PHASE BEHVIOR AND SOLIDIFICATION OF ELECTROSTATICALLY SELF-ASESEMBLED AMPHIPLEXES

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Abstract of the Thesis

Phase behavior and solidification of electrostatically self-assembled amphiplexes

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There has been a steady increase in utilizing nanoporous materials across a wide variety of fields leading to an increased demand for more economical and superior materials. The present work contributes towards addressing these concerns by using commercially and easily available chemicals to synthesize electrostatically self-assembled amphiplexes. These amphiplexes have been prepared by combining polyelectrolyte-surfactant complexes with co-surfactant and oil and they show long range order at the nanoscale exhibiting various morphologies such as cubic, lamellar and hexagonal. Employing small angle x-ray scattering, phase transitions and swelling behavior were investigated in these amphiplexes as a function of ionic strength, co-surfactant concentration and oil concentration.

With the endeavor to capture the nanostructured order demonstrated by these amphiplexes onto a solid polymeric material, the oil phase was polymerized. The polymerization was optimized by two methods. First, the polymerization was successfully delayed using a catalyst poison and second, the catalyst loading was optimized. Upon polymerization, phase transition and swelling behavior studies of amphiplexes revealed no significant influence of ionic strength, co-surfactant concentration and oil concentration on polymerized amphiplexes. A phase separation is observed with the amphiplexes exhibiting a conserved hexagonal phase upon polymerization.

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CHAPTER 1: INTRODUCTION

1.1 Surfactants as building blocks

Self assembly is a universal phenomenon that has been discovered, investigated and explored in a wide range of fields. There exists a plethora of examples and at all scales[1] be it the lipid bilayers of cells, the intricate assembly of ribosome and the accurate folding of proteins to name just a few. Significant effort is being devoted in discovering, understanding and exploiting self assembly for the development of economically and environmentally better technology.

A valuable example and one that has been well explored are surfactants. Surfactants are amphiphilic molecules consisting of hydrophobic and hydrophilic domains together allowing them to self aggregate in a solution thereby forming various morphologies depending on solution conditions. Self assembly of surfactants has intrigued the interests of the scientific community since a long time and exhaustive reviews[2] exist that investigate the same.

In aqueous solution at low concentrations, surfactants exist as free molecules but as the concentration increases there is a threshold known as the critical micelle concentration (CMC) at which these molecules form spherical micelles. The hydrophobic tails form the interior core of the sphere and the polar head groups are exposed to the aqueous environment protecting the hydrophobic tails [3]. At concentrations higher than the critical micelle concentration, surfactants assemble into more complex structures ranging from spherical or cylindrical micelles, bilayer sheets to lyotropic liquid crystals.

A typical lyotropic liquid crystal can exist as hexagonally close packed cylinder (hcpc) phase, cubic phases (bicontinous or micellar) or inverse hexagonal and cubic structures. [3] The significance of investigating surfactants lies in their tunable assembly into organized phases by controlling a number of factors such as hydrophobic chain length, number of tails and spontaneous curvature of the surfactant, temperature and other conditions. Much of the research in this area has been with the endeavor of exploiting the self assembling behavior of surfactants to design functional materials

1.2 Polyelectrolyte-surfactant complexes

An interesting combination and one that has been well established is that of oppositely charged polyelectrolytes and surfactants which leads to the formation of the so called polyelectrolyte-surfactant complexes. Interaction between polyelectrolytes and surfactants is a well studied concept and a topic of numerous reviews [4],[5],[6]. The formation of polyelectrolyte-surfactant complexes is governed by a combination of driving forces that includes charge neutralization that occurs when the two oppositely charged materials interact, hydrophobic interactions between the surfactant tails [7] and the entropic gain associated with the release of counter-ions [8], [9].

When an ionic surfactant is added to an oppositely charged polyelectrolyte solution, the interaction between the two begins with surfactant molecules attaching themselves to the polymer chain. Upon increasing the concentration of the surfactant further, the hydrophobic tails in an effort to avoid exposure to the aqueous environment form micelles along the polyelectrolyte chain in a manner similar to that of a pure surfactant solution. This concentration is termed as critical aggregation concentration (CAC). The binding of polyelectrolytes to surfactants is considered to be a highly co-operative process and the presence of polyelectrolytes causes the surfactant molecules to aggregate at a concentration which is orders of magnitude lower than the critical micelle concentration of the surfactant alone[4].

Depending on whether mixed in a stoichiometric ratio or a non-stoichiometric ratio, the polyelectrolyte-surfactant complexes formed will be insoluble or soluble respectively. Upon stoichiometric mixing, polyelectrolytes and surfactants form a phase separated mixture of two components; the insoluble concentrated phase consisting the polyelectrolyte-surfactant complex and the other phase being a dilute solution of the excess components. There is abundant research on polyelectrolyte-surfactant complexes in non-stoichiometric ratio [10] but since this work primarily deals with complexes in a stoichiometric ratio, the discussion of non-stoichiometric complexes shall be restricted. The interest in polyelectrolyte-surfactant complexes exists owing to their ability to form a wide variety of structures primarily due to surfactants. The rich diversity of phases exhibited by polyelectrolyte-surfactant complexes has been investigated rigorously {[8], [11], [10], [12], [13], [14], [15]} and further being explored towards a diverse set of applications.

1.3 Electrostatically Self-assembled Amphiplexes

Since the past few years, our laboratory has been involved in the investigation of Electrostatically Self-assembled Amphipliexes (ESA) derived from polyelectrolyte-surfactant complexes. As a result of aggregation of surfactant tails, the interior of polyelectrolyte-surfactant complexes is hydrophobic in nature and introduction of a hydrophobic material in this region would allow control over the size of these structures. This would add another factor that could be used to fine tune these materials to our needs. With this intention, we are working towards developing polyelectrolyte-surfactant complexes swelled with a hydrophobic material and we term these complexes as electrostatically self-assembled amphiplexes. Although the hydrophobic region is available for expansion, addition of a hydrophobic material would not directly lead to the expansion of these structures. This can be explained based on the fact that surfactants form micelles having a defined and fixed radius of curvature. This curvature is termed as spontaneous curvature of the surfactant and is an intrinsic property for any surfactant. This restricts the size of the micelle formed[10]. Therefore the strategy to incorporate oil into the hydrophobic regions is accomplished by the use of co-surfactants. Co-surfactants are commonly used for stabilizing microemulsions, and to improve properties of surfactants in solution with short chain alcohols being the most commonly used co-surfactants[16].

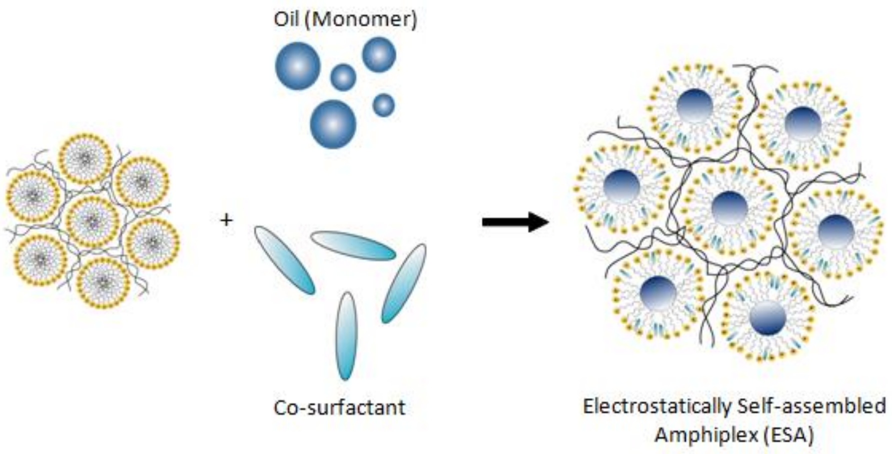

Figure1: Development of Electrostatically Self-assembled Amphiplexes (ESA) from polyelectrolyte-surfactant complexes, co-surfactant and oil

We have explored pentanol and octanol as the co-surfactants for electrostatically self-assembled amphiplexes developed although octanol has not been included here as work on these amphiplexes is still under progress. Pentanol is a weak amphiphile and cannot form micelles of its own[16]. Therefore it enters the amphiphilic region of surfactants between the aqueous and oil phase and reduces the spontaneous curvature of the surfactant layer. This reduction in the curvature affords greater flexibility and therefore allows swelling of the interior hydrophobic region. This is the primary motivation into developing electrostatically self-assembled amphiplexes and figure 1 depicts the formation of these amphiplexes beginning from polyelectrolyte-surfactant complexes, co-surfactant and oil. The polyelectrolyte-surfactant complex shown in figure 1 is a special case and this can be understood when the interactions between polyelectrolyte and surfactants as they form a complex is taken into consideration. The interaction of these two oppositely charged materials begins with surfactant molecules attaching themselves to the polymer chains due to electrostatic interactions. As this continues, charge neutralization and aggregation leads to the formation of micelles along the polymer chain as shown in figure 2 below. These complexes formed are not highly ordered and the polymer chains with micelles are dispersed in the solution.

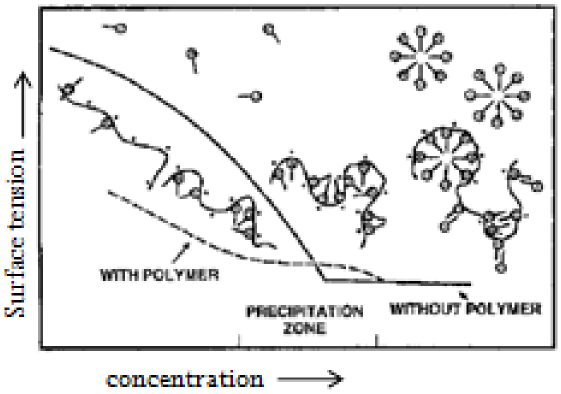

Figure 2: Aggregation of surfactants leading to the formation of polyelectrolyte-surfactant complexes in solution[4]

In contrast, the electrostatically self-assembled amphiplexes that we have developed display long range order at the nanoscale and therefore belong to the special case depicted in figure 1. Long range order simply means that the material displays a defined order and structure at the nanometer level and this order repeats itself over large distances indicative of the monodispersity of the material. This would be further discussed in a later section.

Organized phases of electrostatically self-assembled amphiplexes have been previously explored in our laboratory. We have prepared, electrostatically self-assembled amphiplexes from the combination of oppositely charged poly (acrylic acid) and cetyltrimethylammonium chloride in stoichiometric ratio with pentanol as the co-surfactant and dodecane as the oil phase. In order to investigate the phases that these materials form, we prepared a series of samples with pentanol ranging from 10-60% and dodecane varying from 20-220% with respect to the surfactant. Phases formed by these materials were determined using small angle x-ray scattering as the primary mode of measurement. The results from this work are shown in figures 3 and 4. Long range ordered nanostructures such as the hexagonal (H), lamellar (L), Pm3n cubic (Pm3n) and the Ia3d cubic phases (Ia3d) have been observed as shown in figure 3.

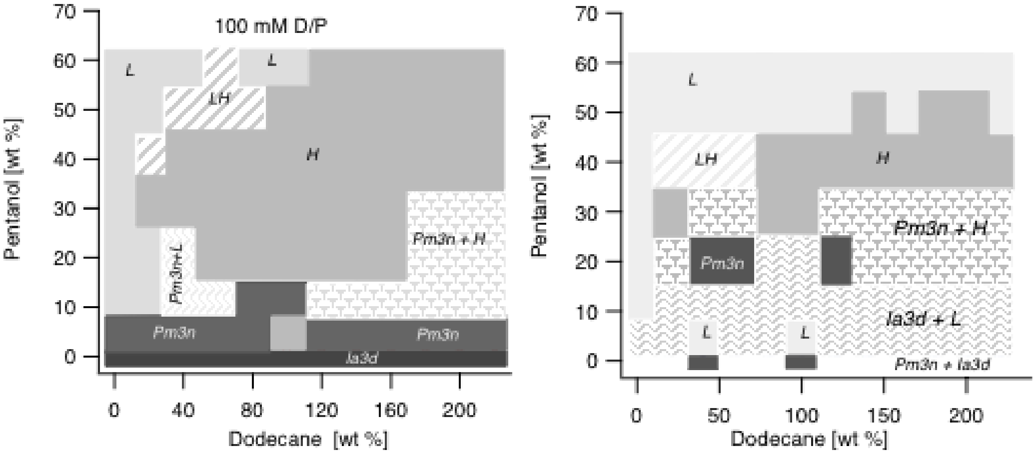

Figure 3: Phase diagram of electrostatically self-assembled amphiplexes as a function of pentanol and dodecane at 100 mM (Left) and 300 mM (Right)

Swelling behavior of these amphiplexes has also been examined and the results as shown in figure 4 which shows plots of unit cell size of these amphiplexes as a function of dodecane (oil) content and pentanol (co-surfactant) content. The unit cell size represents the size of the smallest repeating unit in the structure and the calculation of the unit cell size is discussed ahead. As can be seen there is an observed increase in the hexagonal unit cells with increasing oil and co-surfactant. The increasing co-surfactant content points towards the reduced spontaneous curvature of the surfactant layer as can be confirmed from figure 4. The increasing size of unit cells with additional oil indicates that the oil has been successfully incorporated into the hydrophobic regions of these amphiplexes.

