1.68, 1.51, 1.30. ^{13}C NMR (300 MHz, $CDCl_3$), 18.1, 24.9, 28.4, 28.6, 28.8, 29.0, 29.1, 34.2, 39.0, 39.3, 39.6, 39.9, 40.2, 40.6, 40.8, 71.8, 83.2.

Synthesis of polymer IV: Compound 4 0.1875 g (obtained from Dr Hollingsworth) was dissolved in dichloromethane. Exactly one equivalent (0.0275g) of 2-aminoethanethiol was rinsed into dichloromethane solution of compound 4, mixed and the solvent were evaporated overnight. The mixture was incubated at overnight to obtain polymer IV. ^{1}H NMR (300 MHz, $CDCl_3$), 2.75 (t), 2.52 (d), 2.18 (m), 1.46 (m), 1.26 (m). ^{13}C NMR (300 MHz, $CDCl_3$), 18.1, 24.9, 28.4, 28.6, 28.8, 29.0, 29.1, 34.2, 39.0, 39.3, 39.6, 39.9, 40.2, 40.6, 40.8, 71.8, 83.2. IR($CHCl_3$, NaCl), 3260, 2910, 2120, 1730, 1400, 860, 780, 620

Preparation of the polyethylene supported membrane made of polymer I: Polymer I was designed as a system to imitate the template control over inorganic minerals in the biomineralization process. A few drops of water were put into the ethanol solution of polymer 1 to make it cloudy. Plastic pieces (1 cm x 1 cm) were dipped into the cloudy solution for one hour to be coated. The polymer coated plastic piece was put into water for 10 minutes to remove the excess polymer and the polymer that was not attached well to the plastic substrate. A dialysis bag was filled with water, and the polymer coated plastic piece was put into it before the open end was sealed. The bags were quickly stirred in a supersaturated calcium phosphate solution for different lengths of time.

Preparation of the unsupported membrane made from polymer II: Polymer II, dissolved in toluene, was deposited on top of the cadmium perchlorate aqueous solution. After incubation of 1 day, ordered crystals of cadmium perchlorate was formed under the control of the organic template. The cadmium perchlorate solution was then diluted several times until sodium sulfide tests showed no precipitation. Sodium selenide was put into the aqueous solution and the system was incubated again.

Preparation of the freestanding film made from polymer II: Polymer II was prepared as a very concentrated solution. Fine metal wire loops with diameters of 2-3 mm were dipped into the concentrated solution. A thin membrane was seen formed in the middle of the loop. After the solvent was evaporated, the metal loops were put in water overnight. Cadmium perchlorate and zinc sulfate solutions were used separately to modify the membranes. After one day of incubation, the loops were dipped in water for several minutes to remove the excess metal ions. The loops were respectively put into sodium selenide or sodium sulfide solutions to make CdS, CdSe, ZnS and ZnSe nanostructures.

Preparation of the pinhole supported freestanding film made from polymer II: Polymer II 10 mg was dissolved in 40 ml ethanol and sonicated. Water 40 ml was added to the suspension before another portion of ethanol was introduced. The mixture was sonicated and centrifuged. The upper clear liquid was brushed across the pinhole in a

polyethylene sheet that is drilled by needle with diameter of 500 microns. After solvent was evaporated, the membrane was dipped into water for 1.5 hours. For inorganic phase incorporation, the plastic piece with the membrane was put into cadmium perchlorate solution for one hour, and then water to remove the excess cadmium ions. Afterwards, the membrane was put in a very diluted sodium selenide solution for 6 hours and the membrane prepared was kept in a watch glass.

Preparation of the freestanding film made from polymer III: The primarily polymerized polymer III was dissolved in the least amount of pyridine to form a very concentrated solution. The fine metal wire loop was dipped in the solution of the polymer to form a polymer membrane attached to the loop. The film was air dried, and then put in water overnight. Further inorganic phase modification was achieved by dipping the metal loop into a semiconductor cation salt solution (such as cadmium perchlorate or zinc sulfate). After one day of incubation, the loops were dipped in water for several minutes to get rid of the excess salts or ions. The loops were subsequently put into sodium selenide or sodium sulfide solutions respectively to make CdS, CdSe, ZnS and ZnSe nanostructures. The membrane was further polymerized with irradiation of UV light to crosslink the diacetylene moieties.

Preparation of the unsupported film made from polymer III: Drops of ethyl acetate

solution of the primarily polymerized polymer III were added on top of water. After the ethyl acetate evaporated, the water-supported self-registering polymer membrane was formed at the interface of water and air. To modify the membrane with inorganic elements, cadmium perchlorate hydrate or zinc sulfate was dissolved in the water subphase to form the cation on the organic template. After incubation overnight, the hierarchical material was subjected to UV irradiation for 20 minutes. Aluminum stubs were used to scrape the organic membrane with metal ions chelated from the interface. The aluminum stubs were then put in a bottle containing a mixture of sodium sulfide and sulfuric acid to replace the ions with sulfide.

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CHAPTER 5

EVALUATION AND CHARACTERIZATION OF THE SYSTEMS

ABSTRACT

The three self-registering polymeric systems were evaluated with a variety of methods including laser scanning confocal microscopy, x-ray diffraction and electron scanning microscopy. In the phospholipid membrane mimetics (polymer I) system, the modification of a plastic film and the subsequent deposition of calcium phosphate was confirmed by staining with a cationic dye and the dark field mode of scanning laser confocal microscopy respectively. In the self-registering polymeric system with long saturated fatty acid chains and sulfur functions in the polar region (polymer II) system, lamellar sheet were found to be the dominant morphology. The system displays fluorescence due to the nanoparticles deposited on the membrane surface. In addition, rod shape single crystals were found in the pores distributed on the surface of these lamellar sheets. In self-registering polymeric system modified with polydiacetylene functions in the long fatty acid chain and sulfur functions in the polar region (polymer III) system, lamellar sheets again were found to be the dominating morphology. The fluorescence behavior of the polymer system is greatly modified by different nanoparticle depositions.

