Pedagogical Issues Related to Macromolecular Self-Assembly

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Abstract

Pedagogical issues related to soft materials, including polymers and organics, provide a challenge in the areas of Chemical Engineering, Materials Science, and Materials Engineering. These challenges in education of macromolecular self-assembly will be addressed. Some of these issues involve classroom interactions using Mathcad and other software, classroom presentations, literature reviews and external presentations. A lesson plan is presented for incorporating novel pedagogical strategies for the introduction of concepts related to macromolecular self-assembly. Also included is a survey which provides data on student preferences in the areas of in-class lectures, student class presentations, and other learning tools.

Introduction

The topic of self-assembly is an interesting one that can offer engineering students a new way of looking at their curriculum. The topic itself is broad enough that many examples can be offered and used in a variety of educational settings, depending upon the needs of the instructor. The pedagogical challenges associated with engineering education and of the manner in which the polymerization mechanism and self-assembly can be used will be described. Additionally, examples of polymerization mechanism and self-assembly from the current literature are presented.

Supramolecular self-assembly is the process by which molecules are directed to create highly structured materials in a novel manner. In self-assembly processes, molecules are driven by thermodynamics to form complex macromolecules. This approach is important in the development of materials in many areas of technology including energy, biology, and the environment.

One example of a supramolecular polymer synthesis, which has been done in the Polymer Science and Engineering Laboratory at the University of Nevada, Reno is a supramolecular proton exchange membrane[1]. This membrane is used in hydrogen fuel cells. It offers a unique route in the formation of highly directional and nanostructured materials. These structures possess unique morphologies and are expected to allow the formation of submicron channels, or domains, which will increase the conductivity of protons. The synthesized polymer is supramolecular because of hydrophobic / hydrophilic interactions between the sulfonated polyamide (hydrophilic) and the PBI (hydrophobic) segments. In Figure 1, the hydrophobic and hydrophilic regions of the polymer are shown. These polymers are expected to form “lameller” or layered structures. Also, there is hydrogen bonding between the amphiphile (PDP) and the sulfonic acid group. Proton transfer occurs between the sulfonic acid group and the nitrogen heterocycle in PBI. Mechanical shearing provides orientation within the membrane, shown in Figure 2. Channels of hydrophobic and hydrophilic regions are formed during shearing. These regions provide different proton conductivities in the radial and tangential directions. Therefore, enhanced proton conductivity results tangentially. It is more difficult for protons to cross over the hydrophobic bands formed within the membrane.

The notion of polymer self-assembly relates to the basic chemical engineering curriculum at the University of Nevada, Reno. Examples of such systems can be applied to many of the core classes, thereby introducing the students to new applications for the material they are studying. For instance, freshmen take a series of introductory courses that give an overview of the field of chemical engineering and of the courses that they will take as they continue through the curriculum. Polymer processes and materials can be introduced as part of this cursory introduction in order to excite students to new developments in their field.

Other courses in the curriculum can benefit from using such polymer topics as well. In the transport phenomena series, polymer examples can be used when discussing the topics of viscosity, momentum transfer, or diffusion. Polymer examples are a natural fit for a thermodynamics course as self-assembly is directed by changes in the Gibbs free energy of the system due to the formation of covalent bonds as well as the formation and breaking of non-covalent bonds. Physical properties such as the glass transition temperature can be discussed as can the maximum swelling of a polymer, expressed by the Flory equation, due to a balance in its thermodynamic forces due to solvent swelling and the elastic forces which resist them[2]. A course in reaction kinetics could benefit from concrete examples involving polymer self-assembly.

Besides the chemical engineering curriculum, there are many examples of self-assembly. For instance, the formation of nanotubes[3] is of particular interest to material engineers and mechanical engineers. Also, there are numerous examples of self-assembly in the life sciences and include protein folding and nucleic acid formation.

With so many exciting examples available, it can be difficult to find a way to effectively present the topic of polymer self-assembly, but there are a number of ways to approach this. One can look to the variety of learning elements to determine how this topic of self-assembly can be incorporated into that hierarchical structure. One such structure is the popular Bloom's taxonomy, which has been used extensively since its introduction and continues to be applied in various forms today. Benjamin Bloom introduced what he called a taxonomy of the "cognitive domain", which divided learning objectives into six broad categories that include knowledge, comprehension, application, analysis, synthesis and evaluation[4]. Each successive level of Bloom's taxonomy involves more and more complex learning behaviors.