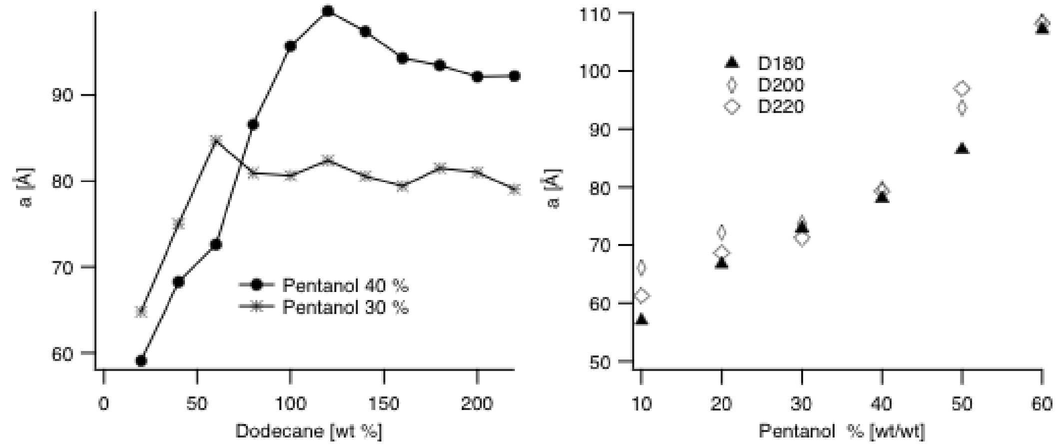

Figure 4: Increase in size of hexagonal unit cells as a function of dodecane (oil) at 300 mM NaCl (L) and pentanol at 100 mM NaCl (R)

Thus we have developed electrostatically self-assembled amphiplexes starting from polyelectrolyte-surfactant complexes at a stoichiometric ratio and adding co-surfactant and oil to swell the hydrophobic interior. The material thus developed displays long range ordered structures and the ability of these amphiplexes to swell upon addition of oil has been established.

The self assembly discussed here is dynamic in nature. Upon mixing the components, they do not immediately form the ordered structures that are seen. Based on the interactions of these materials (hydrophobic, electrostatic) the components arrange or assemble with time. The time required for such equilibration depends on the components, their diffusivities and sizes. Larger molecules would take longer to diffuse and therefore longer time to equilibrate. With time, these amphiplexes form equilibrium structures and the typical time required for the same is 1-2 weeks.

Now that ordered nanostructure has been established in these materials, the next obvious question that could be asked is whether this defined ordered structure can be captured onto a solid material. The motivation behind such a thought would be to develop nanoporous materials. To answer this question, one could think of monomer oil being introduced instead of the oils being investigated here. If the oil phase located inside the hydrophobic regions could be polymerized, the final material formed would exhibit nanoporous order. To this effect, the work presented here specifically aims to investigate the organized phases formed by the combination of the anionic polyelectrolyte poly (acrylic acid) with the cationic surfactant cetyltrimethylammonium chloride (CTACl) at stoichiometric ratios. Monomer oil would be used instead of the oils discussed previously to polymerize these organized phases.

The advantage of such an assembly is that the structured phase that the surfactant forms is used as a template. There are a number of parameters here that can be altered and a systematic study of variation of individual parameters would allow us to investigate the system more closely and fine tune the parameters to our advantage.

1.4 Polymerization in long range ordered structures

In recent years, there has been substantial effort aimed at synthesizing highly ordered nanostructured materials given the need for such materials. There are many ways available and one such way is through template based polymerizations. Given the defined structure and thermodynamic stability, organized media have been used as templates for the synthesis of a variety of solid nanostructured materials. The term organized media here can refer to a wide variety of formulated materials including polyelectrolyte-surfactant complexes, microemulsions, vesicles, surfactant solutions and amphiphilic block co-polymer phases.

Polymerization in and of such organized media is a potent technique to prepare nanostructured materials specifically to capture the organized structure of the media to the polymer [17]. There is abundant literature available on such polymerizations and this has been used to achieve various morphologies like nanoparticles [18], hollow spheres [19] or mesoporous polymers [20] depending on the template type, structure and the reaction conditions. There are a broad possible range of applications of such nanostructured materials from separation media, catalyst supports, drug delivery systems to fuel cell membranes as will be discussed further. [21, 22]

The work presented here is an effort towards polymerization of ordered phase in this case electrostatically self-assembled amphiplexes with the aim of developing solid state materials displaying order at the nanometer level. The type of polymerization attempted here is termed transcriptive templating [21] and involves polymerization of monomer present within the organizing media in this case the electrostatically self-assembled amphiplexes. Another very popular technique available and one that has been successfully employed in a number of cases [23], [24] is synergistic templating that involves use of polymerizable surfactants to capture the organizing template structure. However there are two main disadvantages associated with such systems. The first is that these techniques employ synthetically derived surfactants and the phase behavior of such surfactants is not as easily measured or known as that of common surfactants [3]. The second is that the cost of synthetically designed surfactants is high which can prohibit their use in large scale manufacturing of such materials [22].

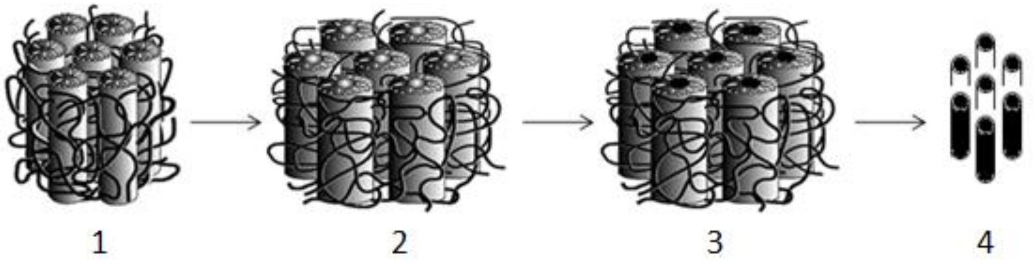

Figure 5: Progression of formation of the final polymer, starting from electrostatically self-assembled amphiplex (1), swelling the amphiplex with oil (2), polymerizing the amphiplex (3) and finally removal of polyelectrolyte and surfactant results in the final polymer with ordered nanostructure

In the present work, the polymerization process is outlined beginning from electrostatically self-assembled amphiplex. Upon introduction of oil, these amphiplexes swell as shown in figure 5. Polymerization of the oil phase results in solid material and upon removal of the polyelectrolyte and surfactant results in the final material with ordered nanostructure.

Polymerization of monomer within an organized phase would be an economically viable and attractive alternative under the following conditions; first that the organized media is prepared from commercial materials reducing the raw material costs involved and second if the polymerized product so obtained displays order. The ability to create ordered nanoporous materials from inexpensive and commercially available raw materials is what makes this work novel and more appealing.

1.4.1 Ring Opening Metathesis Polymerization (ROMP)

The hydrophobic monomer used in the present work is Dicyclopentadiene (DCPD) and it is polymerized via Ring Opening Metathesis Polymerization (ROMP). The reaction is catalyzed through the second generation Grubbs catalyst as illustrated in figure 2.

Dicyclopentadiene is a low cost and highly reactive olefin extracted from Naptha cracking in refineries[25]. It is a commodity chemical costing 45-50 cents/lb depending on the grade of dicyclopentadiene used[26]. Annually, 375 million lbs are produced and upon polymerization, it forms a highly cross-linked material; poly (dicyclopentadiene) which is a mechanically strong material with a high impact resistance. It is manufactured under the trade names Telene and Metton[25], [27] and finds use in plastic moulds for heavy vehicles due to its high impact strength and excellent resistance to harsh chemical conditions[28]. There are several advantages of using dicyclopentadiene as the oil phase in electrostatically self-assembled amphiplexes. One important advantage is that there is minimal chemical shrinkage upon polymerization[29] which implies that there would be negligible volume change upon polymerization. The fact that it is a cheap, highly reactive[28] and easily available material makes the overall work economically more lucrative.

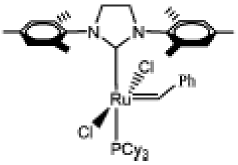

Figure 6: Chemical structure of Second generation Grubbs catalyst [30]

The catalyst used to polymerize is the second generation Grubbs catalyst which is one of the most important organometallic catalysts discovered in recent years[31]. Also known as Benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (tricyclohexyl phosphine)ruthenium[32], it is a transition metal carbene complex and the development of this catalyst system has been tracked[33], [34]. This catalyst is known to have very high activity due to the presence of the N-heterocyclic group at the top of the ruthenium as shown in the chemical structure in figure 6 [35]. It is also known to be very tolerant[36] to other functional groups present and overcomes the disadvantages of other metathesis catalysts used for metathesis based reactions[25].

1.4.2 Mechanism of polymerization of DCPD

The mechanism of polymerization of dicyclopentadiene is as shown below in figure 7.

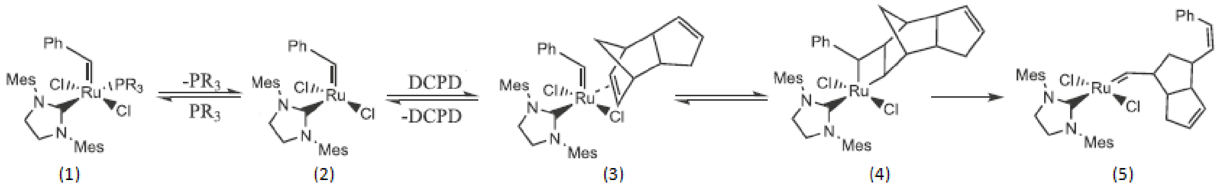

Figure 7: Mechanism of ring opening metathesis polymerization (ROMP) in dicyclopentadiene (Figure adapted from[27])

The first step is the dissociation of the phosphine group (PR_3) from the catalyst that further leads to the formation of the 14-valence electron complex as shown (compound (2) in figure 7). This is followed by cycloaddition of alkene resulting in the formation of the metallocyclobutane intermediate (compound (4) in figure 7). Rearrangement of electrons opens the ring to allow the addition of a new unit to continue the growing polymer chain (compound (5) in figure 7) [27].

1.5 Need for nanoporous materials

The motivation to create such well defined and ordered structures stems from the need for nanoporous materials. There is an imperative need for materials in various areas such as filtration, bio-separations, energy applications, catalysis to name a few. Two important instances where the current research can find applications in are monoclonal anti-body purification and proton exchange membrane in fuel cells.

Monoclonal antibodies are a successful therapeutic product for conditions in cancer, auto immune diseases and infectious diseases [37]. Virus reduction is an important and today a regulated process required for such processes[38]. Several methods exist for virus reduction such as solvent/detergent treatment and treatment with low pH solutions to name a few but removal of non-enveloped viruses such as minute murine virus (MMV) requires physical separation as they are highly resistant to chemical methods[39]. These viruses are in the size range of 150-200Å making them larger than monoclonal antibodies thereby allowing there filtration.

A host of virus filters are available in the market for this purpose but the exceedingly high cost involved forms a bottleneck in the development of these therapeutics. Here the need for developing more economical nanoporous materials is warranted.

Another important area of application where the need for an ordered nanoporous material is critical is the proton exchange membrane in fuel cells. The function of a proton exchange membrane in fuel cells is to transport protons which travel through the membrane to the cathode wherein it reacts with oxygen forming water and releasing energy. Therefore it is required by the membrane to selectively conduct protons only. In the field of fuel cells, the need of the hour is to develop cheaper materials having a defined ordered structure with high proton conductivity, higher operating temperature with the ability to withstand the harsh environment at that temperature in a fuel cell.

The emphasis here is on building materials from commercially and easily available chemicals that are relatively inexpensive. This is reflected from the fact that a major hindrance in the current efforts to develop mesostructured materials lies in expense which remains exceedingly high[40] for mass production. It should be noted that the present work does not directly lead to materials which can be directly employed for these applications. The present work lays the background for the same. These materials can be constructed by modifying the structural components to suit the end need. For instance, tetraalkylammonium functionalized norbornene[36] has been synthesized that forms solid structures which are positively charged subsequent to polymerization. Such monomers could potentially be used as monomers in electrostatically self-assembled amphiplexes for applications in alkaline anion exchange membranes[41].

To this effect, this work presents the ordered phases displayed by complexes formed from the combination of poly (acrylic acid) with cetyltrimethylammonium chloride and using co-surfactant pentanol and oil phase as dicyclopentadiene to form electrostatically self-assembled amphiplexes (ESA). The ordered phases exhibited are explored as a function of ionic strength, co-surfactant concentration and oil concentration. The work then focuses on arresting these ordered phases by polymerizing the hydrophobic region containing the monomer oil dicyclopentadiene. Optimization of polymerization is achieved through the careful selection of the appropriate catalyst loading and poisoning of catalyst to an extent wherein the activity is not affected. The order indicated by the phase behavior of polymerized assemblies is then examined by small angle x-ray scattering to evaluate the retention of order.

