M98-G8
MOLECULAR SPINNERETS FOR POLYMERIC FIBERS

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GOAL/ABSTRACT

The objective of this work is to investigate, design, and synthesize molecular spinning machines that can be shaped in the form of membranes which can control fiber structures and produce nanofibers. Using this design entire spinning units and associated systems, which currently occupy two or three floors, can be made to fit in a small room. Fibers with custom designed structures and properties can be spun with extreme precision and very fine fibers can be spun using this technique. The energy requirements will be diminished by an order of magnitude. The drawing process can be eliminated altogether. Start up and transition time for spinning different polymers will be reduced significantly thus reducing the waste. Eventually, polymerization and spinning can be combined into a single small unit. The development of this technology can revolutionize the fiber, textile, and apparel industry. Identification and development of unique discotic molecules is the key for constructing molecular spinnerets. Using synthetic and computational tools we are developing discotics and discotic membranes. We have synthesized a candidate discotic structure already, and we are using it to build a first generation molecular spinning machines (fig 4).

TECHNICAL DETAILS

The proposed research is directed toward applying advances in nanotechnology in the manufacturing of fibers, an integral component in the Fiber, Textile, and Fabricated Product Complex. The basic idea behind nano-machines has been to tailor a material to function like a machine [1]. Molecular interactions are the basic building blocks of this technology. Naontechnology has been increasingly applied to inorganic systems, especially in microelectronics [2-4]. Also, new developments have been made in relation to nano-tubes, molecular gears, etc [5-9]. Computational and synthetic methods are the two key components in the development of nanotechnology. Computational methods, especially molecular mechanics and dynamics, are employed to design the nano-system theoretically [9-12], and high precision chemical/material synthesis is employed to prepare the system in the laboratory.

The nano-spinning “machine” which we envision consists of a membrane containing discotics (large ring-like columnar organic molecular structures) positioned at designed locations. Discotics are liquid crystals, which are a recent development in synthetic polymer chemistry. In order to achieve the rotational synchronization, the discotics must be connected by molecular hooks (hydrogen bonds). Two different spinning processes are envisioned: (1) spinning fibers from polymer melt or solution (2) spinning fibers from monomers. In case (1), the polymer fluid is supplied at the top of the membrane containing the discotic system. The composite membrane containing the discotic system only serves as the spinneret. Since the structure of the fiber is formed within this membrane, the discotic system must be designed appropriately to create the desired structure in the fiber. In case (2), monomer components are supplied above the membrane. The first layer of the membrane is designed such that these monomers can be reacted to form a polymer chain. These chains are then pulled through the discotic system, as in Case (1), to form the fiber. As the discotics rotate, using hydrogen bonding and other non-bonded interactions, they can pull polymer molecules supplied at the top surface of the membrane, align them within the membrane, and release fiber at the bottom surface. In order to develop this system, the discotics must be designed and positioned such that they can attract and pull certain polymer molecules in the prescribed sequence, and assemble and orient them together as a fiber with the required structure. In order to produce fibers with a specific molecular structure, exact rotational synchronization must be achieved for the discotics. The rotation of the discotics will be achieved by the application of a magnetic field.

Computational Approaches

The structure and location of the discotics are the key to success. They have to be designed for specific polymer systems to be spun. The design of the discotics and their arrangement in the membrane will be extremely complex. Molecular modeling [11-18] techniques are applied in the design and positioning of the discotics, since such “virtual” machine designs can be carried out with good computational precision. Qualitative patterns will be more reliable than quantitative predictions even with the advanced molecular modeling techniques. However, the mostly qualitative predictions on the molecular interactions can be used in identifying the chemical functional groups required for the discotics, and their geometrical specifications (i.e., location, size, etc.). Discotics must spin molecules into molecular assemblies of fibers using non-bonded interactions between the discotic molecules and polymer molecules. Using molecular dynamics, these interactions can be simulated. Chemical compositions of the discotics can redesigned for improving specific interactions with the polymers, and the locations of discotics can be changed until the spun polymer molecules attain the desired structure. Discotic structures obtained from molecular modeling analysis will be synthesized and tested.