Bloom's Taxonomy and Learning Style Models

The first element of Bloom's taxonomy is "Knowledge" which is defined as the process of retrieving information from memory[4]. In other words, knowledge is the storage and recall of definitions and facts. At this basic level, students can begin to learn about the topic of polymer self-assembly through a set of basic definitions and examples. This step is important for all students that are new to a topic, but may be especially useful to freshmen in an introductory class as a novel example of a chemical product.

Next is "Comprehension", the largest group of skills from the taxonomy. Comprehension involves taking in new information from a source (whether it be verbal, written, symbolic, or experimental) and understanding meaning. Additionally, the comprehension level includes the acts of translation (putting information into one's own words), interpretation (reorganizing ideas), and extrapolation (using knowledge to make predictions)[4]. This element, then, comprises the bulk of a student's basic learning through lectures and readings.

The third element "Application" involves the use of the previous two elements. At this level, students are able to generalize comprehension and use the knowledge in an appropriate manner[4]. Working simple problems from a textbook is one example of this level, as students' learn from putting the material into practice.

"Analysis" is the fourth element of Bloom's taxonomy where students find relationships among parts of knowledge. In particular, they utilize comprehension and evaluation to compare and contrast ideas[4]. Fabrication of variations of self-assembled polymer by systematically varying the temperature and pressure is an example of analysis.

The fifth element is "Synthesis" and it is defined as the use of the all of the previous elements learned, combining and forming them into new organizations, ideas, and material. The process of synthesis requires some degree of creativity, in that new connections are made between the materials learned[4]. Synthesis activities typically involve communicating ideas. The conceptualization of the addition of functional groups to a polymer backbone which would result in self-assembly is an example of synthesis.

The last element in Bloom's taxonomy is "Evaluation". This category is defined as the critical examination of the materials learned for the purpose of making an opinion or forming a qualitative or quantitative judgment. When students are using Bloom's evaluation element, they are thinking independently, making extrapolations based upon their learning at all other levels[4]. Selection of the reactants for the self-assembly process require high level of understanding and is therefore part of the evaluation concept.

There may be a tendency for educators to look down on those most basic elements of the taxonomy (knowledge and comprehension) and instead focus on higher elements (synthesis and evaluation). The elements of the taxonomy, though, all depend on the other elements. A foundation of learning must first be must exist, set by building strength in the seemingly trivial elements, before the higher elements can be explored in depth. A student of organic chemistry often begins learning through a system of rote memorization, drilling repeatedly with flashcards to retain the names and particulars of a list of reactions. Once knowledge is achieved, comprehension and application can occur through further lecturing, reading, and lab experiences.

Taken individually, undergraduate classes generally promote Bloom's elements of knowledge, comprehension, and application, with an emphasis on lectures, homework, and exams. Graduate classes, on the other hand, tend to emphasize analysis, synthesis, and evaluation in the coursework, as less class time is reserved for lecture. This frees more of the class for discussions where these elements can be explored while knowledge, comprehension, and application are left for outside study. An example of the difference between the undergraduate learning of concepts related to self-assembly is that they will focus more on application such as monomers which are presented in the literature and at the graduate level the focus will be more on consider of new functional groups.

While Bloom's taxonomy addresses the different elements of learning, it does not help to explain how to best present material to students. Attempts have been made to characterize students by the manner in which they learn best, dividing students based upon their preferential ways of absorbing new information[5-9]. Although there is some controversy regarding the very idea of learning styles[8], such models still have utility in the design of a classroom curriculum. The central theme of all learning style models is that students learn differently and that, by recognizing and addressing these differences, can learn more effectively[10-13].