CHAPTER 2: OPTIMIZATION OF POLYMERIZATION

2.1 Delay of polymerization

2.1.1 Introduction

The polymerization of dicyclopentadiene by Grubbs catalyst is a very rapid reaction. Following initiation, the polymerization proceeds to form the final polymer within a few minutes alongwith a rapid rise in temperature[42]. The reaction is highly exothermic with the average enthalpy of reaction reported to be 461±14.1 $J.gm^{-1}$ [29]. Given the particularly high activity, if not poisoned the catalyst would immediately cross link any dicyclopentadiene that it comes in contact with and would lead to an irregular distribution of the catalyst and thereby the product formed would have an asymmetrical distribution of polymer. For this purpose, the polymerization needs to be delayed.

Based on the mechanism of polymerization discussed earlier, it is evident that dissociation of the phosphine group is a necessary step for propagation of polymerization thereby making it a rate limiting step [43], [27]. Controlling the dissociation of phosphine group on the Grubbs catalyst should be a possible way to control the rate of polymerization. This fact has already been investigated in literature and it has been established that addition of triphenylphosphine delays the catalyst activity[27].

An analogous strategy has been adopted for electrostatically self-assembled amphiplexes in this case wherein the catalyst activity is delayed with the addition of triphenylphosphine. The thought behind this idea was to enable efficient distribution of the catalyst upon mixing the catalyst solution in the microemulsion. During polymerization, there is a rise in temperature owing to the exothermic nature of the reaction. This temperature profile can be monitored as a function of time and the effect of addition of triphenylphosphine can be observed. The addition of excess triphenylphosphine can lead to an irreversible reduction in the activity of the catalyst[27].

Before attempting to delay polymerization in the amphiplexes, experiments to delay polymerization were initially attempted in pure dicyclopentadiene with the intention of identifying a suitable loading of the poison triphenylphosphine that would ensure that the activity of the catalyst does not decrease. With the optimal loading for triphenylphosphine in pure dicyclopentadiene, the experiments were extrapolated to amphiplexes to ensure successful polymerization.

2.1.2 Materials and Methods

Stock solution of catalyst with benzene was prepared under an argon atmosphere. A scintillation vial was flushed with argon before being used. An arbitrary amount of catalyst was added to this vial inside the glove bag filled with argon. The vial was transferred out of the glove bag, weighed and transferred back inside the glove bag. The amount of benzene that would be required for a 0.05 mg/μl solution was added and the scintillation vial was sealed with paraffin film so that it could be stored for further use.

For delay of polymerization experiments, glass scintillation vials were filled with 1 ml of dicyclopentadiene (DCPD) and weighed. The base of the vial was glued to the plate of a rotating turntable and a thermocouple was attached to the side to measure the temperature of the vial which would represent the temperature of the dicyclopentadiene catalyst mixture. An appropriate amount of catalyst-benzene solution was added to the vial, closed immediately and the temperature noted as a function of time. With time, the solution viscosity increased as could be seen as the vial revolved and it increased to a point when the temperature started to increase rapidly to form a hard polymer. The temperature was noted and the profiles plotted.

In order to determine the optimum concentration of triphenylphosphine (TPP) to be added to microemulsions, experiments to polymerize pure dicyclopentadiene with and without poison were performed. Beginning from a 1:5 molar ratio of catalyst to triphenylphosphine, experiments were performed upto 1:25 molar ratio in 5 steps increasing the ratio 5 times each step.

	Catalyst:DCPD- 1:2500	**Catalyst:DCPD- 1:5000**
Catalyst:TPP	1:5	1:5
Catalyst:TPP	1:10	1:10
Catalyst:TPP	1:15	1:15
Catalyst:TPP	1:20	1:20
Catalyst:TPP	1:25	1:25

Table 1: Molar ratios of catalyst to triphenylphosphine used to polymerize pure dicyclopentadiene at catalyst loadings (catalyst:dicyclopentadiene = 1:2500 and 1:5000)

2.1.3 Results and Discussion

Based on the fact that the reaction is highly exothermic in nature, figures 8 shows the temperature profiles for polymerization of pure dicyclopentadiene in the presence of increasing amount of catalyst poison triphenylphosphine. For the case of catalyst:DCPD = 1:2500, at catalyst:TPP = 1:5 the rise in temperature occurs near 4 minutes which is indicative of the propagation in polymerization of dicyclopentadiene and the end material resulting is a hard polymer. At a higher ratio of poison (1:10), this rise in temperature exhibits a shift at 7 minutes thereby demonstrating a delay in polymerization. The same is true for the case of catalyst:DCPD = 1:5000 however greater amount of triphenylphosphine results in inhibition of polymerization with no polymerization occurring at a catalyst:TPP of 1:20. The solution remains in a viscous form and does not harden with time.

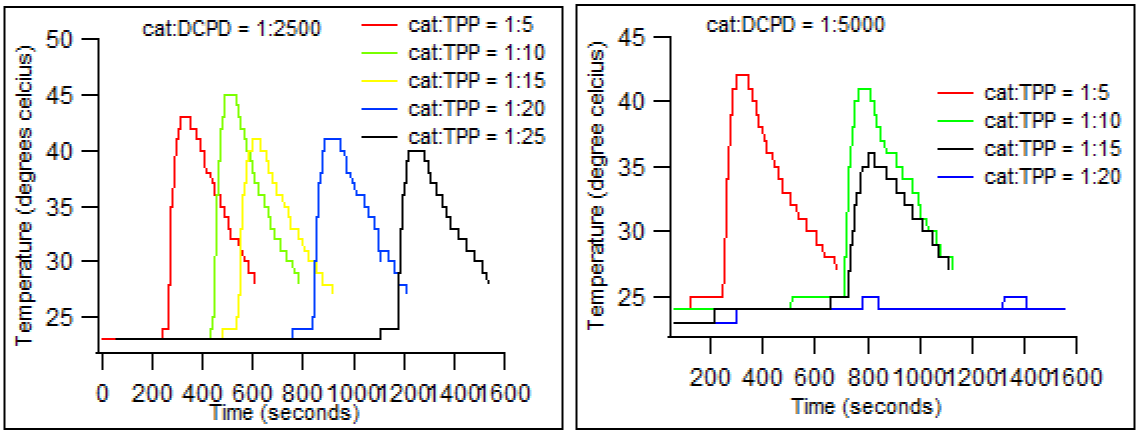

Figure 8: Temperature profiles for polymerization of pure dicyclopentadiene at two catalyst loadings [cat:DCPD =1:2500 left and cat:DCPD = 1:500 right] under increasing triphenylphosphine concentrations

Given that Grubbs catalyst is in equilibrium with the dissociated species, free triphenylphosphine in this case, addition of free triphenylphosphine shifts this equilibrium backwards towards the initial Grubbs catalyst causing a delay in polymerization. Excess triphenylphosphine however leads to inhibition of polymerization altogether. Previous literature on this topic reports a reduction in the enthalpies of reaction and the glass transition temperature of the final polymers upon increasing the triphenylphosphine loading[27]. This would represent a change in material properties thereby affecting the overall property of the polymer material. To avoid any changes to the material properties of the final polymer, the catalyst:TPP loading chosen for further experiments was 1:10. At this concentration, the polymerization was delayed by around 7 minutes which is adequate for distribution of the catalyst throughout the amphiplex.

2.2 Optimization of polymerization

Polymerization of dicyclopentadiene would occur in the hydrophobic regions of the amphiplexes. The need to optimize polymerization in amphiplexes is due to the presence of other components in the mixture. The polymerization is now evaluated at different concentrations of catalyst given the fixed amount of triphenylphosphine. Optimization polymerization was performed after optimizing the delay in polymerization because triphenylphosphine is already present in the catalyst solution. Once the polymerization is optimized, a greater variety of samples can be explored to evaluate the effect of different components.

2.2.1 Materials and Methods

Poly (acrylic acid sodium salt) (PAA) with MW= 5100 g/mol, cetyltrimethylammonium chloride (CTACl) 25% solution in water by weight, 1-Pentanol 99% pure and Octanol were purchased from Sigma Aldrich. Dicyclopentadiene (≥ 95% pure by GPC) was obtained from Sigma Aldrich. 2.8% of 5-ethylidene 2-norbornene was added to dicyclopentadiene in order to maintain the dicyclopentadiene liquid at room temperature as described in literature[44]. Millipore water was used to make poly (acrylic acid) solutions while other chemicals were used as received.

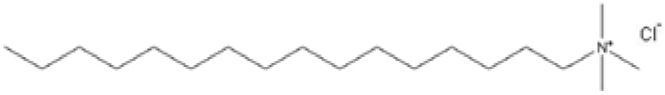

Figure 9: Chemical structures of Cetyltrimethylammonium chloride $CH_3(CH_2)_{15}NCl(CH_3)_3$ Figure adapted from[45],[46]

For optimization of polymerization experiments, one set of amphiplexes with 10% (w/w) Pentanol with respect to surfactant (CTACl) and varying amount of dicyclopentadiene (0 – 220% w/w with respect to surfactant) were selected. Samples were prepared in Teflon tubes in bulk. Polyelectrolyte and surfactant solutions were mixed in a stoichiometric amount yielding precipitated insoluble complex. To this mixture, appropriate amounts of co-surfactant (Pentanol) and oil (dicyclopentadiene) were added to prepare the amphiplexes, vortexed for 10 minutes and left to equilibrate for a week.

For polymerization experiments, the amphiplex was prepared, equilibrated and upon centrifugation isolated in a glass vial. The polymerization was performed in an argon atmosphere in the glove bag. A fixed amount of triphenylphosphine was added to a freshly prepared catalyst-benzene solution to poison it and appropriate volume of this catalyst solution was added to the vial. Upon polymerization, a portion of the sample was transferred to a plastic plate for x-ray measurements. The sample was washed with water before measurements to remove all the surfactant and polyelectrolyte.

The ratio of catalyst:triphenylphosphine at 1:10 was fixed for all amphiplexes and experiments were performed at different concentrations of catalyst. For this the molar ratio of catalyst:dicyclopentadiene was varied starting from a low concentration (catalyst:dicyclopentadiene = 1:10,000). The ratios of catalyst:dicyclopentadiene investigated are as shown in table 2.

	Catalyst Loading
Catalyst: DCPD	1:1000
Catalyst: DCPD	1:2500
Catalyst: DCPD	1:5000
Catalyst: DCPD	1:10000

Table 2: Molar ratio of catalyst to dicyclopentadiene for amphiplexes at a fixed loading of triphenylphosphine (catalyst:TPP = 1:10)

2.2.2. Results and Discussion

Amphiplexes that were polymerized at a catalyst ratio 1:10000 did not polymerize. They remained as a viscous complex even after 24 hours. The same is true for catalyst loading of 1:5000 as well. Given the presence of other components in the mixture, the amount of catalyst actually accomplishing contact with dicyclopentadiene would be limited. This limits the amount of catalyst available for the monomer and would warrant the need for a higher amount of catalyst in the mixture. At a higher concentration of 1:2500, the sample was polymerized but still was soft as compared to the hard polymer obtained in the previous experiments with pure dicyclopentadiene. Finally for the catalyst concentration of 1:1000, the resulting polymer was a hard material. Based on the fact that the highest concentration of triphenylphosphine was successful in polymerizing the amphiplex, the catalyst:TPP ratio of 1:1000 was chosen for further experiments.

CHAPTER 3: PHASE TRANSITIONS AND SWELLING BEHAVIOR STUDIES OF AMPHIPLEXES

3.1 Introduction

The experimental design here was to investigate phase behavior of electrostatically self-assembled amphiplexes with monomer oil to observe long range order if any. The question addressed here is whether electrostatically self-assembled amphiplexes formed using monomer oil display long range order and to examine the swelling behavior under increasing oil content in the hydrophobic region. The phase behavior was investigated for the unpolymerized amphiplexes as a function of three parameters namely, co-surfactant concentration, oil concentration and the salt concentration. The amount of co-surfactant in the amphiplexes was varied from 10 to 60% (weight percent) with respect to surfactant in intervals of 10%. Similarly the oil concentration was varied from 20% to 220% (weight percent) with respect to surfactant in steps of 20% each. For adjusting the ionic strength, solutions of poly (acrylic acid) sodium salt were prepared at 100 mM, 300 mM and 500 mM NaCl salt concentrations by adjusting the concentration at 1.08, 4.57 and 13% by weight in water respectively.

Upon preparation of the range of amphiplexes, small angle x-ray scattering (SAXS) was the primary mode for studying these materials. From the results thus obtained, phase diagrams were plotted as a function of co-surfactant content and oil content. Unit cell sizes were calculated for all the amphiplexes which represents the size of the smallest repeating unit in the structure. Swelling behavior was plotted which was simply a plot of the unit cell sizes as a function of the oil concentration.

