PART B

INDEPENDENT PROPOSAL

Liquid Crystalline Dendrimers with Multi-functional Groups

Note: The independent proposal is an exercise designed to evaluate the ability to synthesize an original problem and will not be performed as part of the dissertation. The Department of Chemistry issues guidelines for this section, and in our research group these are augmented with American Chemical Society guidelines. This proposal is written in the format of an ACS type AC grant disregarding the word limit, citation format, and spacing requirements.
PRF#____________

AC

THE PETROLEUM RESEARCH FUND
AMERICAN CHEMICAL SOCIETY
1155 16th Street, NW, Washington, DC 20036

PROPOSAL SUBMITTED FOR CONSIDERATION FOR A RESEARCH GRANT

TYPE AC

(Please refer to Page 3 for statement of eligibility, terms and conditions.)

PRIVILEGED COMMUNICATION

This proposal is intended for review exclusively by ACS-PRF staff, members of the PRF Advisory Board and outside reviewers officially asked to furnish scientific comments. It may not be transmitted to other parties, copied, or retained for future reference. Please return to the PRF office, or destroy, in accord with instructions.

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Brief Descriptive Title of Proposed
Liquid Crystalline Dendrimers with Multi-functional Groups

Requested Start Date:     Feb 1, 2005     End Date: May 31, 2007

Amount Request: $30,000       $30,000       = Total $60,000
(First year)        (Second year)

Principal Investigator: ____________________________________________________  (Signature)  (Date)

Officer of the Institution
Endorsing the Proposal:
__________________________________________________  (Signature)  (Title) (Date)
I. PERSONAL AND PROFESSIONAL VITA

a. Indicate academic degrees, when and where received; previous faculty and other principal positions; awards and honors; and other pertinent biographical material. A selected list of recent publications from the last five years should be included or attached.

- Ph.D. Chemistry Louisiana State University, USA 2005
- M.S. Chemistry Shandong University, P.R.China 1997
- B.S. Chemistry Qingdao University, P.R.China 1994

Publications from last 5 years: They are ready to be published.

b. Do you currently hold a tenured or tenure-track position? No
   If not, please explain the nature of your position. Graduate Student

II. RECENT RESEARCH ACCOMPLISHMENTS

(Provide a brief narrative statement indicating the nature of your current and recent activities. These activities need not be related to the research proposed herein.)

We are studying the self-assembly of amphiphiles such as arborol gels, poly-peptides and lipids. Two directional arborol ([9]-10-[9]) forms gel in water. We found that the assembly size of arborol in dilute solution could be controlled by filtration and increased day by day because of its self-assembly. By adding one-directional arborol ([9]-6) the speed of self-assembly was reduced. In addition, we have been studying the size change of liposome (DOPC) by adding various amounts of [9]-10-[9]. The main techniques used include dynamic light scattering, static light scattering, and fluorescence photobleaching recovery, but other supporting techniques are available. The present proposal is not related to these projects.

III. CURRENT RESEARCH ACTIVITIES

a. List any active research grants or other financial support received for research. Give titles, amounts (annual direct costs; if more than one PI, indicate only your share of the granted amount), sources, time, periods of awards, and relationship to this PRF proposal. Use separate page if necessary; indicate “none” if applicable.

   None

b. List any other research grant applications pending. Give titles, amounts requested, sources and relationship to this PRF proposal. Use separate page if necessary; indicate “none” if applicable.

   None
c. How many graduate students are currently doing research with you? 2

d. How many post-docs are currently doing research with you? 3

e. How many undergraduates are currently doing research with you? 4

IV. SUGGESTED REVIEWERS

Please furnish the names and complete addresses of at least four experts in the field of the proposed research, whether or not you are known to them. Do not include collaborators, former mentors, former students, or colleagues at your current or former institutions. Include the first name, middle initial (if any), and full current mailing address with zip code. It is suggested that you include the names of experts residing in the United States.