One learning style model is termed the Visual, Aural/Auditory, Read/write, and Kinesthetic, or VARK model[9]. Based on VARK, students are categorized into four learning styles: Visual, Aural/Auditory, Read/write, and Kinesthetic. Students who predominantly have a visual learning style tend to catch information most easily through charts, graphs, flow charts, pictures, and symbolic arrows. For students with a preference for aural/auditory information, it is helpful to learn via group discussion, lectures, tapes, web chat, and speaking. The read/write type of students is able to learn most effectively through reading the textbook and from taking the time to write notes covering important material. Students with a kinesthetic learning style learn and gain a better understanding of some problems by experience and practice. For instance, kinesthetic students may benefit most by practicing some lecture material in a hands-on, laboratory setting[9]. For students who favor visual learning the chemical structures of the reactant molecules and microscopy results will provide a deeper understanding of the self-assembly process.

Another model of learning styles is that proposed by Felder and Silverman[7], who looked specifically at engineering education. The model contains four scales each of which reflects a student's particular element of their learning style. They are: (1) sensory versus intuitive learners, (2) visual versus verbal learners, (3) active versus reflective learners, and (4) sequential versus global learners[7]. Each of these metrics is a continuum, reflecting the degree to which a student falls into either category.

Sensory learners tend to prefer facts and other concrete information while intuitive learners tend to prefer more abstract material like theories or mathematical models. Visual learners are defined by their preference to images and demonstrations while verbal learners get the most out of lectures. Engaged discussions are best for active learners while reflective learners are more introverted and perform best when given time to process the material in private. Lastly, sequential learners require structured lessons that progress in increments. Global learners, instead, often need to know the "big picture" before understanding how new material fits into what they already know.

It has been demonstrated that many professors have teaching styles that are significantly different than the learning styles of their students and design their courses based upon their own preferences[8, 11]. For instance, most science and engineering classes are taught primarily as a series of lectures, favoring those students who are intuitive, reflective and sequential learners. However, it is reported that the majority of engineering students are active and sensory learners[8]. While it is impossible to design a course which addresses the learning styles and needs of each individual student, teaching methods that address many styles of learning are shown to be more effective than those that do not[8, 11, 13].

For the topic of self-assembling polymers, the variety of learning styles can be addressed in a number of ways. Both visual and verbal learners can benefit from a lecture that has many examples of self-assembly through verbal description along with diagrams showing the mechanism. Physical models showing the polymer chain or the complex can help as well. Sensory and intuitive learners can both be accommodated through course material that balances concrete facts and calculations with the underlying theory. For instance, a discussion on the formation of self-assembling polymers may contain calculations for the determination of the specific volume of a polymer in various solvents, a discussion of the ideas of excluded volume in both a good solvent and a Theta solvent, and how this affects the process of self-assembly[2]. Active learners would benefit from discussing their solutions to important homework problems, while reflective learners would be comfortable with the time spent in preparation of their solutions. Finally, global learners could be accommodated through discussions relating polymer engineering to highlights from previous courses (thermodynamics, fluid dynamics, heat transfer, mass transfer, reaction kinetics, etc).

Once the different ways that students learn are observed, the quality of their learning can be examined. Felder suggests[8] that student learning can be defined as "superficial", "deep", or "strategic" and that the deep approach to learning, where understanding the material is more important than simply memorizing it, is the most rewarding. Students with a superficial learning approach, on the other hand, are concerned with learning in as much as simply to get through the course, or to gain just enough knowledge so as to solve a homework problem. Strategic learners are organized and efficient and strive for achievement for the sake of being on top rather than for an understanding of the material.

Students can be motivated into going beyond the simple, superficial learning approach through a number of techniques. For instance, using inductive teaching methods[8], where students learn through somewhat large problems or projects, can stimulate a class. Also active learning[8], such as where students lead discussions regarding homework solutions, can motivate a deep approach to learning. Cooperative learning[8] can be useful as well, where class projects, working together on homework, or collective discussions of topics and underlying principles. For the polymer engineering course there are opportunities for all of these approaches. Students must frequently discuss their homework solutions as well as the underlying theory and physics related to the problem. Collaboration also often occurs through these discussions. Lastly, opportunities for active learning are available as both undergraduate and graduate students often have the option of working with the professor and graduate students of the polymer engineering research group, helping to see their classroom knowledge applied to real problems. An example of superficial learning might be the memorization of the chemical reactions which take place, while deeper, strategic learning would be exemplified by identification of new monomers for the synthesis.