Upon investigating the unpolymerized amphiplexes, these amphiplexes were polymerized according to the protocol discussed later. The set of amphiplexes prepared were in the same range as that for the unpolymerized amphiplexes. Results from small angle x-ray scattering experiments were used to plot phase diagrams and swelling behaviors to examine the effect of polymerization of monomer oil in these materials. The phase diagrams and the swelling behavior data for the unpolymerized and the polymerized amphiplexes are presented together to afford an effective comparison.

3.2 Methods

3.2.1 Preparation of unpolymerized amphiplexes

For X-ray measurements, samples were prepared in a Teflon 96 well plate. This well plate was developed in our laboratory for organic molecules that are incompatible with plastic well plates and can be pressure sealed at both ends with mylar sheets to prevent evaporation or leakage. Upon adding the surfactant solution to polyelectrolyte in the Teflon well plate, an insoluble white precipitate appeared. To this complex, required amount of co-surfactant and oil were added. The plate was vortexed for 5 minutes at 1500 rpm and left to equilibrate at room temperature for 7 days before polymerization or measurement. Prior to measurement of the unpolymerized samples, the mylar film was punctured with a pin and centrifuged to remove the salt solution in which it was equilibrating inorder to ensure the selective scattering of sample only.

3.2.2 Preparation of polymerized amphiplexes

The entire polymerization reaction was carried out in an argon atmosphere using a glove bag. The well plate containing the equilibrated samples and all the necessary equipments were placed inside the glove bag before sealing it. The glove bag was evacuated using a pump and upon complete evacuation, argon gas was introduced to maintain an inert atmosphere and the polymerization reaction was then carried out in this argon atmosphere. The Teflon well plate was punctured to remove salt solution in which it was equilibrating and one face of the plate was disassembled to perform the reaction. Previously calculated amount of poisoned catalyst-benzene solution was added to each well. The complex was mixed to ensure homogeneity of the catalyst within the sample. After completion, the plate was sealed and left in the argon atmosphere. The samples were transferred to a plastic 96 well plate sealed with sticky mylar sheets for x-ray measurements. The samples were washed with water to remove surfactant and polyelectrolyte prior to measurement.

3.2.3 Small angle x-ray scattering (SAXS) measurements and data analysis

Synchrotron based small angle x-ray scattering was the primary method employed for studying the unpolymerized and polymerized amphiplexes. Experiments were performed at beamline X6B at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratories (BNL). The incident wavelength was 1.2Å and the sample to detector distance was about 100 cm. This distance allowed us to investigate the q-range of 0.02 - 0.39 $Å^{-1}$. Here q represents the scattering vector which is given by q =

4πsinθ/λ, where λ is the wavelength of the incident X-ray and 2θ is the scattering angle. Calibration was performed using silver behenate as the standard. The X-ray measurements were carried out in an automated fashion using a motorized stage developed at the beamline with the support of Elaine Dimasi at BNL. This facilitates the measurement of upto 3 well plates in one run. The X-ray scattering data obtained were angularly averaged to give X-ray scattering profiles using Igor Pro software package (Wavemetrics)[47].

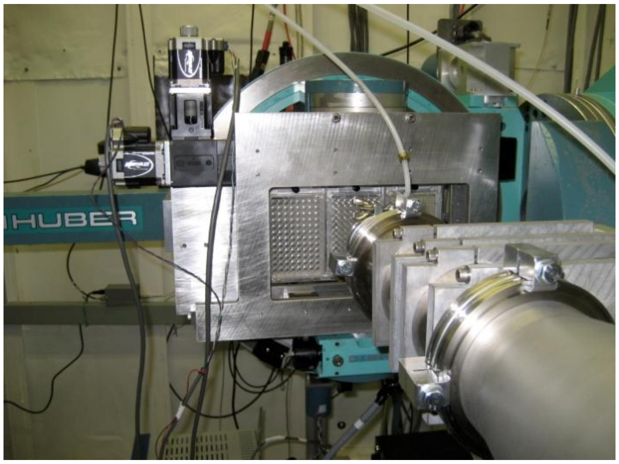

Figure 10: Set up for small angle x-ray scattering at Beamline X6B, NSLS consisting of a automated x-y translation stage

Upon characterization of samples using small angle x-ray scattering, three key parameters can be obtained from the scattering plots. The first is the type of structure of the material determined from the ratios of location of peaks on the plot. The size of these structures obtained from the location of peaks and finally long range order can be evaluated from the width of the peaks. The width of the peak is inversely proportional to the degree of order in the structure. Thus, a scattering plot with broad peaks would represent a disordered state and narrow peaks would be representative of long range ordered structures. Although the extent of long range order for the samples has not been reported here, a sample value of the width of peak is 0.0249Å. This can point to a long range order of upto 253.1 Å. The data that we have investigated exhibits narrow peaks as mentioned here across all co-surfactant and oil concentrations. Based on this fact, we state that the amphiplexes investigated here exhibit long range order.

Small angle x-ray scattering (SAXS) curves of the various samples have been used to put together phase diagrams. The various phases observed were identified based on the ratios of the peaks of intensities on the scattering curves. The Pm3n cubic phase was identified by peaks which were located in the ratio of √2, √4, √5, √6, √8, √10 and √12. For the cubic phase, in most samples the peaks in the ratio of √4, √5 and √6 were the strongest peaks representing the 200, 210 and 211 planes[8] . The hexagonal phase has peaks at the ratios of 1, √3, √4, √7 and √9 that represent the 100, 110, 200, 210 and 300 planes. The lamellar phase was identified by peaks in the ratio of 1, 2 and 3 representing 100, 200, 300 planes [8].

The swelling behavior of these amphiplexes was examined by calculating the unit cell size for the samples. The unit cell size refers to the size of the smallest repeating unit for that phase. The unit cell size is calculated using the following equations [8]:

For cubic, $\frac{1}{d_{hkl}} = \frac{\sqrt{(h^2+k^2+l^2)}}{a}$

For hexagonal, $\frac{1}{d_{hk}} = \frac{2\sqrt{(h^2+hk+k^2)}}{a.\sqrt{3}}$

Where, ‘a’ is the unit cell parameter, d is the interlayer spacing (d-spacing) obtained from x-ray scattering curves.

The phase diagrams for unpolymerized and polymerized amphiplexes prepared at various salt concentrations are shown and in these figures, the hexagonal phase is represented by H, lamellar by L and Pm3n cubic by C. LH and CH represents the co-existence of the lamellar-hexagonal and cubic-hexagonal phases respectively. This notation would be used throughout the text. Swelling behavior is represented as a plot of unit cell size in Angstroms (Å) versus the dicyclopentadiene content. The term “weight%” in all the figures refers to the percentage by weight of that component relative to that of the surfactant (cetyltrimethylammonium chloride). To get an idea of the fractions of the components in the total amphiplex, a sample calculation has been shown below.

Sample combination prepared:

PAA – 228.94 μl

CTACL – 30 μl

Dodecane – 9.02μl

Pentanol – 3.1μl

Based on the knowledge of the densities of the components, the theoretical weights of the components calculated are

PAA – 2.45 mg (1.08% solution – 100mM)

CTACL – 7.438 mg (25% w/w solution)

Dodecane – 6.765 mg

Pentanol – 2.525 mg

Total water – 249.04 mg (water in PAA + water in CTACl solutions)

To find the weight of the individual components, there can be two assumptions made here:

a) No water in the complex

Under this assumption, Weight fractions of the components –

PAA – 12.78%

CTACl – 38.7%

Dodecane – 35.2%

Pentanol – 13.16%

b) Water in complex

After preparing the complex and equilibration, the sample was centrifuged and the excess water was removed. Based on the initial weight of the water and the weight of the water removed, an estimate can be made for the amount of water present in the complex.

Weight of water present in the complex (experimentally) – 32.3 mg

Therefore performing the same calculations the fractions of each components are,

PAA – 4.76%

CTACl – 14.45%

Dodecane – 13.14%

Pentanol – 4.9%

Water – 62.7%

It is important to note here that the weight fractions indicated here are purely theoretical. For the experiments, the weight fractions that have been used for the samples are with respect to the surfactant and not with the amphiplex due to the difficulty associated with making these calculations. Also, these calculations might not reflect accurate amounts of the materials. This is primarily based on the fact that the amphiplex precipitates out of the solution. As the co-surfactant and the oil would have some defined solubility in water, the amounts of co-surfactant and oil calculated using the above calculations would not be accurate, therefore these values cannot be included as part of the results. The values provided above are merely an illustration of the range of variation discussed here.

3.3 Results and Discussion

3.3.1 Evaluation of amphiplexes at 100 mM salt concentration

Phase Transition

Results for the unpolymerized amphiplexes at 100 mM salt concentration are as shown below. The amphiplexes in the unpolymerized state display ordered nanostructured phases showing lamellar and hexagonal phases. There are two trends that can be observed as is evident from figure 11. First, at low concentrations of pentanol ranging from 10-30%, there is a phase transition from lamellar to hexagonal phase with increase in dicyclopentadiene concentration. Second, there is a noticeable phase transition from the hexagonal to lamellar phase as the co-surfactant concentration increases. At low co-surfactant concentrations ranging from 10 to 30%, the predominant phase observed is hexagonal. However there is a distinct phase transition from hexagonal to lamellar phase as the co-surfactant concentration increases that passes through a region where the two phases co-exists which has been previously observed [48].

Upon polymerization, amphiplexes exhibit a consistent hexagonal phase at all co-surfactant and oil concentrations as can be observed in the phase diagram in figure 12 below. Upon polymerization, all the phases observed in the unpolymerized state transform into a hexagonal phase and there is no phase transition irrespective of changes in oil content or the co-surfactant content.

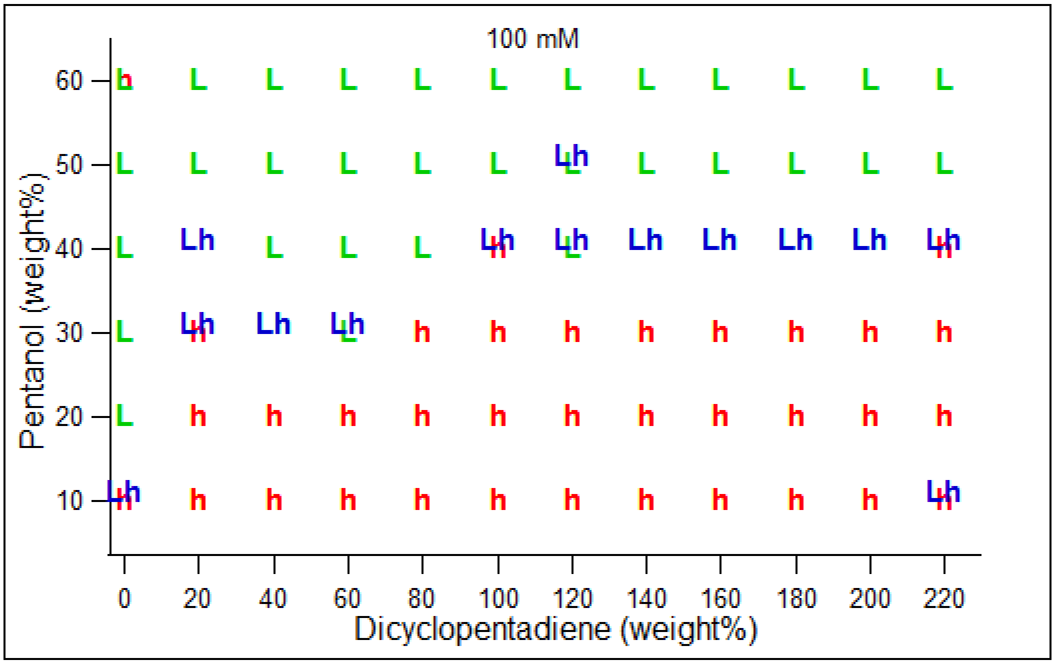

Figure 11: Phase diagram for unpolymerized amphiplexes showing pentanol and dicyclopentadiene variation relative to surfactant at 100 mM NaCl

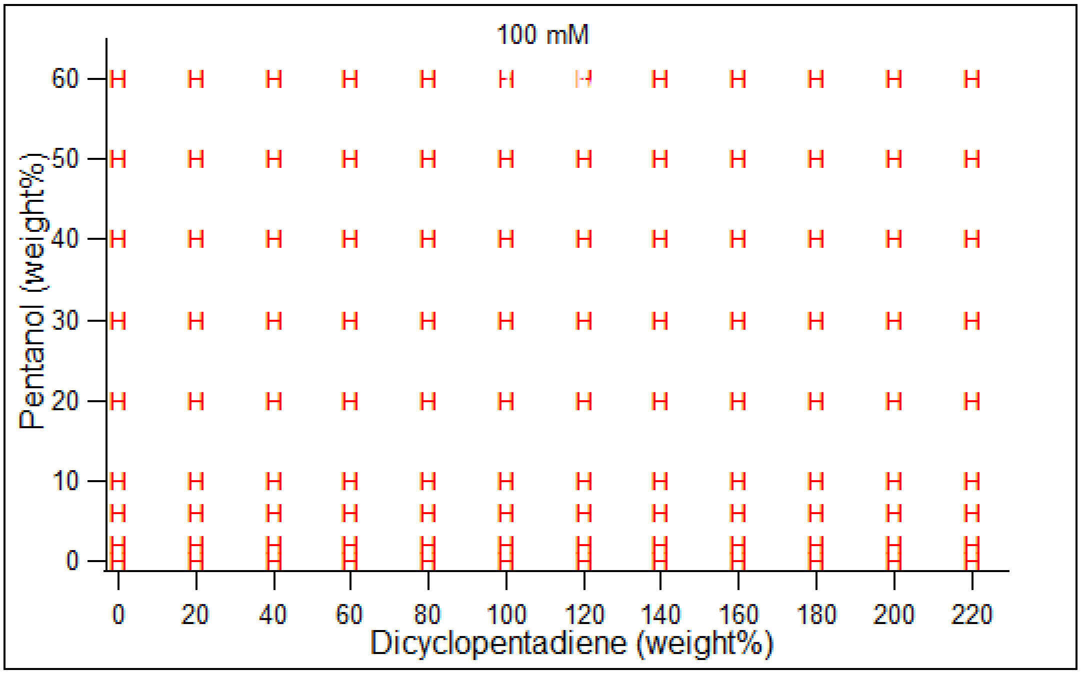

Figure 12: Phase diagram for polymerized amphiplexes showing pentanol and dicyclopentadiene variation relative to surfactant at 100 mM salt concentration

Swelling behavior

The swelling behavior of amphiplexes is investigated by examining the unit cell size as a function of oil content for the corresponding co-surfactant content and reveals more information regarding the assembly of these amphiplexes and their behavior with variation of these parameters. For the case of 100 mM salt concentration, the unit cell size variation is affected by two major factors; co-surfactant concentration and oil concentration and the results are as shown.