In this chapter, we used a variety of methods such as laser scanning confocal microscopy, atomic force microscopy, x-ray diffraction and electronic scanning microscopy to evaluate the self-registering polymer systems that we developed. Three systems were developed: a phospholipid membrane mimetic (polymer I), a self-registering polymeric system with long saturated fatty acid chains and sulfur functions in the polar region (polymer II) and a self-registering polymeric system modified with polydiacetylene functions in the long fatty acid chains and sulfur functions in the polar region (polymer III). Polymer I was developed as a supported (substrate deposited) 2-dimensional membrane system. For polymer II and polymer III, two kinds of membranes were prepared for each. An unsupported membrane system which was formed at the interface of an aqueous phase and an immiscible organic phase was one membrane system. The membrane can be lifted from the interface and applied to different substrates or supports for further characterizations or for use in various applications. The other system studied was a self-standing edge-supported membrane. This was formed inside of a circular metal wire loop or a pinhole in a polyethylene sheet. These systems were then subjected to further modifications such as the incorporation of inorganic phases.

5.1 Evaluation of surface coverage of a polyethylene substrate by polymer I and characterization of the modified surface after calcium phosphate deposition

Verification of modification of polyethylene by staining with a cationic dye

Modification of the polyethylene film with polymer I should lead to the formation of an array of phosphate groups on its surface similar to the array formed on the surface of a cell. The cationic dye crystal violet (structure shown in figure 5.1) interacts strongly with cell membranes and should therefore stain the polyethylene film if it was successfully coated. The comparison between a sample of an uncoated polyethylene film and a coated film after staining with crystal violet was shown in Figure 5.2. The coated film is stained much more purple by crystal violet than the uncoated one. This result confirms that the surface was successfully modified and should be capable of functioning as a template or foundation for the deposition of calcium phosphate.

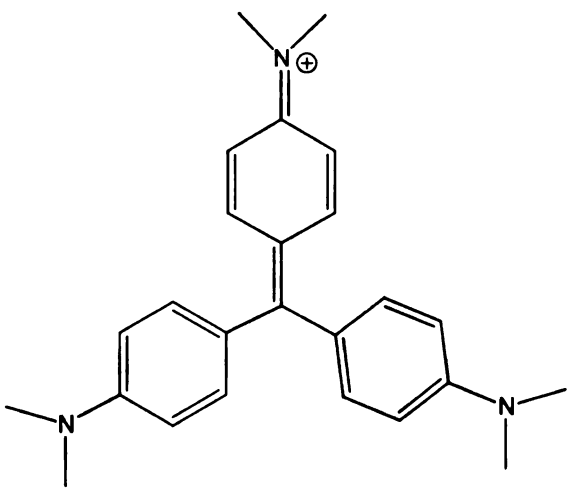
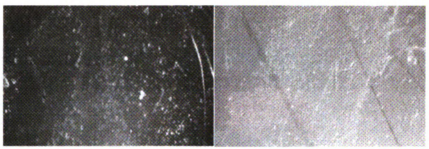


Figure 5.1 Structure of cationic dye crystal violet

Figure 5.2 Comparison of bare polyethylene piece (left) and polyethylene piece modified with polymer I (right) after crystal violet treatment. Notice that the polymer coated piece is stained more purple by crystal violet

Study of calcium phosphate deposition on the polymer I modified polyethylene

The calcium phosphate deposition on the polymer I modified polyethylene was studied by optical laser scanning confocal microscopy in dark field mode. In dark field microscopy, transparent areas will appear to be dark and highly refractile areas (e.g. those modified by salt deposition) will appear to be bright. This mode of light microscopy is therefore an excellent one for evaluating the deposition of highly refractive inorganic materials on a transparent organic matrix. In figure 5.3A, the polymer I modified polyethylene, which was kept in the presence of calcium and phosphate ions for one week, shows early stages of mineral deposition and partial coverage (i.e. more dark regions). While in figure 5.3B a similar substrate after five weeks of calcification shows complete coverage (i.e. more dark regions). The deposition difference can also be seen by the naked eye (figure 5.4). The plastic piece on the left doesn't have any coverage, therefore is very transparent. The polymer I modified polyethylene is much more opaque due to the polymer and its inorganic phase coverage.



A B

Figure 5.3 Dark field optics micrographs of polymer modified polyethylene calcification A: one week of deposition with partial inorganic phase coverage; B: 5 weeks of deposition with complete inorganic phase coverage. Notice that there are more darker areas (i.e. no salt deposition) in A the substrate area in B is very bright, indicating complete salt deposition over the whole surface

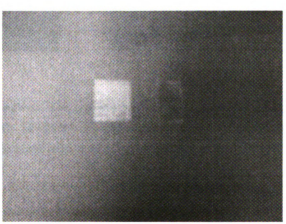


Figure 5.4 Comparison between a polymer I modified surface and a bare ethylene surface. Left: transparent unmodified ethylene surface; Right: opaque polymer I modified surface

5.2 Fluorescence and morphology study of unsupported membrane prepared with self- registering polymer II and the observation of rod shape CdSe single crystals

With cadmium selenide modification, different morphologies such as lamellar phases sheets, macroporous hexagonal networks (beehive architecture), vesicle spheres, and

combinations of these were all observed by laser scanning confocal microscopy under fluorescence optics (figure 5.5). Among these possible morphologies, the lamellar morphology dominated.