Integration of Theory Into the Classroom

There are many pedagogical challenges related to polymer education. For instance, the field is constantly evolving, bringing new technologies and new materials. Other chemical engineering departments are looking for new ways to expose students to this exciting topic, such as through composing learning modules that introduce "cutting-edge" content[14]. Ultimately, though, the solution to the pedagogical challenges faced in macromolecular self-assembly lies in the ability to touch and feel the unique materials that are synthesized using these approaches. Students are able to use their tactile and visual capabilities to a greater extent than for more subtle problems in chemistry, physics, and mathematics. Another aspect relates to relevancy or global impact. Students understand that advanced materials are useful in emerging applications including: energy, biomedical, and environmental

To help with the development of a learner-centered module on the topic of supramolecular self-assembly, the schematic shown in Figure 3 was created. This figure presents the main elements of the integration approach for teaching the concepts of macromolecular self-assembly. The "learner centered" ideas are characterized by the learning styles listed in the center of the figure. The learning elements include: in-class lectures / student presentations, laboratory experiences, textbook, and exam / homework content. Within the laboratory experience area, experiments related to emulsion formation and phase separated membranes will be presented. Several classroom elements were devised to support the varied learning styles of the students and to help ensure a teaching approach that integrates the needs of the students with the needs of the subject matter.

A survey, shown in Figure 4, was given to the students of the Chemical Engineering 406 polymer science and engineering class in an attempt to explore ways of meeting their preferred learning styles and to improve the class structure. Questions focused on measuring the perceived usefulness of six learning tools: textbooks, lectures, homework, student class presentations, laboratory practice, and exams. Within each of these categories, options were presented to cover a variety of learning styles. The average response value of each question is also shown.

From the results of the survey, it has been determined that the preferred method of learning is through the textbook. Students expressed interest in having a book that provides lots of solved example problems. Additionally, students preferred to gain practice through end-of-chapter problems. On the other hand, students showed a preference for such problem solving over the inclusion of more theory and abstract concepts. This may indicate that the students who participated in the survey prefer a sensory learning style.

Students expressed an interest in using class-time to present and discuss their homework solutions to the class instead of exploring and presenting related topics through their own literature reviews. Students also expressed an interest in sticking closely to the textbook and its problems and the challenge of creating their own assignments was not expected. Furthermore, the utilization of class time for problem solving rather than through traditional lectures to understand self-assembly issues was a top choice of the students. In class demonstrations of self-assembly processes, such as an experiment related to emulsion formation and phase separated membranes, was the highest choice to facilitate self-assembly understanding. For the final tool concerning exam issues, a take-home format and/or open book exams were preferred than close book and in class exams. These results would indicate the desire for a reflective learning environment.

In order to address these issues while still maintaining a course that acknowledges the variety of learning styles, a sample lesson plan was created (Table 1). In it, the area of supramolecular self-assembly is broken down into topics and corresponding student activities. These activities are examined to see how they relate to Bloom's Taxonomy.

Much of the introductory material involves learning in the knowledge, comprehension, and application domains of the taxonomy. This is to be expected, as a foundation of understanding must be present before the other levels of the taxonomy can be utilized. With the introduction of calculations and problem solving, Bloom's analysis level is developed. Lastly, the exploration of the topic through laboratory experiences can bring the remaining elements of the taxonomy, synthesis and evaluation, into the class experience.

Differences in learning styles are addressed as well. Active learners get a chance to engage the material through the lab experiences while those that are reflective learners may prefer the readings and the lectures. The topic of polymer self-assembly is ripe for both sensory learners and intuitive learners. Demonstrations and laboratory experiences would be ideal for those students with a sensory preference while the underlying thermodynamic concepts may appeal to the intuitive learners. The characterization of polybenzimidazole phase separated membranes is an example of appeal to student with sensory learning style. Global learners can see how the topic of self-assembly fits into the overall framework of thermodynamics and polymer chemistry through homework problems, lectures, and laboratory experiences. Sequential learners may rely on the textbook to satisfy their learning style preferences

Conclusions

The pedagogical challenges associated with macromolecular self-assembly and the connection to supramolecular chemistry is discussed. Issues related to learning style and how they related to many areas within chemical engineering are included. The relationships of learning are connected to Bloom's Taxonomy. An integration scheme is presented showing the 'learner centered" relationship to pedagogy. A survey was carried out which determined student preferences for learning the module of macromolecular self-assembly. Based on the results of this survey a lesson plan was created in order to efficiently present the content. Students emphasized the importance of solved problems in the textbook for increased learning.