Figures 13 and 14 below show the change in unit cell size for unpolymerized amphiplexes from 10% to 60%. At 10% pentanol relative to surfactant (CTACl), the hexagonal phase grows from 49.94Å to 68.6Å with addition of dicyclopentadiene. At 20% pentanol, this swelling increases from 56.4Å to 80.35Å. At 30% pentanol, the observed swelling is the maximum with the hexagonal phase enlarging from 54.85Å to 88.23Å. Performing a similar comparison at higher pentanol range (40-60%) reveals that the amount of co-surfactant does not affect the unit cell size further. With increasing oil, at 40% pentanol, the lamellar phase shows a growth from 41.8Å to 46.73Å. At 50% and 60% pentanol, this change is from 39.5Å to 46.7Å and 40.9Å to 47.2Å respectively as can be seen in figure 14.

For the same amount of oil in the amphiplex, increase in the amount of pentanol from 10% to 30% causes a concomitant increases the unit cell size as is evident from figure 13 indicating incorporation of increasing amount of co-surfactant in the surfactant layer. The existence of pentanol in the surfactant layer allows the swelling of the phases in figures 13 and 14 however the swollen phases at high pentanol contents do not increase in size as they did at lower co-surfactant concentrations. As the co-surfactant molecules enter the surfactant layer, there would be a reduction in the curvature as the co-surfactant molecules wedge in between the surfactant layers. Upon increasing the pentanol concentration above 40%, the spontaneous curvature is reduced to zero which can noted by the observation of lamellar phases at high concentration of pentanol.

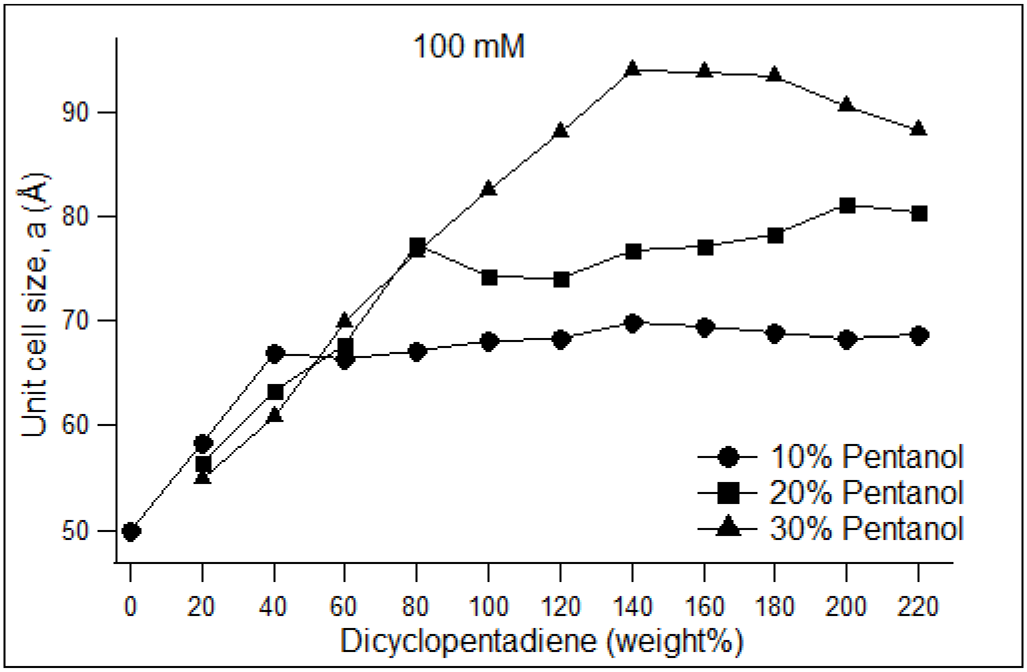

Figure 13: Variation of unit cell size as a function of dicyclopentadiene for the hexagonal phase at 100 mM from 10 to 30% pentanol

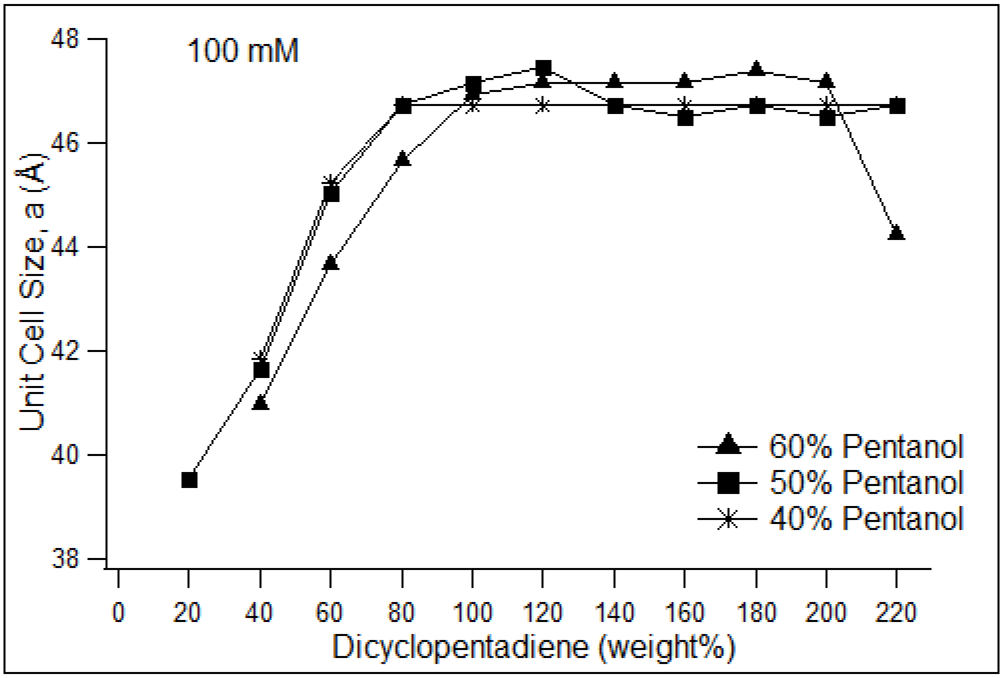

Figure 14: Variation of unit cell size as a function of dicyclopentadiene for Lamellar phase at 100 mM salt concentration from 40 to 60% pentanol

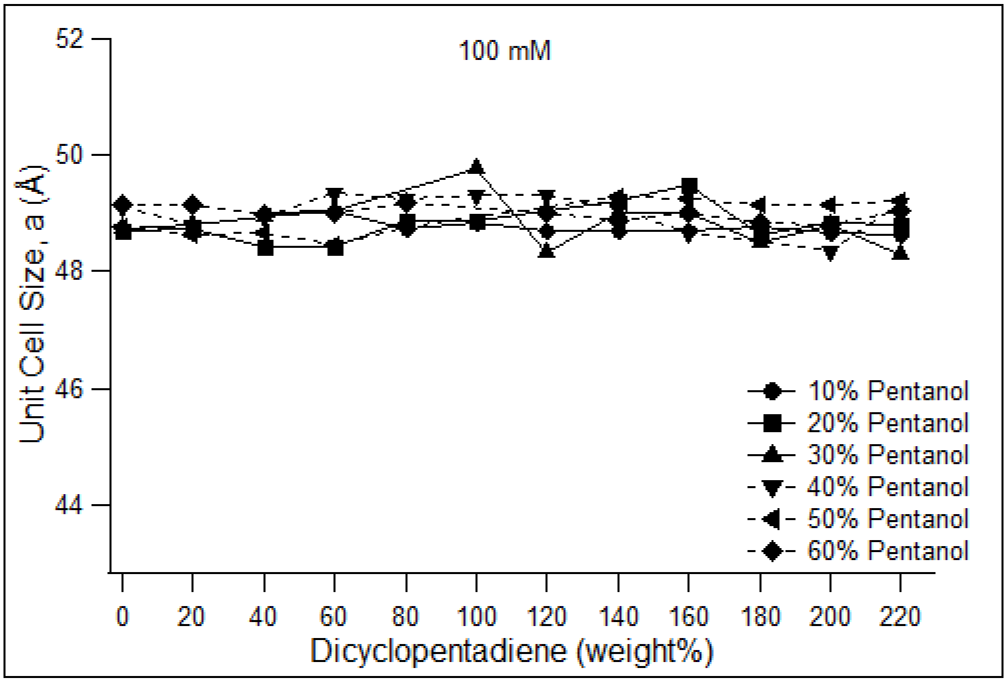

Figure 15: Variation of unit cell size (hexagonal phase) for polymerized amphiplexes as a function of dicyclopentadiene at 100 mM salt concentration

The swelling behavior of polymerized amphiplexes across all pentanol and dicyclopentadiene concentrations is similar in nature as summarized in figure 15 above. There is no swelling observed and the range of variation of the unit cell sizes encompassing all pentanol and dicyclopentadiene concentration lies in a tight range of values from 48.29 Å to 49.73 Å. The reason behind such behavior would be discussed in a later section.

3.3.2 Evaluation of amphiplexes at 300 mM salt concentration

Phase Transition

At 300 mM salt concentration, the phase diagram for unpolymerized amphiplexes is shown in figure 16. A similar observation can be made for the case of 300 mM as was for 100 mM. Referring to figure 16, there are two key observations; first a phase transition to a lamellar phase with increasing co-surfactant concentration. Second, a phase transition with increasing amount of dicyclopentadiene from the lamellar phase to a coexistence phase displaying both hexagonal and hexagonal phases.

Upon polymerization, there is significantly better conservation of order as compared to the case of 100 mM salt concentration. The region of lamellar phase above the 40% pentanol concentration is retained after polymerization as can be seen by comparing figures 16 and 17. For pentanol concentrations in the range of 10-30%, there is an incomplete retention of order as some of the hexagonal phases transform into a lamellar phase.