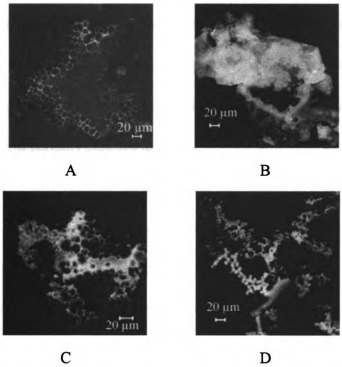


Figure 5.5 Fluorescence micrograph of cadmium selenide modified unsupported membrane made from polymer II (A) macroporous hexagonal networks (B) lamellar phases (C) combination of macroporous hexagonal networks and lamellar phases (D) vesicles phases

In the macroporous morphology, hexagonally shaped pores are packed closely in arrays with diameters of 10 to 20 microns. The most likely arrangement is one in which the amphiphilic molecules form double layer structures with the polar heads facing towards the open areas of the pores, which are highly hydrated, and the hydrophobic tails are within the double layer. This is essentially the same as the hexagonal inverted phase

the amphiphilic molecules form double layer structures with the polar heads facing towards the open areas of the pores, which are highly hydrated, and the hydrophobic tails are within the double layer. This is essentially the same as the hexagonal inverted phase observed in biomembranes. The macroporous morphology has an intermediate stability. It is a mesophase and much more unstable than the lamellar phase because the hydrophobic tails are still partially exposed to water.

The vesicular phase is nominally the most stable of the three because no edges are exposed. However it is kinetically unfavored, therefore in some systems it might not be as common as the lamellar morphology.

Lamellar phases were by far the most common morphology observed. The size of the folded sheets was often 1 mm in length and 500 microns in width. With higher magnification, small pores with diameters of about 200 nm could be seen on the surface of the sheets. Rod shape particles were observed lying on the surface of the sheets. The size, shape and morphology of these particles indicate that these are microstructured CdSe single crystals which were formed using these porous templates as "molds".

Using a porous template as the matrix to produce a high aspect ratio microstructured material has been widely studied because it is one of the most efficient and facile methods[1]. Anoidic alumina oxide and nuclear track etch polymer membranes are two commonly used templates[2]. One interesting work regarding the synthesis of Metal-CdSe-Metal nanowires is illustrated in figure 5.6[3]. The preparation process of

Au-CdSe-Au is shown on the left side of figure 5.6. A polycarbonate template was coated on one side with Ag (A). The template was then filled with approximately 1 micron of Ag (B). An Au segment was deposited (C), followed by the CdSe layer (D) and another Au layer (E). In the end, the Ag backing and the membrane were dissolved and the free-standing nanowires were formed (F). The right side of figure 5.6 shows the SEM images of 350-nm diameter Au-CdSe-Au nanowires.

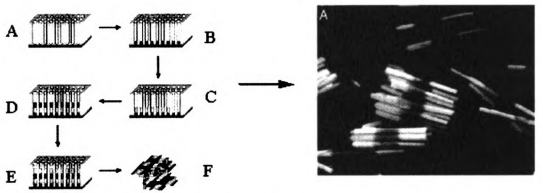


Figure 5.6 Template growth and release of Au-CdSe-Au nanowires (left) and SEM images of Au-CdSe-Au nanowires (right) (Adapted from reference 3)

The unsupported membrane system formed from our polymer II as templates provided size and crystal structure control over the microstructure of CdSe to yield a monodispersed, single crystal micro-rod array by a similar mechanism. When the unsupported polymer II membrane was overlayed on cadmium perchlorate solution, cadmium ions diffused into the pores of the lamellar sheets and were trapped inside. The pores protected the cadmium ions through the washing process afterwards. When selenide ions were introduced into the system, they combined with the cadmium ions to

nucleate crystallites that even finally grew into uniform sized single crystals whose dimensions were controlled by the dimensions of these pores.

When this sample was observed under a laser scanning confocal microscope, local heating by power dissipation of the laser induced phase transitions in the membrane, including melting, and the CdSe single crystal was released. In figure 5.7, the free CdSe single crystals with widths of 2 microns and lengths of 20 microns can be observed lying on the amorphous membrane surface. The widths corresponds to the diameter of the pores and the lengths to the thickness of the polymer II template.

In figure 8a, pores that contain the cadmium selenide single crystals appear to be very bright under dark field optics because of the high refractility of inorganic crystals. They have diameters of about 2 microns, which agree with the size of the CdSe single crystals observed. Some empty pores with the same size can also be seen. In other areas, such as shown in figure 8b, the distribution of pore-template CdSe single crystals is more compact.

Some smaller sized rods were observed under phase-contrast optics as shown in figure 5.9. These rods are 500 nm in width and 5 microns in length, and the occurrence is fairly rare. None of the rods were fluorescent because they are not of the correct length scale (a few nanometers) in any dimension to display this property. However, as seen earlier (figure 5.6), the surface of the membrane evidently contained nanoparticles of the appropriate size to display fluorescence.

Here we observed the formation of monodispersed rod-shape CdSe single crystals with assistant from porous membrane templates. These high aspect ratio semiconducting materials hold promise for a wide range of potential applications, including chemistry, physics, electronics, optics, material science, and biomedical sciences.

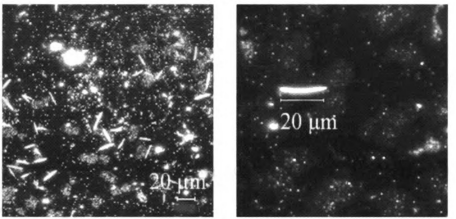


Figure 5.7 Single crystals of cadmium selenide under dark field optics (Left: CdSe single crystals dispersed on an amorphous substrate; Right: one common CdSe single crystal with length of 20 μm and width of 2μm)

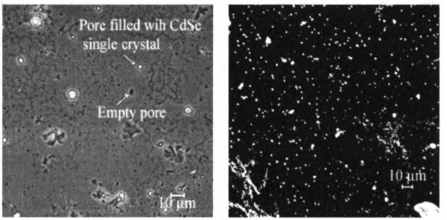


Figure 5.8 A dark field micrograph of CdSe single crystal (Left: the pores in a lamellar membrane with growing CdSe single crystals and without; Right: compact dispersion of CdSe single crystals)

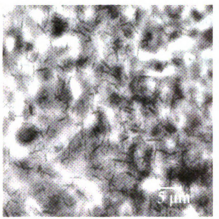


Figure 5.9 Phase contrast micrograph of smaller sized rods dispersed on porous membrane

5.3 Fluorescence study of a self-standing edge-supported membrane prepared with the self-registering polymer II

Self-standing edge-supported membranes were prepared by two similar methods. The first method involved dipping the self-registering polymer II membrane attached to a metal loop in water overnight. The membrane was treated with the appropriate metal salt solution and then with the desired anion. We called this edge-supported self-standing membrane. The other method involved painting the polymer II solution across a pinhole with a 500 micron diameter in a polyethylene sheet. We called the membrane prepared this way pinhole supported self-standing membranes.