Listed in alphabetical order:

Professor Gudrun Schmidt, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803
Professor Paul Russo, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803
Professor Robin McCarley, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803
Professor Robert Hammer, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803

V. THE PROPOSED RESEARCH

Abstract

A new liquid crystalline dendrimer with multiple meso-groups on a carbosilane dendrimer matrix is designed. Three different type meso-groups, schift base type, biphenyl type with chiral carbon and azobenzene type, will be synthesized and attached with various mole ratios on a carbosilane dendrimer with 12 arms each of which features a 6 carbon chain cushion. The chemical structure of the final product and intermediates will be characterized by FT-IR, NMR and MALDI-TOF. Polarized optical microscopy (POM) with hot stage, differential scanning calorimetry (DSC) and X-ray diffraction will be used to study the liquid crystal phase properties. Dielectric measurements and electooptical invetigations will be carried out to understand the final dendrimer better.

Introduction

Liquid Crystal: “Over the past 30 years 'liquid crystals' have gone from being an academic curiosity to the basis of a $15 billion display industry - from watches and calculators to mobile phones and lap-top PCs. Before long they are expected to replace cathode-ray tubes in televisions. All this has been made possible because of the developments in liquid crystal materials.”—by David Coates
It is well known that substances have three states, gas, liquid and solid. Liquid crystals are materials having both long-range ordering like crystals and flow properties like liquids. Liquid crystal materials were discovered in 1888 by an Austrian botanist, F. Renitzer when he studied the cholesteryl benzonate. O. Lehmann found its birefringence properties and named it as liquid crystal. Liquid crystal materials are extensively developed in the past thirty years because of their application in electronically driven displays.

There are two main kinds of liquid crystals based on the type of phase transition: thermotropic and lyotropic. A thermotropic liquid crystal exhibits phase changes that relate to the change of temperature (Figure 1). A lyotropic liquid crystal depends on the solvent and its concentration (1). While thermotropics are presently mostly used for technical applications, lytropics are important for biological systems, e.g. membranes. In this research we mainly focus on thermotropic liquid crystals.

**thermotropic liquid crystals**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Crystal</th>
<th>Liquid Crystal (mesophases)</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-D lattice</td>
<td>orientation</td>
<td>fluid</td>
<td>isotropic</td>
</tr>
<tr>
<td>solid</td>
<td>1- (2-)D lattice</td>
<td>orientation</td>
<td>fluid</td>
</tr>
<tr>
<td>anisotropic</td>
<td>anisotropic</td>
<td>anisotropic</td>
<td>isotropic</td>
</tr>
</tbody>
</table>

**Figure 1:** liquid crystalline mesophases between the solid and isotropic liquid phase (From: [http://moebius.physik.tu-berlin.de/lc/lcs.html](http://moebius.physik.tu-berlin.de/lc/lcs.html))

Several liquid crystalline phases are known to date. They can be divided into nematic, smectic phases. At isotropic state the rod-like molecules are randomly distributed. At nematic phase, the rod-like molecules have an orientational order which is perpendicular to the layers and also called director (Figure 2). The smectic phase has orientational orders both in layer and among layers. The flow intensity is disappearing as the molecules are gaining order. Eventually the molecular can’t flow anymore at solid state.
Figure 2. Schematic drawing of anisotropic (rod shaped) molecules in the solid (3D order), smectic (2D order) and nematic (1D order) liquid crystal and isotropic liquid (zero order) phases (From: http://www.rsc.org/lap/educatio/eic/2000/coates_nov00.htm#x)

The range of liquid crystal phase is always a hot topic. MBBA (4-methoxy benzylidene-4′-butylaniline) is the first room temperature nematic liquid crystal (2, 3), but the temperature range is short (4). It is then discovered that eutectic mixtures of MBBA with other compounds in its homologous series could broaden the temperature range to extend from below -40 degree centigrade to over 100 degree centigrade. Though the mixtures are unstable and not useful in display at the beginning, it gives a creative suggestion for the liquid crystal display. After several years’ investigation, stable, lower transition temperature and wider range liquid crystal mixtures are prepared and ready to be used (5-8). Now almost all of the liquid crystal displayers, such as Twisted Nematic (TN), Supper Twisted Nematic (STN), Thin Film Transistor (TFT) and so on are using liquid crystal mixtures.