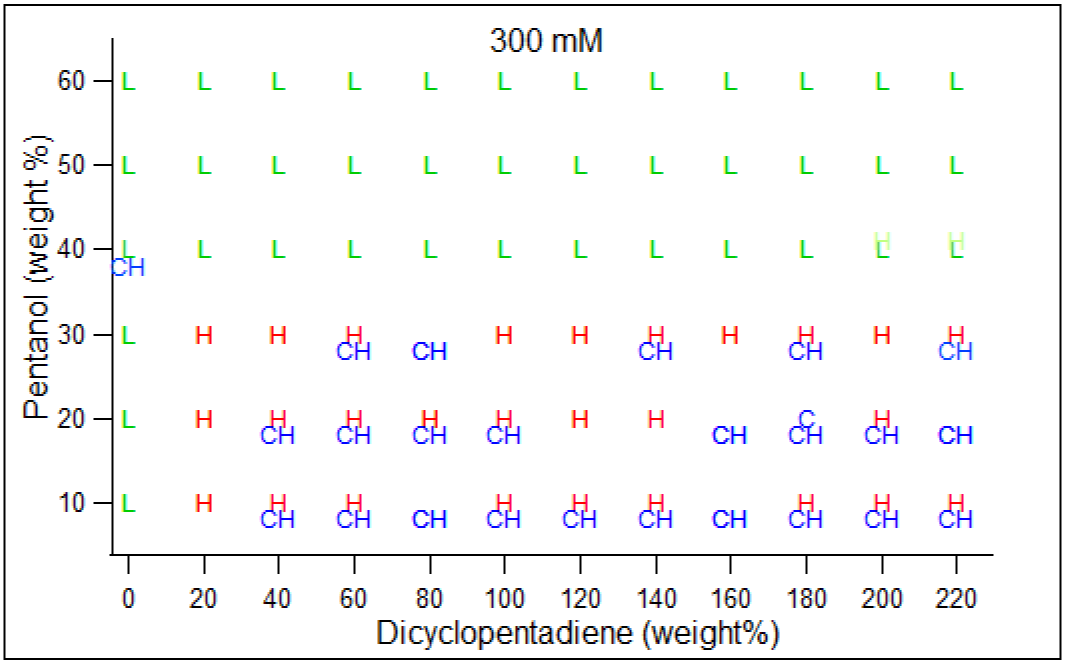

Figure 16: Phase diagram for unpolymerized amphiplexes showing pentanol and dicyclopentadiene variation relative to surfactant at 300 mM NaCl salt concentration

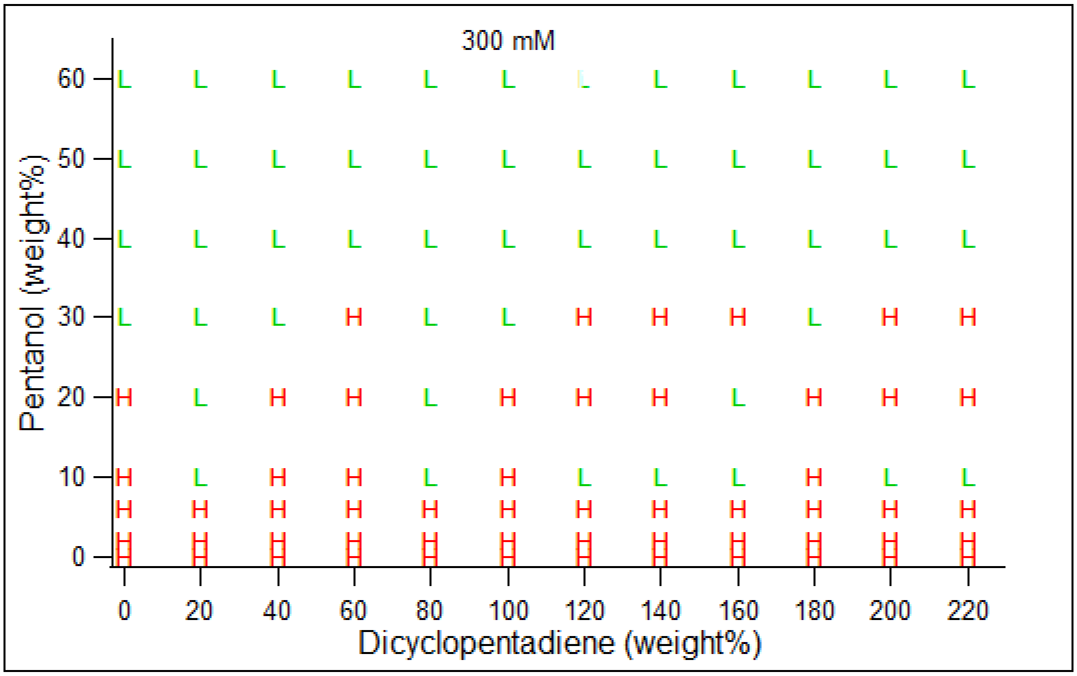

Figure 17: Phase diagram for polymerized amphiplexes showing pentanol and dicyclopentadiene variation relative to surfactant at 300 mM NaCl salt concentration

An illustration of phase transition of amphiplexes from lamellar to hexagonal to a hexagonal-cubic co-existence can be seen in figure 18. The leftward shift in the scattering curves moving from lamellar to hexagonal to hexagonal-cubic coexistence indicates the swelling of the amphiplexes with increasing amount of dicyclopentadiene.

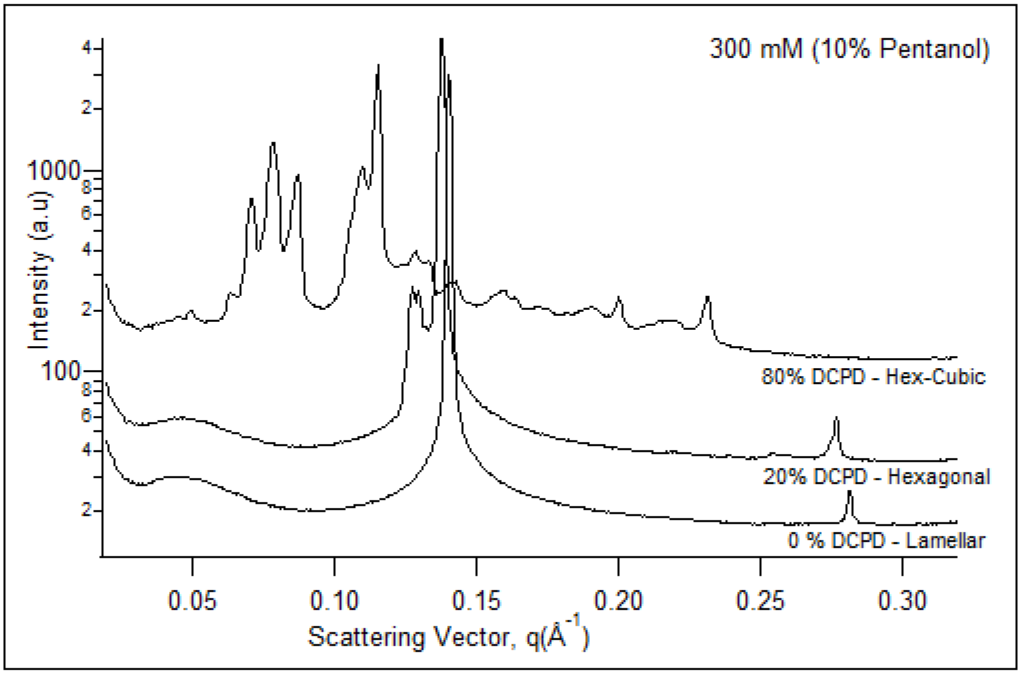

Figure 18: Phase transition for unpolymerized amphiplexes showing transition from lamellar to cubic-hexagonal coexistence phase with increasing dicyclopentadiene

Swelling behavior

The swelling behavior of unpolymerized and polymerized amphiplexes is summarized in figures 19, 20 and 21 below. A similar trend is observed as in the case of 100 mM. The hexagonal phases in the 10% to 30% range show a marked swelling as is apparent from figure 19. At 10%, the hexagonal phase swells from 56.5 Å to 71.15 Å. At 20% and 30%, the increase in swelling is greater. The increase in swelling is 24% in the case of 20% pentanol from 66.7 Å to 82.9 Å. The corresponding increase at 30% is much higher at 70.9% with the hexagonal unit cell swelling from 56.2 Å to 96.1 Å. This is indicative of the increasing capacity of the surfactant layer to incorporate oil and confirms the result discussed previously in the case of 100 mM. From figure 20, the effect of pentanol on unit cell size is not significant at concentrations of pentanol higher than 40% although the swelling of amphiplexes is evident indicating uptake of dicyclopentadiene. This will be further discussed in a later section. For the polymerized amphiplexes, lamellar phases being observed in majority are plotted in figure 21. Pentanol and dicyclopentadiene have no effect on swelling of the amphiplexes upon polymerization and the unit cell sizes lie in a tight range of values between 42.7 Å and 45.9 Å.

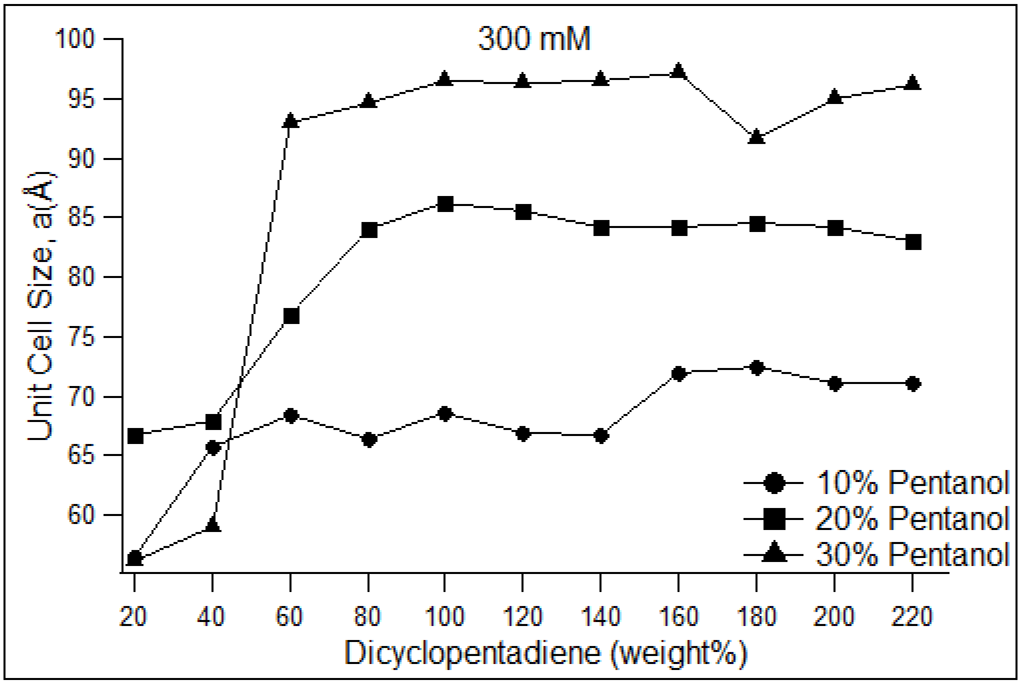

Figure 19: Variation of unit cell size (hexagonal phase) as a function of dicyclopentadiene for unpolymerized amphiplexes at 300 mM

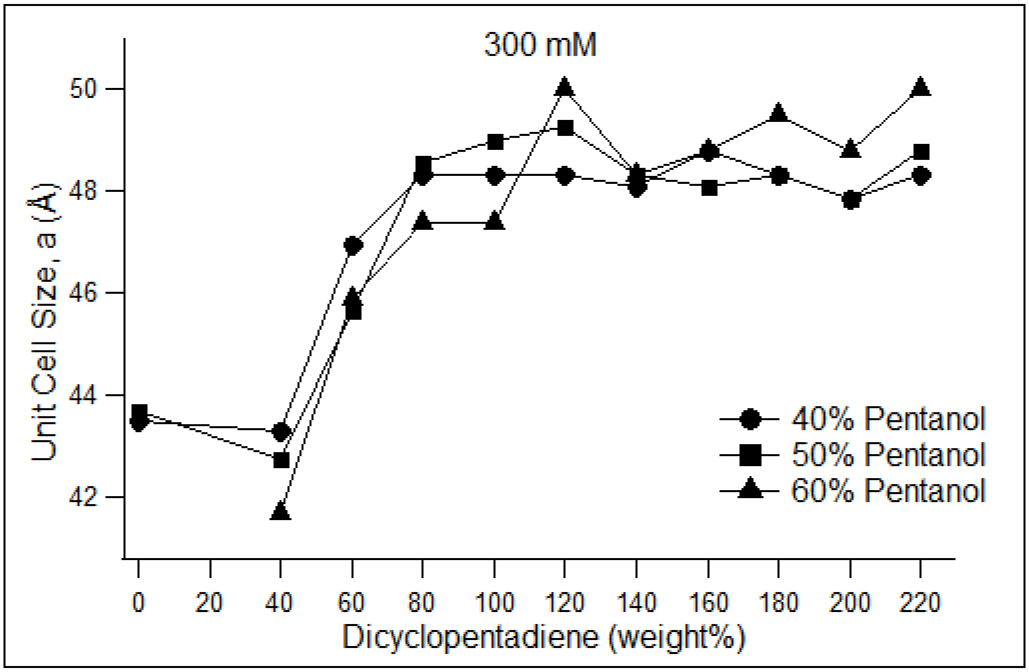

Figure 20: Variation of unit cell size (lamellar phase) as a function of dicyclopentadiene for unpolymerized amphiplexes at 300 mM from 40% to 60% pentanol