Lamellar sheet phases are the main morphology observed in self-standing edge-supported membranes made from self-registering polymer II. In the pinhole supported self-standing membrane modified with CdSe, a flat fine sheet with fluorescence across the entire visible light range was observed under fluorescence optics

(figure 10). Red, green and blue fluorescence was observed at excitation wavelengths of 543 nm, 488 nm and 633 nm, respectively. The blue fluorescence was probably due to frequency doubling phenomena, which was evidence of a distribution of different sizes of nanoparticles. The red, green, blue fluorescence opens up possible applications of this material for ultra-thin color displays based on photostable (non-bleachable) fluorescence and blue laser development.

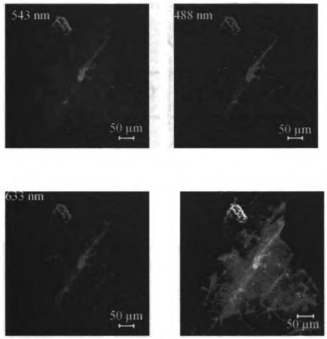
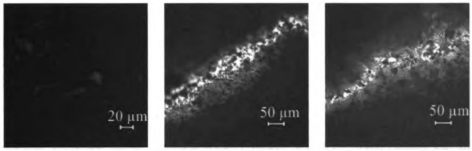


Figure 5.10 Fluorescence micrograph of cadmium selenide modified pinhole supported membrane made from polymer II. Notice that the membrane is a fine flat sheet displaying fluorescence across the entire visible spectrum.



A B C

Figure 5.11 Fluorescence micrograph of a free-standing membrane prepared with polymer II (A: dark unmodified polymer II membrane; B: ZnS modified polymer II membrane with pink/purple fluorescence; C: CdS modified polymer II membrane with blue/green fluorescence). The membrane is not laying flat on the substrate and the figures show the top of a ridge or undulation that is in the focal plane.

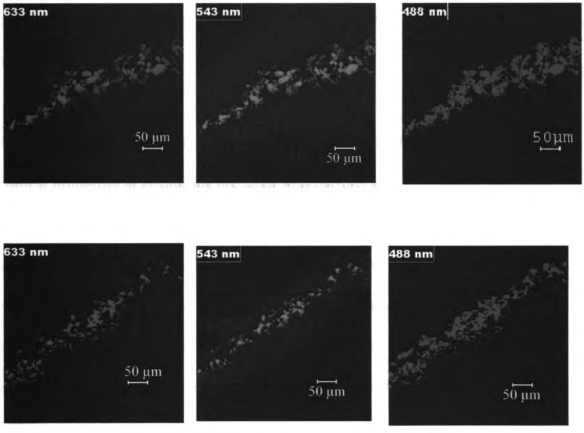


Figure 5.12 Fluorescence micrograph of self standing membrane prepared with polymer II modified with CdS (upper row) and ZnS (lower row), both display fluorescence across the entire visible spectrum

Before deposition of the inorganic phases, the edge-supported self-standing polymer II membrane showed weak fluorescence (figure 5.11A). Deposition of the different inorganic systems onto the polymer membranes led to a display of different fluorescent properties. The CdS modified membrane displayed blue/green fluorescence (figure 5.11B) and the ZnS modified membrane displayed pink/purple fluorescence (figure 5.11C). These systems also displayed fluorescence across the entire visible spectrum (figure 5.12).

5.4 Optical property and High long range order of system III

Optical properties of membrane prepared with polymer III

The membrane prepared from polymer III exhibited the typical light and solvatochromatic properties for polydiacetylene polymers (figure 5. 13). The blue membrane was colorless when placed on a glass slide as a thin film and it turned blue on irradiation with UV light at 233 nm and 365 nm for half an hour. The blue color turned red on contact with organic solvents such as chloroform and pyridine or longer time of UV light irradiation (figure 5.14).

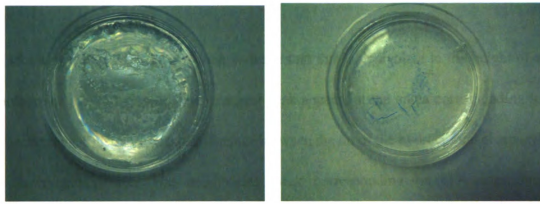


Figure 5.13 The membrane prepared from Polymer III (left) becomes blue after UV excitation (right) due to the photopolymerization of diacetylene units to form an extended conjugated system

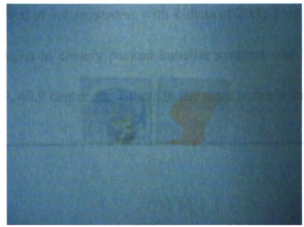


Figure 5.14 Chromatic alteration of polydiacetylene after UV irradiation (left: after 0.5 hr, right: after 6 hrs)

High long range order of diacetylene containing self-registering polymer

X-ray diffraction experiments were carried out on a layer of polymer IV (which is an analog of polymer III), in order to characterize the degree of order and to quantitate aspects of the organization of the system (figure 5.15). The X-ray powder diffraction patterns were sharp and intense, and contained higher order reflections indicating a high degree of order in the polymer systems. There was a diffraction peak at 2 θ corresponding

to 45.1 angstroms. Molecular models indicate that this is equivalent to the height of a monolayer of the 2-D system. The strongest peak appears at the angle corresponding to 27.1 angstroms. This represents the distance between the tip of the hydrocarbon chain and the diacetylene groups. The neighboring peak corresponding to 13.4 angstroms corresponded to the distance between the diacetylene groups and the polar region. A sharp peak in the wide angle region corresponding to the inter-chain separations of the alkyl groups was observed at 4.4 angstroms with 2-theta at 20.1. This is the characteristic separation for alkyl chains in closely packed lamellar systems (the L_α). Higher order reflections at 26.9, 33.9, 40.9 degree for 2-theta in the same series were observed.