**Dendrimer:** Now dendrimer is a well accepted name for highly branched, monodisperse compounds. Newkome and Tomalia prepared dendrimers around the same time separately in the beginning of 1980’s (9-12). From then on, dendrimers have been rapidly expanding for both basic and applied reasons. Dendrimers have their advantage to the traditional liner polymer because their size and architecture can be well controlled. They have many chain-ends that can be functionalized so they can be constructed with discrete domains having different properties. They can be used as nanoscale catalysts and reaction vessels (13, 14), micelle mimics, agents for delivering drugs into cells, chemical sensors, light sensors (15), adhesives and coatings and so on.

According to the way in which the dendrimer grows, there are two main ways to synthesize dendrimers, divergent and convergent. In the early dendrimer syntheses, the divergent way was predominant. It starts from a reactive core, a generation is grown, and then the new periphery of the molecule is activated for reaction with more monomers. The two steps can be repeated. The convergent way begins at what will end up being the surface of the dendrimer, and works inwards by gradually linking surface units together with more monomers. When the growing wedges are large enough, several are attached to a suitable core to give a complete dendrimer. For both divergent and convergent ways the reactions have to be performed at many sites on the same molecule simultaneously. It is very important to keep the reaction very clean and high yield (16-21).
**Liquid Crystalline Dendrimer:** Liquid crystalline dendrimers refer to dendrimers that have liquid crystalline properties.

We will use one carbosilane dendrimer (19, 20) as scaffold and functionalize it by putting meso-groups on its surface. As we discussed in the liquid crystal part, mixtures of liquid crystals are used in the LCD to get a wider transition temperature than single liquid crystal. We plan to put two or more different meso-groups on the same dendritic scaffold. By doing this, the good liquid crystalline properties of small molecules liquid crystals are united with the good material properties of dendrimers. With various meso-groups such as chiral group and azo-group, on the same dendrimer, a nanoscale molecule with multi-functions can be prepared. The development of liquid crystalline dendrimers can be an exciting design to prepare advanced functional materials that self-organize into materials with desirable functionalities and physical properties at nano- and mesoscopic length scales. It also can be an approach to get advanced materials with low cost.

**Results of Previous Studies**

Since this is a new area of research for our group, we do not have any preliminary data. We will present some of the data from references (22-29) to demonstrate the capabilities of this method. In 1996 Zhang’s group (23, 24) prepared liquid crystalline dendrimers with 12 azobenzene meso-group terminals on a carbosilane dendrimer. In the next year they reported another liquid crystal crystalline dendrimers with 12 chiral meso-group terminals. Bobrovsky (22) studied the photo-optical behavior of an eight-terminal azobenzene liquid crystal dendrimer. Both of these groups found the wider temperature range of liquid crystal behavior. Figure 3 gives the structure of the liquid crystalline dendrimer and its possible packing scheme in the smectic phase.
Figure 3. (a) Structural formula of the dendrimer of the first generation with azobenzene end groups and (b) Scheme illustrating the packing of dendrimer molecules in the SmA phase. (Adapted from Bobrovsky, A. Y.; Pakhomov, A. A.; Zhu, X. M.; Boiko, N. I.; Shibaev, V. P. Polymer Science Series A 2001, 43, 431-437.)

Tsiourvas’ group (26-28) also found that a broad thermal range of SmA phase (from 150 up to 210 °C) when they functionalized the poly(propylene imine) dendrimers with cholesterol moieties. His group also identified a new mesophase type with unique properties from a carbosilane based dendrimer with banana-shaped mesogenic units. The new mesophase was stable and had a low conductivity, and the liquid crystalline phase occurred over a broad temperature range.

Recently Saez and Goodby reported a new class of Liquid crystal with two different halves, chiral and achiral halves (30). ‘The new liquid crystals selectively reflected light and could be used in filters and coatings.’ They could made materials with molecule weight 14,000 Da and the mesophases of the materials existing from room temperature to 80 °C.