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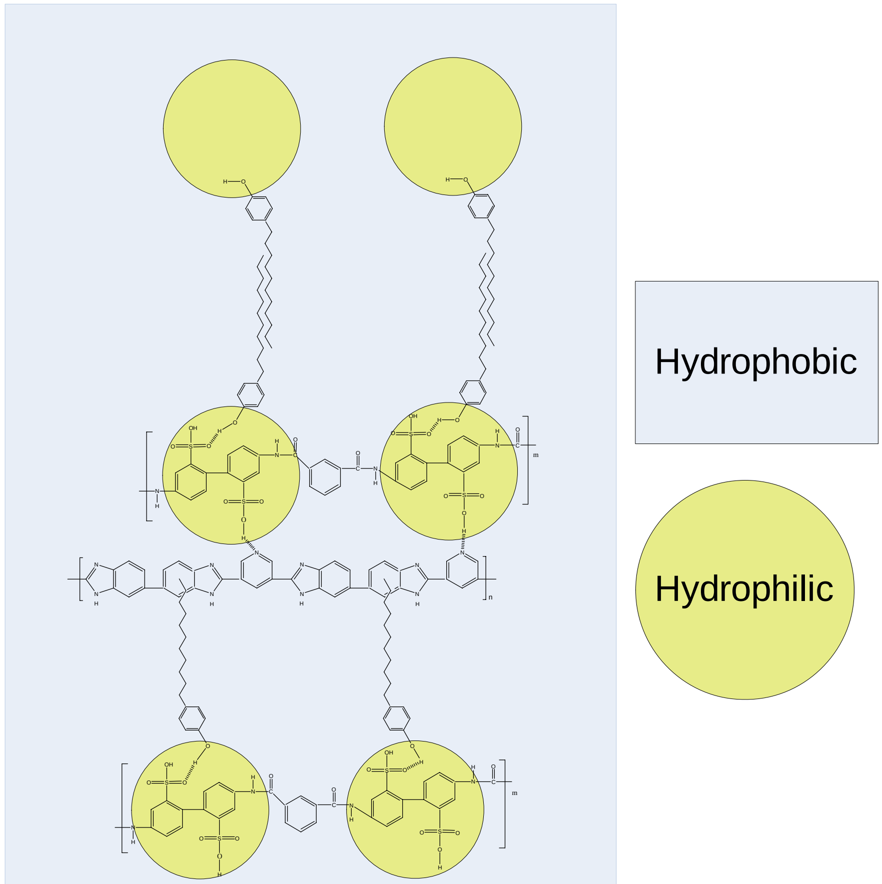

Figure 1: Representation of the hydrophobic and hydrophilic region of PBI and sulfonated polyamide[1].