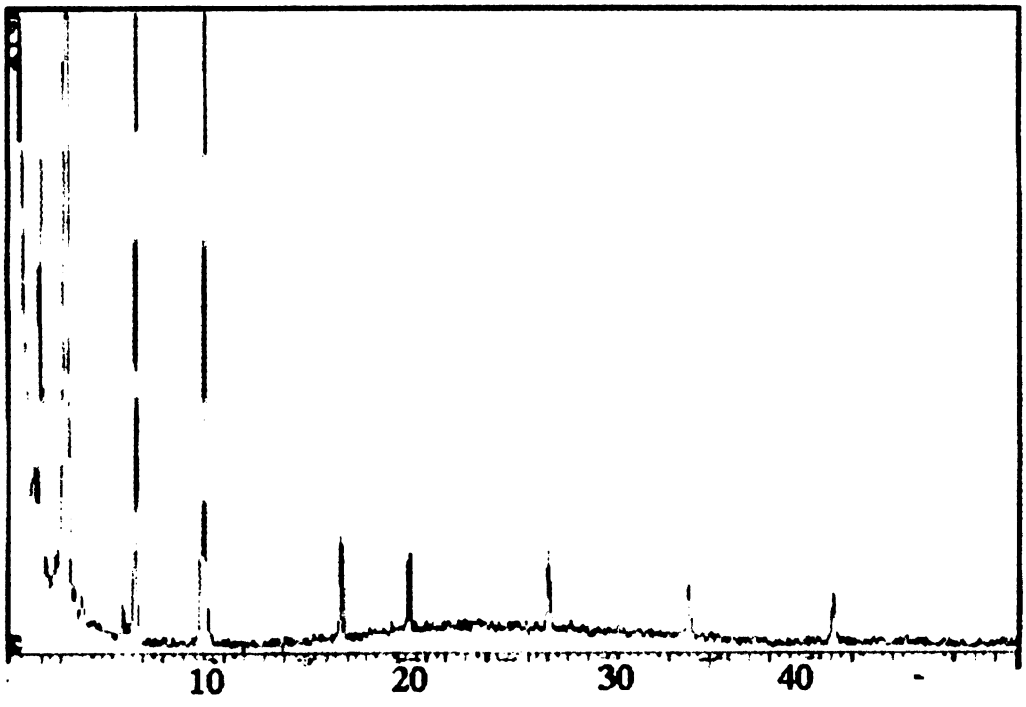


Figure 5.15 X-ray spectra for system III

5.5 Microscopy study of self standing membrane prepared with polymer III

The main morphology of the system was flat lamellar sheets, some of which tended to curl at the edge probably to reduce the alignment of the dipoles in the chiral headgroups. An example of this is shown in figure 5.16. The tubular structure formed by curling displays much brighter longer wavelength fluorescence than the substrate. This could be attributed to the differences in diacetylene cooperated side chains packing close to and far away form the twisting region. In regions close to the twist, the chains should be more disoriented and appear red as was observed in chain disorientation due to heating and solvent treatment (figure 5.13, 5.14).

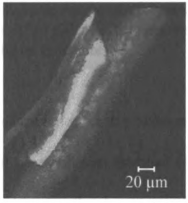
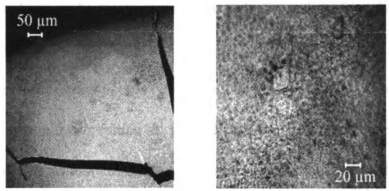


Figure 5.16 Curling structure of self standing membrane prepared with polymer III

Figure 5.17 shows the lamellar sheets on a macroscopic scale. The surface appears uniform over most of its area. When it is observed with higher magnification, porous structures can be observed. The sizes of the pores are around two microns. One possible

origin for their formation is through an inversed hexagonal phase transition such as those observed in biomembranes.



A B

Figure 5.17 Micrographs of self-standing membranes prepared from unmodified polymer III membrane. A: lamellar unmodified polymer III membrane in dark field optics; B: porous surface of unmodified polymer III membrane

As we mentioned above, lamellar phases are the main morphology in self standing polymer III membrane and the same membranes modified with CdS, CdSe, ZnSe, ZnS. Figure 5.18 shows the lamellar structures that have been observed. In the membranes prepared from polymer III, large dull green low fluorescence with more intense purple and much more intense but smaller pink regions were observed. This is probably due to different local ordering patterns or domain structures. High wavelength fluorescence is characteristic of higher ordering and conjugation. Typical membrane systems exist in a form where some regions are highly ordered, some are partially ordered and others are disordered. The diacetylenic functions in highly ordered regions are readily polymerized

if the chain alignment is favorable. These regions will give rise to much brighter fluorescence at much longer wavelength than more disordered regions. Further expansion of the ordered regions by mechanical stress or solvation will lead to a further red-shifting of the fluorescence.

Fluorescence spectroscopes were used to characterize the modification of the membrane system by deposition of zinc and cadmium salts. The fluorescence properties of the modified membranes were completely different to those of the unmodified membranes. For example, ZnSe modified membranes mainly displayed red fluorescence, while CdSe and ZnS modified membranes displayed more purple fluorescence.

5.6 Scanning Electronic Microscope (SEM), Atomic Force Microscopy (AFM) and fluorescence characterization of unsupported polymer III membrane and the membranes incorporated with CdS or ZnS

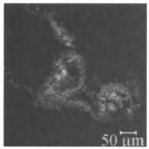
Under polarization microscope, the unsupported film deposited with ZnS shows maltese cross spatial pattern in figure 5.19. The maltese cross pattern is characteristic of the smectic C phase (chiral lamellar system) expected for the polymer layers[4]. It indicates the parallel-polarization component existence. The parallel-polarization component will evolve into far-field pattern in the form of maltese cross or optical four leaf clover. In other words, the system has a highly ordered multilayer structure.