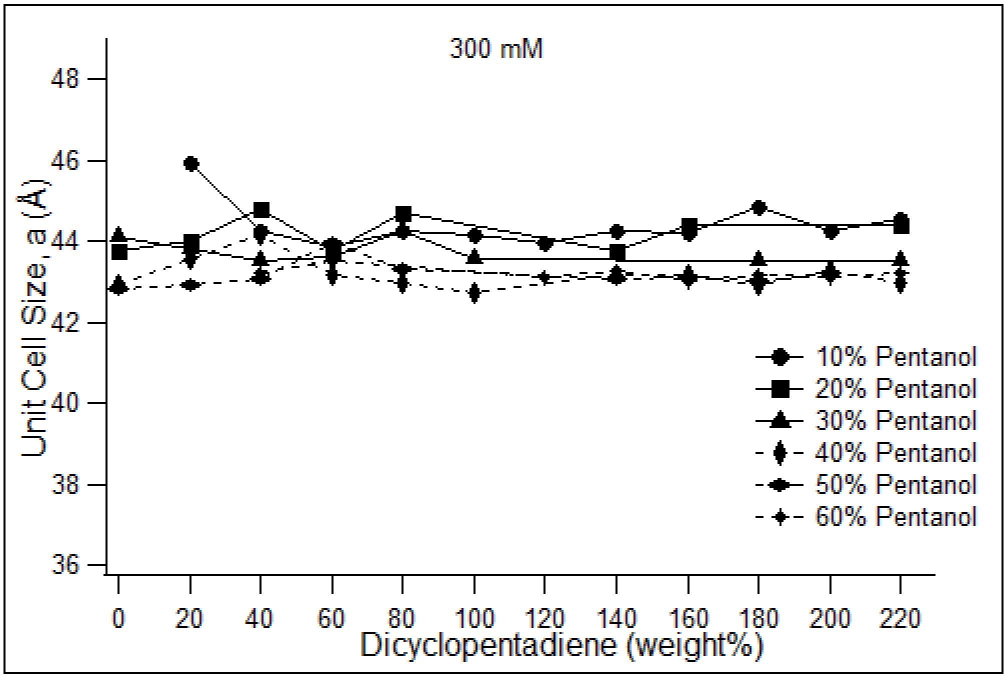

Figure 21: Variation of unit cell size (lamellar phase) of polymerized amphiplexes as a function of dicyclopentadiene at 300 mM from 10% to 60% pentanol

3.3.3 Evaluation of amphiplexes at 500 mM salt concentration

Phase transitions

The effect of increasing ionic strength is most apparent in the case of 500 mM wherein richer phase diversity is observed. Hexagonal phases are not limited to the range of 10-30% pentanol concentrations as observed previously as can be seen in figure 22 with hexagonal phases observed at higher pentanol concentrations as well. The existence of cubic phases is seen at multiple locations mostly at dicyclopentadiene concentrations above 40% and distributed across all values of pentanol concentrations. The transition to the lamellar phase at high pentanol content (above 40%) that was evident for 100 mM and 300 mM phase diagrams is now found only at 60% pentanol content representative of the weakening of interactions at high salt concentrations.

Based on the knowledge of the fact that the strength of interactions between polyelectrolytes and surfactants reduces at high ionic strengths [15], this permits the formation of ordered phases which was not possible earlier due to the high affinity binding. This makes the assemblies more flexible than before and is reflected in the diversity of phases displayed in figure 22.

The polymerized amphiplexes display hexagonal and lamellar phases as can be seen in figure 23 but there is no clear trend or pattern that can be observed in the phase transitions as a function of co-surfactant and oil content. The swelling behavior would reveal more information regarding these phases formed.

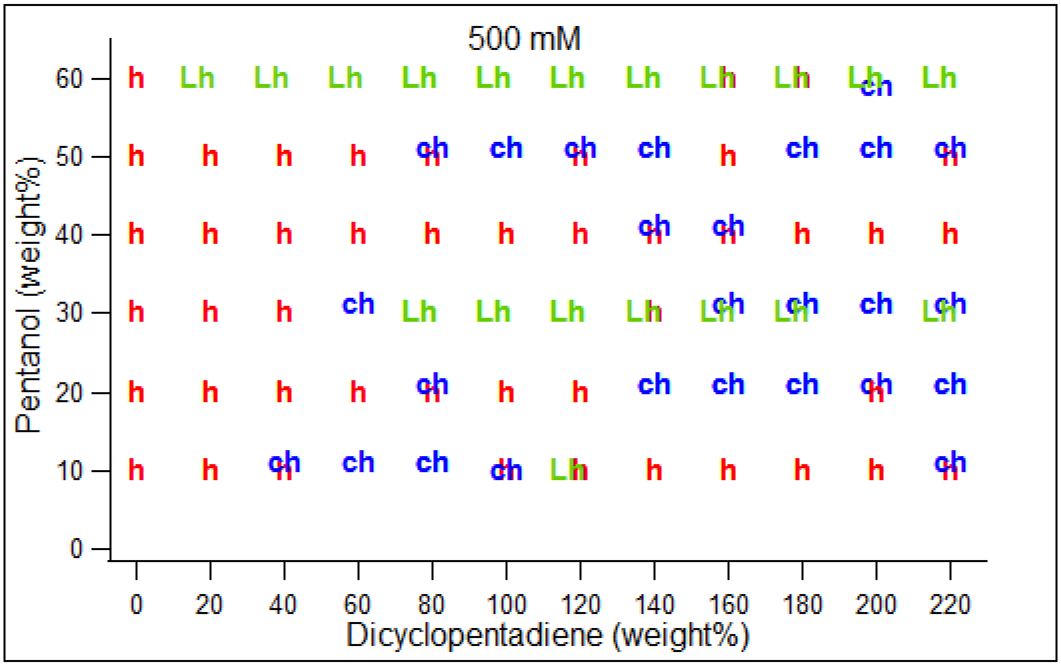

Figure 22: Phase diagram for unpolymerized amphiplexes showing pentanol and dicyclopentadiene variation relative to surfactant at 500 mM ionic strength

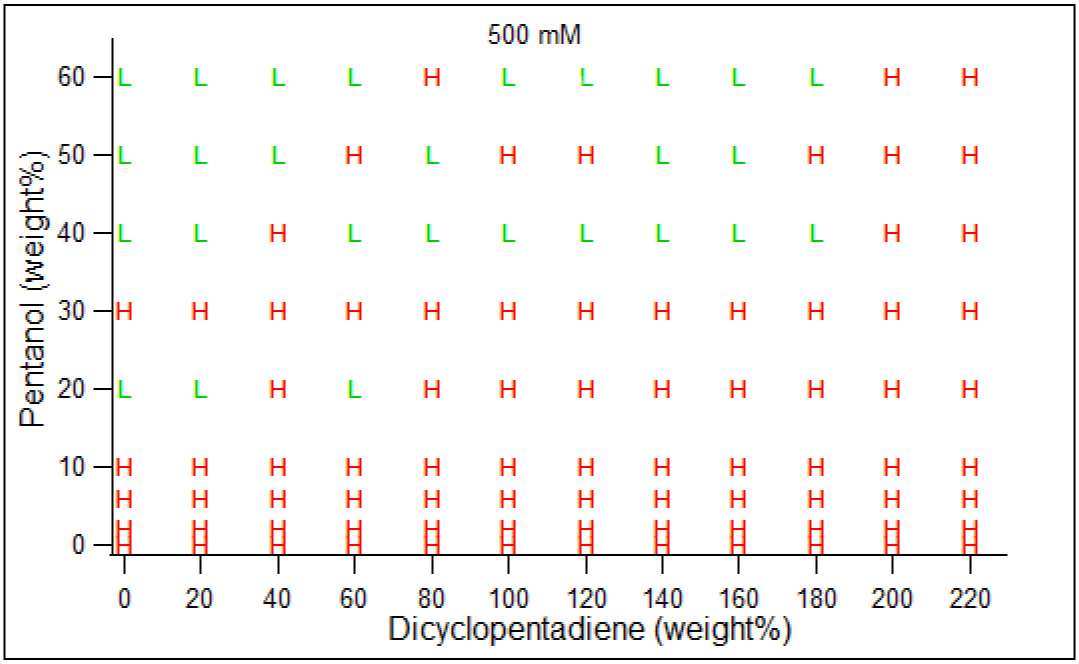

Figure 23: Phase diagram for polymerized amphiplexes showing pentanol and dicyclopentadiene variation relative to surfactant at 500 mM ionic strength

Swelling behavior

The swelling behavior for amphiplexes at 500 mM shows a non-uniform increase. At 10% pentanol, there is a 62% increase in the hexagnol phase from 56.56 Å to 91.6 Å. The swelling in the case of 20% pentanol is 74% from 56.95 Å to 99.1 Å. 30% pentanol shows the highest amount of swelling with the hexagonal unit cell swelling 157% from 54.9 Å to 141.5 Å. The increase in swelling as seen in figure 24 is the greatest at 500 mM salt concentration as compared to the 100 mM and 300 mM case representing the weaker interactions as discussed earlier. Upon polymerization, the swelling behavior shows a similar trend as was observed for the case of 100 mM and 300 mM in figures 15 and 21 respectively. There is no swelling observed and the unit cell sizes lie in a range of values between 42.7 Å and 45.9 Å as shown in figure 25 and 26.

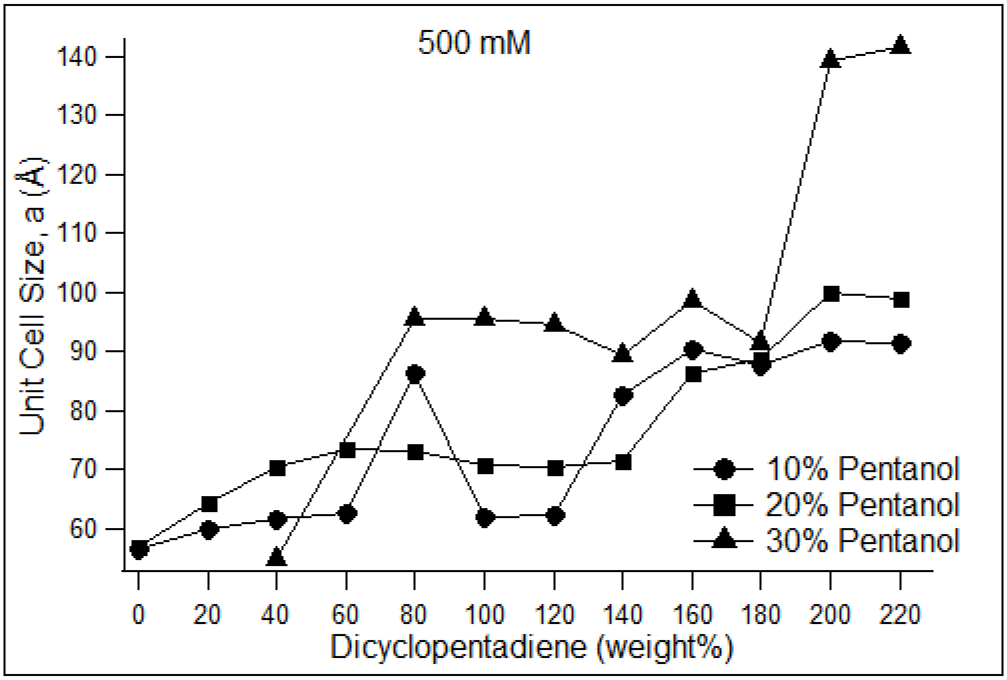

Figure 24: Variation of unit cell size (lamellar phase) of polymerized amphiplexes as a function of dicyclopentadiene at 300 mM from 10% to 60% pentanol

The reason for the non-uniform swelling behavior can be explained by looking at the swelling behavior of all the phases observed. Because of co-existence of more than one phase, the partitioning of the oil (dicyclopentadiene) is not consistent as in the pure phase systems. This can be seen from Table 3 below wherein the unit cell sizes for amphiplexes of pentanol at 10% and 500 mM salt concentration are given.

Oil (weight %)	Unit cell size (Å) Hexagonal phase	Unit cell size (Å) Cubic phase
20	59.9	
40	62.64	
60	62.54	175.44
100	62.05	172.41
140	92.02	

Table 3: Unit cell sizes for amphiplexes in the hexagonal and cubic phase at varying concentrations of oil at 10% pentanol concentration and 500 mM salt concentration

The hexagonal phases of amphiplexes at 10% pentanol show an increase in unit cell size with increasing amount of oil from 20% to 40%. However at 60% pentanol, the existence of cubic phase suddenly causes a reduction in the unit cell size of the hexagonal phase. This could be explained by a competition between the phases for incorporating the oil phase and therefore the swelling behavior follows a non-uniform increase in the unit cells size. Since this is just a speculation, confirmatory experiments to prove the same would be needed.