With condensed functional groups on a matrix, the liquid crystalline dendrimers could enhance the performance of small molecular liquid crystals, even provide unexpected functions.
VI. RESEARCH PLAN

It is proposed to use a 1st generation carbosilane dendrimer what has 12 arms as matrix and meso-groups are linked to this matrix through an aliphatic spacer composed of six methylene units. Meso groups are listed in Figure 5.

1. Preparation of Carbosilane Dendrimer

The 1st generation carbosilane dendrimer will be prepared according to Zhang’s paper (23, 24). The procedure is indicated in Figure 4.

![Figure 4 Scheme to prepare 1st generation carbosilane dendrimer](image)

2. Preparation of Meso-groups

There are only three meso-groups in Figure 5, but more options can be tried besides these three. The schift-base type meso-group is selected because of its low transition point and it is widely used in TN type displayer. Biphenyl type one has chiral group which has ferroelectric potential, and the azobenze meso-group has non-liner potential and can form complex with platinum or other transitional metals to be used as carriers of catalysts. The proposed procedures to prepare these meso-groups are shown in Figure 6.
Figure 5. Meso-groups used in this project

One option to prepare the meso-groups are listed in Figure 6.

1. \[
\text{HO-}
\text{CHO + H}_2\text{N-}
\text{CHO + H}_2\text{N-}
\text{Schiff base type meso-group}
\]

2. \[
\text{HO-}
\text{OH + Br-}
\text{Biphenyl type meso-group with chiral carbon}
\]

3. \[
\text{H}_2\text{N-}
\text{NO}_2 + \text{HNO}_2
\text{Azobenzene type meso group}
\]

Figure 6. Synthetic Scheme of meso-groups

3. Put Meso-groups on the Dendrimer
The meso-groups react with $\omega$-bromohexanol respectively to get the corresponding meso-units (See Figure 7).

![Figure 7 Scheme of preparation of Meso-units](image)

The meso-units are added one by one and react with the dendrimer matrix in certain mole ratio. The ratio of meso-units is changeable. Figure 8 gives an example. The mole ratio of shift base type meso-unit to biphenyl one to azobenzene one and to dendrimer matrix is 6:4:2:1 respectively. If the attaching process starts from shift base type meso-unit, there are at least 10 conformations of the final compound. One of the possibilities is indicated in Figure 8. As we mentioned in the introduction, usually the liquid crystals are used in mixture to get a broader liquid crystal phase, so the existence of different conformations will be ignored for this reason.
Figure 8. Attaching meso-unit to the dendrimer
4. Characterization

The regular instruments such as FT-IR, NMR MALDI-TOF etc. will be used to confirm the completion of reactions and the chemical structures of the products. Polarized light optical microscopy (POM) with hot stage, differential scanning calorimetry (DSC) and X-ray will be used to study the liquid crystal phase properties, dielectric measurements to get the dielectric constant $\varepsilon_1$ which is important parameter of the current response of liquid crystals. Electro-optical investigations can be carried out in transparent sandwich type capacitor cells consisting of two indium-tin oxide (ITO) coated glass plates (Thickness = 5 µm). Nonlinear optical effects (NLO) and ferroelectric (FE) properties will be checked.

VII. FUTURE WORK

The liquid crystalline dendrimers react with transitional metal, and the product can be tried as catalyst for heterogeneous reaction. The Varying the chain length between the meso-groups and matrix, using high generation dendrimers, trying different meso-group ratios can be tried.

VIII. SUMMARY

A new liquid crystalline dendrimer with multiple functional groups is designed. By putting small molecule meso-groups on a carbosilane dendrimer, the good functionality of small molecules and advance material properties of dendrimer might be united to obtain a new product with wider liquid crystal phase range, higher response speed and lower threshold pressure. These materials can, therefore, be utilized in liquid crystal displayers, optical sensors, catalysts carriers or some other applications.

Reference List