The unsupported self-registering polymer III membrane treated with cadmium sulfide

displayed strong fluorescence properties. Against the weak green fluorescence of the substrate, CdS nanoparticles exhibited purple fluorescence as shown in figure 5.20. Here polymer III forms a patterned lamellar structure in which cadmium sulfide clusters are incorporated. The membrane treated with ZnS nanoparticles also displayed much enhanced fluorescence properties. They formed delicate bright fucia petals.

The main morphology of unsupported membranes is the lamellar sheets as shown in figure 5.21. Again, the purple and red spots in the fluorescence micrographs indicate that the membrane is not of uniform crystallinity. Polarized light microscopy clearly demonstrated the presence of ordered chiral crystalline domains. In this technique a polarizing filter called an analyzer is oriented so as to cancel the polarization of the laser, thus leading to a situation where no light reaches the detector. If a polarizing substance is injected between the laser and the analyzer, the plane of polarization would be rotated, and light would then be seen through the analyzer. If the membranes were achiral, the plane of rotation of the polarized laser light would not change after going through the layer, and would have been blocked by a cross polarizer. In this case only a black background would be observed. Regions of the membrane that can be observed using the polarized light microscopy are chiral with very ordered arrangements that are different to the bulk material.

Figure 5.18 A photo gallery of fluorescence micrographs for lamellar self standing polymer III membranes and polymer III membranes modified with ZnSe, CdSe, ZnS and CdS. A and B are unmodified polymer III membrane (A: small areas of intense purple and pink fluorescence were observed against a background with low dull green fluorescence; B: blown-up for a small area with intense purple fluorescence), C and D are ZnSe modified membranes (similar with unmodified membranes), E and F are CdSe modified membranes (mainly display red fluorescence), G and H are ZnS modified membranes (areas with purple fluorescence is greatly enhanced), I and J are CdS modified membranes (areas with purple fluorescence is greatly enhanced)



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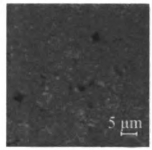

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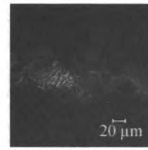

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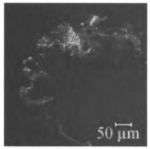

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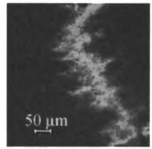

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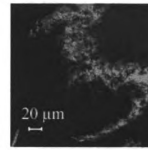

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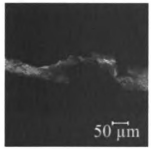

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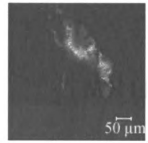

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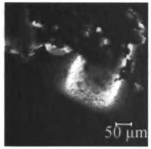

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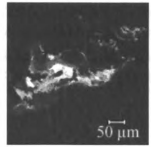

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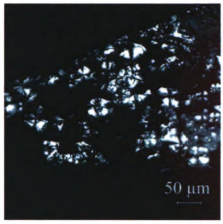
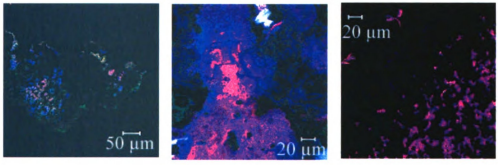


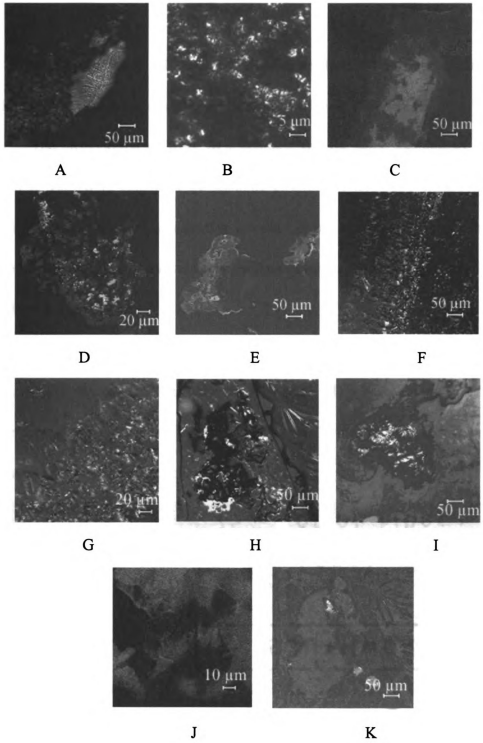
Figure 5.19 Maltese cross pattern under polarization microscope



A B C

Figure 5.20 Comparison of unsupported membrane prepared with polymer III (A) and the ones that incorporate with CdS (B) and ZnS (C). A: untreated system III with small areas of intense purple and pink fluorescence against a background with low dull green fluorescence; B: CdS treated system III with big area of intense purple fluorescence; C: ZnS treated system III with delicate bright fucia petals

Figure 5.21 A photo gallery of fluorescence micrographs for lamellar self-standing polymer III membranes. A and B are polarized optical images of an unmodified polymer III membrane, indicating the chirality and ordered arrangements of the membrane; C, D and E are fluorescence micrographs showing that the membrane is not of uniform crystallinity; F and G are polarized optical images of polymer III membranes modified with ZnS; H and I are polarized optical images of polymer III membrane modified with CdS; J and K are fluorescence images of polymer III membrane modified with CdS, bigger area of purple fluorescence was observed

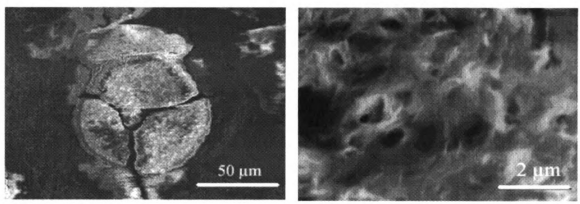


Scanning Electronic Microscope (SEM) characterization of unsupported polymer III membrane and the membranes incorporated with CdS or ZnS

Scanning Electronic Microscope (SEM) characterization of unsupported polymer III membrane and the membranes incorporated with CdS or ZnS

The unsupported polymer III membrane and the same membranes incorporating CdS or ZnS were examined by scanning electronic microscopy without coating. The sharp images obtained indicate that the unmodified polymer III membrane and those modified with CdS or ZnS were very conductive without the usual coating with carbon or gold to aid in imaging.