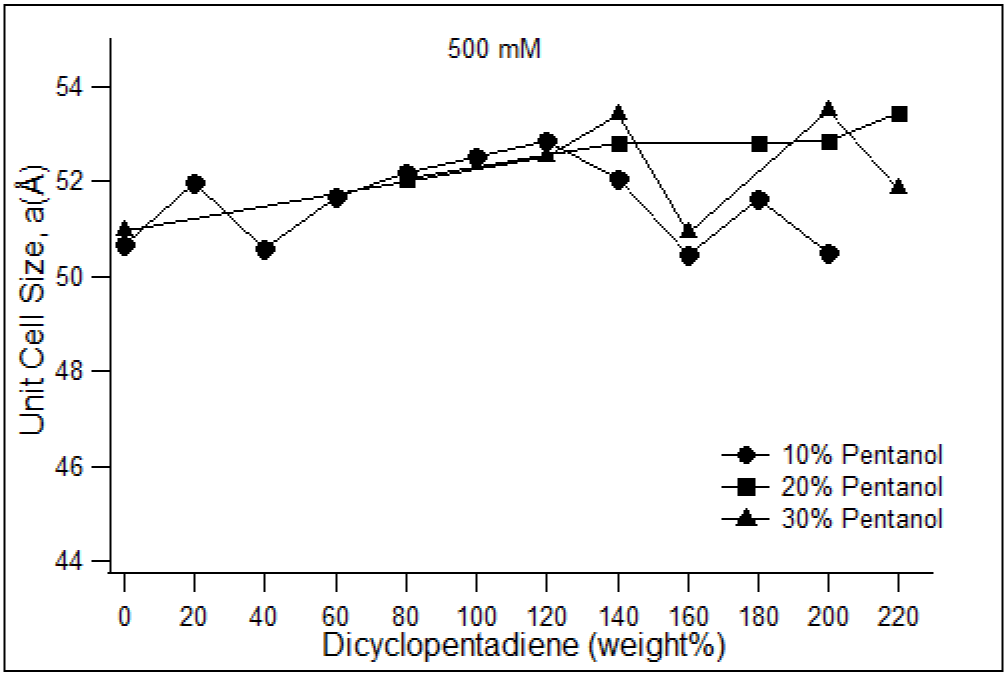

Figure 25: Variation of unit cell size (hexagonal phase) of polymerized amphiplexes as a function of dicyclopentadiene at 500 mM from 10% to 30% pentanol content

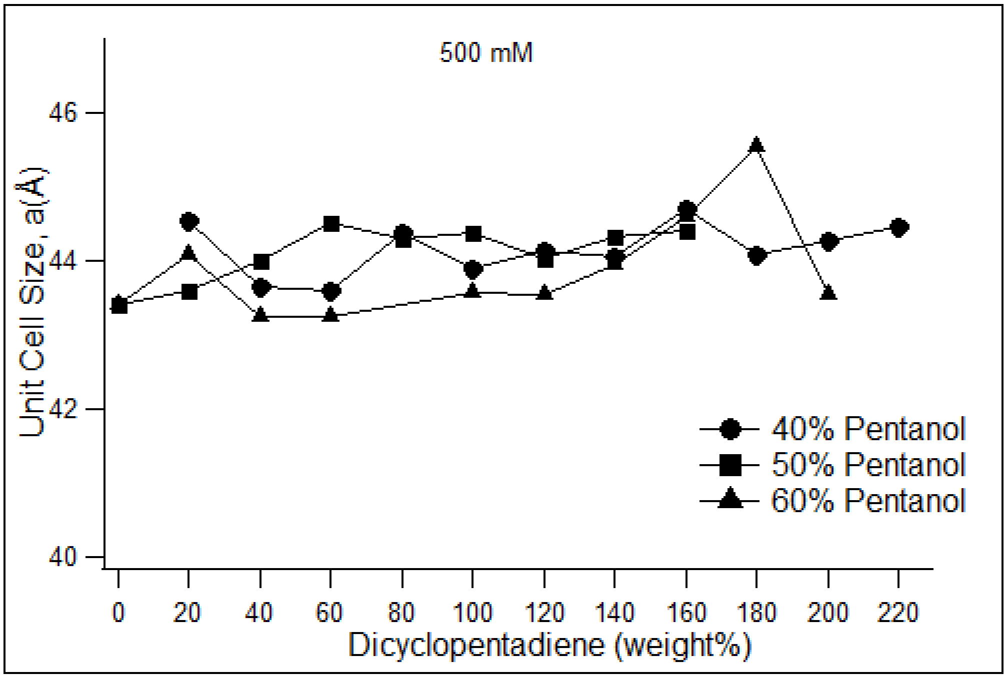

Figure 26: Variation of unit cell size (lamellar phase) of polymerized amphiplexes as a function of dicyclopentadiene at 500 mM from 40% to 60% pentanol content

3.3.4 General Discussion

Effect of Ionic Strength:

An increase in unit cell size with increasing ionic strength was observed by comparing figures 12, 18 and 23. This fact is not new and it has been well established that interaction between polyelectrolytes and surfactants weakens with increasing ionic strength [49], [50]. This weakening of interactions results in reduced attraction between polyelectrolyte and the surfactant [6] thereby causing an increase in the unit cell size as has been observed previously [8] and also in this study. Apart from the larger unit cells observed, another effect which is apparent is the formation of hexagonal and cubic-hexagonal co-existence phases at higher ionic strengths that were not observed at low ionic strengths. This can be attributed to the greater flexibility afforded due to the weakening of the interactions between polyelectrolytes and surfactants.

Effect of oil

Upon increasing the concentration of dicyclopentadiene in amphiplexes, the unit cell size reaches a maximum and does not increase as has been seen in the swelling behavior of amphiplexes at almost all concentrations of salt and co-surfactant. This plateau can be explained based on the following justification. Pentanol as a co-surfactant has a finite solubility in the oil phase and it is known to partition into the oil phase in certain microemulsions [51]. As the amount of dicyclopentadiene in the amphiplex increases, pentanol begins to solubilize into the oil phase. The reduction in the amount of pentanol available in the surfactant layer limits its spontaneous curvature resulting in the plateau that is seen in the unit cell sizes at high oil concentrations. This needs to be investigated further to confirm the theoretical explanation.

Effect of co-surfactant

Comparison of swelling behavior at increasing co-surfactant concentration reveals the effect of addition of short chain alcohols in this case, pentanol to electrostatically self-assembled amphiplexes. There are two main observations, first at low concentrations in the range of 10 to 30%; there is an increase in the unit cell size on addition of pentanol. This can be explained by the fact that pentanol is incorporated in the surfactant layers causing the structure to enlarge as has been documented previously[52]. The second observable trend is that at higher concentrations of pentanol, the structures tend towards forming lamellar phases irrespective of the oil concentration or the ionic strength. This can be explained by the fact that co-surfactant molecules enter the amphiphilic (surfactant layer) region of these complexes between the larger surfactant molecules thereby causing a reduction of the spontaneous curvature. Upon increasing the pentanol concentration above 40%, the spontaneous curvature reduces to zero which is evidenced by the observation of lamellar phases at high concentration of pentanol for the case of 100 mM and 300 mM amphiplexes. At 500 mM, as the interactions have weakened, lamellar phases are not observed.

Effect of polymerization

Polymerization of electrostatically self-assembled amphiplexes has not led to retention of the exact order as displayed by the unpolymerized amphiplexes. At 100 mM, the consistent hexagonal phases that are observed irrespective of the pentanol and dicyclopentadiene concentration point towards phase separation of the polymerized phase and this is confirmed by the swelling behavior. At 300 mM, there appears to be a partial retention of order but the swelling behavior reveals that all the phases exhibit the same range of unit cell sizes at all range of co-surfactant and oil concentrations. The same is true for the case of 500 mM and phase separation is a plausible explanation for the observed behavior of polymerized amphiplexes.

Achieving a 1:1 direct templating from the liquid crystalline phase to a solid polymer has been a formidable task and previous work aimed at retaining order within a mesophase upon polymerization has led to a disruption of phase [53], [54]. What is different in the present work is the fact that although phase separation is present, it has led to a material with defined long range ordered phase and uniform unit cell sizes as can be confirmed from the phase transitions and swelling behavior of polymerized amphiplexes at the different range of ionic strengths, co-surfactant concentrations and oil concentrations. The highly conserved order across all range of co-surfactant and oil variation suggests that although phase separation occurs, nanostructure is retained upon polymerization. Although this work is still less understood, a similar phenomenon has been reported in literature for the polymerization of acrylamide monomer within ordered microemulsions [55]. Polymerization of the monomer led to phase separation but the final polymerized product demonstrated order in the submicron to micron range.

Two possible speculations to explain the observed behavior can be made. The first is that mixing of the catalyst solution with the amphiplex leads to a disruption of ordered phase which is seen in the final structures. As the catalyst is mixed, the defined structure of the amphiplex is disturbed and as the polymerization occurs rapidly, these structures do not have sufficient time for equilibration.

Polymerization of dicyclopentadiene is a fast and highly exothermic reaction. Upon dissociation of the phosphine group from the Grubbs catalyst, addition of dicyclopentadiene to this reactive intermediate is highly favored. Thus the dicyclopentadiene present in the amphiplex would be pulled out of these equilibrium structures. This might result in the monomer oil forming a separate phase of its own which is seen as the polymerized material. The remaining polyelectrolyte and surfactant would form a separate phase which is detected during small angle x-ray scattering. Thus we hypothesize that the separation of the monomer oil during the polymerization reaction might be the reason for this observed transition. This could also explain the highly conserved hexagonal and lamellar phases observed. However further experiments need to be done to corroborate these explanations.

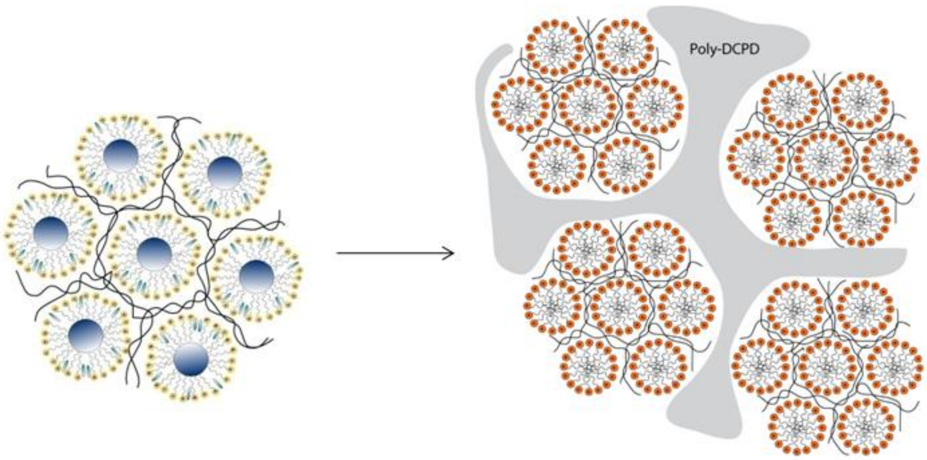

Figure 27: Separation of monomer oil during polymerization resulting in phase transition

Given that the transcriptive templating attempted here has not led to a perfect retention of order, the ordered phases observed here exhibit long range order and this order is conserved across varying various parameters such as ionic strength, co-surfactant and oil concentration. This could imply that the lyotropic structure of these amphiplexes perhaps governs the creation of the growing polymer chain thereby leading to the highly conserved hexagonal phases.

CHAPTER 4: CONCLUSION

Electrostatically self assembled amphiplexes have been prepared by swelling hydrophobic region of stoichiometric polyelectrolyte-surfactant complexes of sodium polyacrylate and cetyltrimethylammonium chloride with pentanol as the co-surfactant and dicyclopentadiene as the oil phase. Small angle x-ray scattering has demonstrated that these amphiplexes exhibit long range ordered structures under varying ionic strength and also at various concentrations of the co-surfactant and oil as noted from the phase diagrams and swelling behavior studies.

In an effort to capture the ordered nanostructure, ring opening metathesis polymerization of the monomer dicyclopentadiene has been achieved using the second generation Grubbs catalyst. Polymerization of dicyclopentadiene has been successfully delayed using catalyst poison. Polymerization of dicyclopentadiene in amphiplexes has been optimized through careful selection of reaction conditions.

X-ray scattering experiments have demonstrated that subsequent to polymerization, these self assembled amphiplexes illustrate structures with long range order at the nanoscale but different from that of the original amphiplexes. There has not been a one-to-one retention of order upon polymerization and results indicate occurrence of phase separation upon polymerization. Factors used to investigate the phase transition and swelling behavior; co-surfactant concentration, oil concentration and ionic strength had an insignificant effect on the phase and the swelling behavior of the final polymerized product.

Although the transcriptive templating attempted here has been unable to replicate the exact structures, polymerization in these ordered amphiplexes has led to polymerized structures which exhibit a highly conserved structure across varying parameters such as co-surfactant and oil concentrations.

Future Directions

The reported work is not complete and there exists much more untapped potential by exploring other avenues available at our disposal. The work presented here represents preliminary efforts at developing nanoporous materials by exploiting the diversity of long range ordered phases demonstrated by electrostatically self assembled amphiplexes. Examination of the structure using small angle x-ray scattering alone is insufficient. Transmission electron microscopy would allow a complementary corroboration of results obtained.

Recently, efforts towards development of photoactivated Grubbs catalyst have been reported [56]. Dissolving the photoactivable catalyst with dicyclopentadiene could potentially allow equilibration of the oil phase with the catalyst. Thus polymerization would be confined only to the hydrophobic regions allowing a better control over polymerization.

Since the amphiplexes developed here are thermally stable, temperature offers another window of opportunity towards successful polymerization and retention of order. Dicyclopentadiene can be maintained in the liquid state near 0^{o}C with addition of 5-ethylidene 2-norbornene as reported earlier. A solution of cooled dicyclopentadiene mixed with catalyst can be used as the oil phase for equilibration of electrostatically self assembled amphiplexes. After equilibration under cooling, the gradual heating of these amphiplexes would activate the catalyst and lead to polymerization. This is another way to confine the catalyst enabled polymerization inside the hydrophobic regions.

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