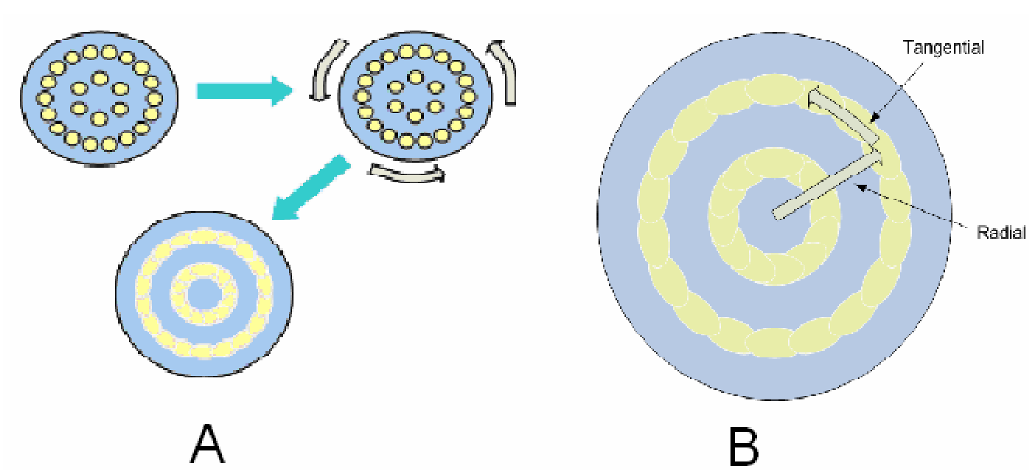

Figure 2: A) Illustration of shearing process. B) Illustration of Conductivity measurement in tangential and radial direction[1].