Figure 5.22A shows an image of an unmodified sample of this material showing it to be a multiple layered porous polymer membrane. The morphology of the polymer membrane is flat lamellar, but the material was evidently very fragile because most images showed evidence of damages of the topmost layer.

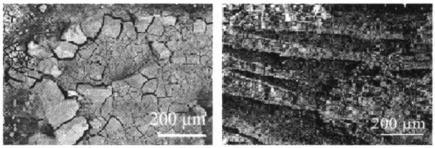


A B

Figure 5.22 Scanning electronic microscope image of unsupported polymer III membrane A) multiple layered porous polymer III membrane B) magnified view of top surface shown in A (x25) showing 1 μ pores.

The pieces shown in the picture have widths between 25 microns to 50 microns and lengths around 40 microns. Several pores could be observed distributed over the surface of the membrane. The pores had diameters of around 1 micron and are probably due to local inverted hexagonal phases.

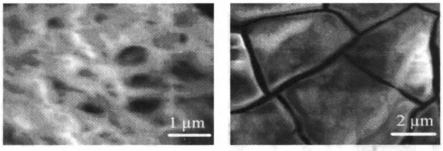
The CdS or ZnS modified polymer III membranes appeared to be very brittle and showed cracking patterns on the surface as indicated below in figure 5.23. The comparison between SEM images of unsupported polymer III membrane and the membranes incorporated with CdS or ZnS indicate that the modification of CdS or ZnS bestows the polymer III membranes some inorganic characters.



A B

Figure 5.23 SEM micrograph of CdS (A) and ZnS (B) treated polymer III membrane with cracking patterns

SEM micrographs of higher magnification for CdS (figure 5.24a) and ZnS (figure 5.24b) treated polymer III membrane show no sign of inorganic particles that were resolvable at the highest magnification studied where morphologies of 1 micron could be readily discerned.



A B

Figure 5.24 higher magnification of SEM micrograph of CdS (A) and ZnS (B) treated polymer III membrane showing no sign of large crystals

Atomic force microscopy (AFM) characterization of unsupported polymer III membrane and the membranes incorporated with CdS or ZnS

Atomic force microscopy is used to characterize the packing and surface coverage of polymer III and size, distribution, general shape and morphology of the nanoparticles formed with the polymer as template. The systems were formed on the surface of flat silicon wafers.

The untreated polymer membrane has very rough surfaces compared to the CdS or ZnS treated ones. After the metal ion treatment, the membrane becomes flat, smooth and thin. When the polymer membrane is coated with metal ions, it starts to get charged. The repelling effect of the charges distributed on the surface makes the membrane expand to form the flat, smooth and thin morphology. The charged layers are also more solvable. This results in thinning and evening of the layer. Figure 5.25 shows comparison between the membrane treated with CdS and the unmodified silicon wafer surface. The

highest points on the particles were around 54 nm above the silicon substrate.

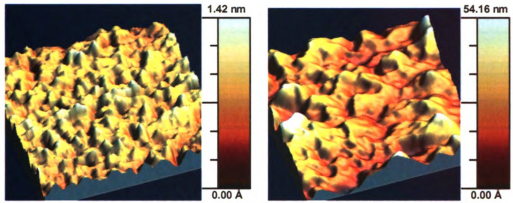
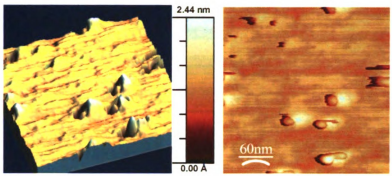


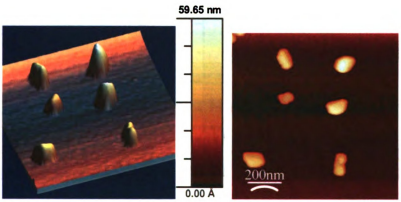
Figure 5.25 The flat, smooth thin surface of the membrane treated with CdS (right) on a clean silicon wafer surface (left) at 300 nm, the highest point on the particles were around 54 nm above the silicon substrate

Coverage by CdS or ZnS was not very uniform. For example, for ZnS treated membrane as shown in figure 5.26, in some areas, the particles are isolated. In some other areas, confluent coverage with layers of ZnS can be observed. Similar phenomenon is observed in CdS treated membranes as well. The diameters of the nanoparticles vary from a few nanometers to around a hundred. The small nanoparticals will display fluorescence. The highest points on the particles against the silicon substrate on a bigger scale are around two hundred nanometers.

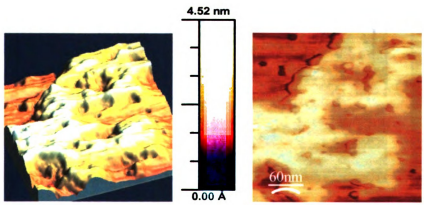
Figure 5.26 Different distributions of nanoparticels. Sparsely distributed nanoparticles of ZnS (A, 300 nm) and CdS (B, 500 nm); confluent coverage of nanoparticles of ZnS (C, 300 nm) and CdS (D, 500 nm); evenly distributed nanoparticles of ZnS (E, 500 nm); From A to E, three-dimensional images are on the left side, and two-dimensional images are on the right side; CdS (F) and ZnS (G) modified membranes with highest point at 236 nm and 190 nm respectively observed at 2 micron



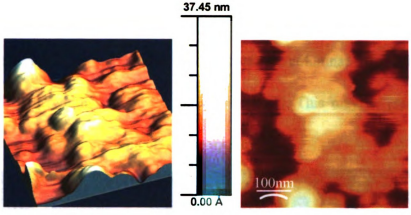
A



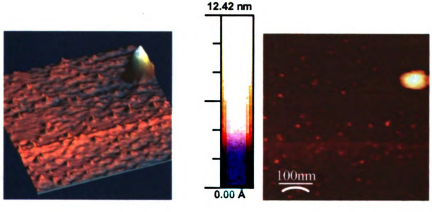
B



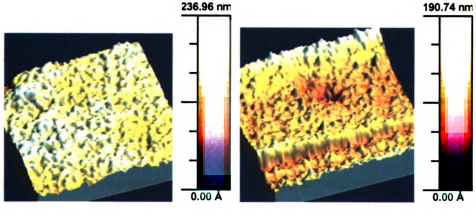
C


37.45 nm
0.00 Å
100nm

D


12.42 nm
0.00 Å
100nm

E


236.96 nm
0.00 Å
190.74 nm
0.00 Å

F G

Part of the polymer membranes shows distorted columnar structure under high magnification with widths around 20 nm (figure 5.27). This may be caused by screw delocalization of the stacking lipid crystal molecules.

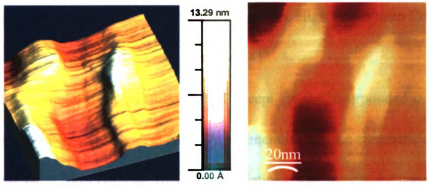


Figure 5.27 Distorted columnar structure of polymer membrane observed at size 100 nm shown in three dimensional (right) and two dimensional (left)

5.7 Conclusion

Form the evaluation results, we can conclude that we have successfully developed three multiple functional self-registering polymeric systems with unique properties that can be applied in a variety of fields.

Phospholipid biomimetic system, referred as system I, has been successfully coated onto a polyethylene surface as demonstrated by a cationic dye experiment. Further deposition of calcium phosphate was found to increase with incubation time in calcium phosphate solution. System I resembles collagen templates in cells and can be developed into biomimetic material with potential application as bone filler or scaffold of bone tissue engineering.

System II with sulfur function and saturated fatty acid chain was prepared into two different kinds of membranes: unsupported and edge-support self-standing membranes. Morphologies such as beehive macroporous phases, vesicle phases and lamellar sheets were observed. Among them lamellar structure dominates. High aspect ratio CdSe single crystals with rod shape of 2 x 20 microns were formed.

System III has similar design with system II except for the incorporated diacetylene functional group in the long fatty acid chain. Experiments verify the chromatic change of membranes prepared form polymer III under irradiations. The membrane appears to be blue with UV light irradiation for a couple hours due to the photopolymerization of diacetylene groups, and becomes red after 4 more hours of UV irradiation or organic solvent treatment. The polydiacetylene function groups bestow the system with an electronically and optically responsive region. For system III, we did X-ray diffraction experiment which provides strong evidence that the system bears high long-range order. The modification effects of nanoparticles on morphology of the membranes were confirmed through scanning electronic microscopy (SEM) and atomic force microscopy (AFM). The sharp images obtained from SEM experiments also tell that system III is very conductive.

System II and system III serve as templates for nanoparticles formation. This enables the nanoparticles to be synthesized with mild conditions. The nanoparticles formed display fluorescence across visible spectrum. For system II and system III, due to the

stablization coming from polymerization, the membranes prepared are robust enough to self support or be applied on different substrates for coating and properties modification after their formation. This greatly enhances the possibility of practical applications of the systems that we have developed.

5.8 Experimental Section

Cationic dye staining experiment: A polyethylene film and the polymer I modified polyethylene film were dipped in a crystal violet solution separately and immediately taken out. The excess dye solution was then removed by delicate task wipers. Digital camera was used to record the images. Images in this thesis are presented in color.

Laser scanning confocal light microscopy experiment: These experiments were performed on a Zeiss 210 instrument with laser wavelengths at 488 nm, 543 nm, 633 nm. Images were obtained in dark-field, phase contrast, polarization and fluorescence modes. For the polarizing mode experiments, an analyzing cross-polarizer was placed on the objective lens. For self-standing film preparation, the film was attached to a clean glass slide directly, and for unsupported film preparation, polymer membrane was taken from the interface and deposited on a clean glass slide which was left in a horizontal position at room temperature for two hours to allow the solvent to evaporate. Images in this thesis are presented in color.

X-ray diffraction experiment: This study was performed on a Rigaku instrument with a Rotaflex rotating copper anode operating at 45 kV with a current of 100 mA. The X-ray beam was collimated with a 1/6 slit and the K_α line was selected. A pinch of polymer IV was dissolved in 8 drops of methanol, and the mixture was sonicated for 10 minutes. One drop of a mixture of methanol and water (2:1) was added, and the mixture was sonicated for 10 min again. The polymer IV suspension formed was kept in oven at 70 °C for 15 min, then left at room temperature for half an hour. The slurry was transferred to the glass slide, and air dried for one day. The solid deposited on the slide was used for the x-ray measurement. After the measurement was performed, the part under the x-ray beam turned to blue, the part without x-ray irradiation is still white.

Scanning electronic microscopy experiment: The experiment was performed on a JEOL (Japan Electron Optics Laboratories) 6400V with a LaB6 emitter (Noran EDS). The electronic beam intensity was 7 kV. The unsupported membranes prepared from polymer III and those modified with nanoparticles were mounted on the SEM aluminum stub probes by peeling the membranes from the surface of aqueous subphases with the aluminum stubs.

Atomic force microscopy experiment: These analyses were performed using a Nanoscope III instrument operating in tapping mode. The film was mounted on a clean

silicon wafer by peeling the membranes or those modified with nanoparticles from the surface of aqueous subphases with the clean silicon wafer. Images in this thesis are presented in color.

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