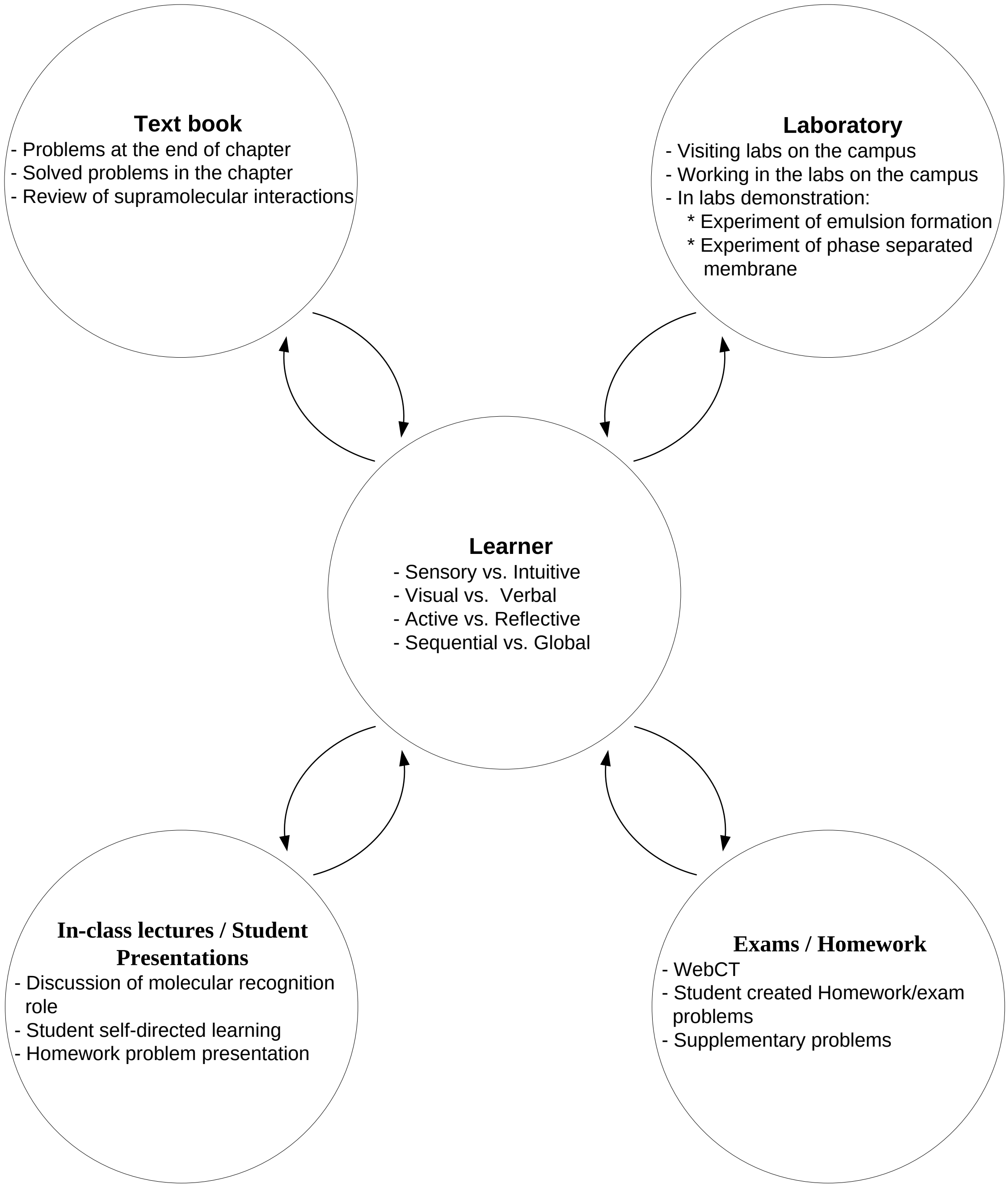

Figure 3: Integration scheme showing the relationship of the learner to pedagogical tools.

Figure 4: Survey and Results for Undergraduate Polymer Science and Engineering Class

Macromolecular self-assembly is the process by which molecules are directed to create highly structured materials in a novel manner. This approach is important in many areas of technology including: energy, electronics, biology and environmental applications. This complex topic is based on an understanding of issues involving chemistry, physics and thermodynamics of materials.

The purpose of this survey is to determine how to best modify the CHE 406 (Introduction to Polymer Science and Engineering) course in order to incorporate this concept into the class. It is requested that you indicate which areas you consider to be the most important to provide high quality learning of this topic by circling the appropriate rating below. (5 is most useful and 1 is least useful):

What learning tools would be the most useful for this topic?	Average points
a) Text book	
1) Many problems at the end of the chapter	3.47
2) Many solved problems in the chapter.	4.33
3) Additional readings beyond textbook	2.87
4) Theory rather than problems	2.80
5) Review of supramolecular interactions	3.40
6) Class notes	4.00
b) Laboratory	
1) In class demonstrations	
Experiment related to emulsion formation	3.00
Membrane which phase separates	3.00
3) Visiting labs on campus	2.80
4) Working in labs on campus	2.80
5) Plant trips	2.33
6) Students hypothesize how to create macromolecular self assembled materials	2.40
c) Student class presentations	
1) Literature review	3.13
2) Homework problem presentations	3.47
3) Assigned topic presentation	3.20
d) Homework	
1) End of chapter problems	3.53
2) Supplementary problems to bring in additional concepts	3.20
3) Student created homework problems	2.47
e) In-class lectures	

1) Problem solving	4.13
2) Discussion of connection to thermodynamics: enthalpy/entropy	3.40
3) Discussion of role of molecular recognition	3.40
4) No lectures at all	1.47
5) WebCT based	2.27
6) Student self-directed learning (students teaching other students)	2.73

f) Exams

1) Student created exam problems	2.40
2) In class	3.33
3) Take home	3.80
4) Quizzes	2.73
5) WebCT	2.07
6) Open book	3.80
7) Close book	2.73

Additional Comments:

Table 1: Lesson Plan for Module on Macromolecular Self-Assembly

Lecture Content	**Student Activity**	**Bloom's Level**
Introduction – definition of macromolecular self-assembly	Lecture – Energetics, chemistry, characterization. Literature review – ACS and APS journals	Knowledge Comprehension Application
Supramolecular Polymers	Textbook – Principles of Polymer Systems - Rodriguez	Knowledge Comprehension Application
Molecular Recognition	Utilizing antigen / antibody interactions Molecular imprinting	Knowledge Comprehension Application
Thermodynamic Issues: enthalpy / entropy balance	Students calculate free energies	Comprehension Application Analysis
Examples: a) experiment related to suspension polymerization, formation b) phase separated membrane	Laboratory experience – suspension polymerization with fluorinated monomers, Laboratory experience – characterization of phase separated polybenzimidazole membrane. Laboratory experience – Thermal analysis, dynamic mechanical analysis and differential scanning calorimetry Laboratory experience – atomic force microscopy to image nanostructured materials	Comprehension Application Analysis Synthesis Evaluation
Applications: a) Energy b) Environment c) Biological d) Intelligent	Field Trip – Ballard Corporation, Vancouver, B.C. Laboratory experience – supramolecular polymer gels Laboratory experience – synthesis proton exchange membrane, Laboratory experience – use proton exchange membrane in a fuel cell.	Comprehension Application Analysis Synthesis Evaluation