Designing the membrane structure containing discotic molecules that can rotate in specific directions under externally applied fields (such as magnetic fields) is a major challenge in this investigation. The molecular spinning machine, designed in the form of a membrane, must be designed such that discotics which make up the membrane will rotate freely in the desired direction, while remaining at the same position in the membrane. This design has to be achieved using molecular hooks such as hydrogen bonds that can connect different discotic molecules to provide rotational freedom without any translational freedom.

Computational models are being developed to study the kinetics of fiber formation within the membrane. The design of the discotic system that can provide the desired fiber structure has to be determined using computational tools. A detailed molecular modeling study will be conducted to understand structure formation for polymer molecules under selectively and dynamically confined configurations, while they are moving through the membrane spinnerette. Computational results on the design of discotic membranes will be used to synthesize the nano-spinning system. Computational modeling and synthesis of candidate structures will be conducted simultaneously.

Synthetic Approaches

The discotic systems to be used for spinning alone will be synthesized based on the outcome of computational approaches. Supply of polymers or monomers should be provided in the solution form. Since the purpose of the functional groups in the discotic system are to assemble and structure the polymer molecules to form a fine filament, greater understanding of the interactions between polymer molecules and the discotic system has to be developed. For assisted spinning of fibers using external fields, developments have been made in the synthesis of discotics with embedded metal atoms, making them sensitive to changing external magnetic/electric fields. There has been a significant amount of work done at Oak Ridge National Lab., NASA Ames Research Center, and other research facilities in this area. The results of their investigations will be used to guide the present work on synthesizing discotics that can behave as electric motors facilitating effective spinning of polymer fibers.

The first synthetic model that we have studied is based on taper-shaped monoesters of oligo(ethylene oxide) with tris(p-dodecyloxybenzyloxy)benzoic acid polymethacrylates. These systems have been shown to form tubular supramolecular architectures involving a columnar mesophase. These systems have been shown to self-assemble to form almost identical supramolecular tubular architectures because of the presence of the tapered exo-receptors attached to the polymethacrylate backbones. Exo-molecular recognition generated by the similar sized and shaped surfaces results in spontaneous self-organization to form cylindrical-shaped assemblages remarkably similar in shape to molecular rotors. 3,4,5-Tris(p-alkyloxybenzyloxy)benzoic acids are flat molecules which are triangular in shape and which self-assemble like slices in a pie to form columnar mesophases.

Methyl 3,4,5-trihydroxybenzoate was purchased from Aldrich. We have synthesized p-dodecyloxybenzaldehyde by the reaction of p-hydroxybenzaldehyde with n-dodecylbromide**.** p-Dodecyloxybenzyl alcohol was obtained by the reduction of p-dodecyloxybenzaldehyde with sodium borohydride. p-Dodecyloxybenzyl alcohol was reacted with thionyl chloride to produce p-dodecyloxybenzyl chloride. p-Dodecyloxybenzyl chloride was reacted with methyl 3,4,5-trihydroxybenzoate to form methyl tris(p-dodecyloxybenzyloxy)benzoate which was hydolyzed with potassium hydroxide in ethanol to form tris(p-dodecyloxybenzyloxy)benzoic acid [1]. 2-[2-(2-Hydroxyethoxy)ethoxy]ethyl 3,4,5- tris(p-dodecyloxybenzyloxy)benzoate [2] was formed by the reaction of tris(p-dodecyloxybenzyloxy)benzoic acid with triethylene glycol. [2] was reacted with methacryloyl chloride to from 2-[2-(2-methacryloyloxyethoxy)ethoxy]ethyl 3,4,5-tris(p-dodecyloxybenzyloxy)benzoate [3] which undergoes free radical polymerization initiated by 2,2-azoisobutyronitrile (AIBN) at 60^0C in benzene. The polymer has been isolated and characterized by IR and NMR spectroscopy.

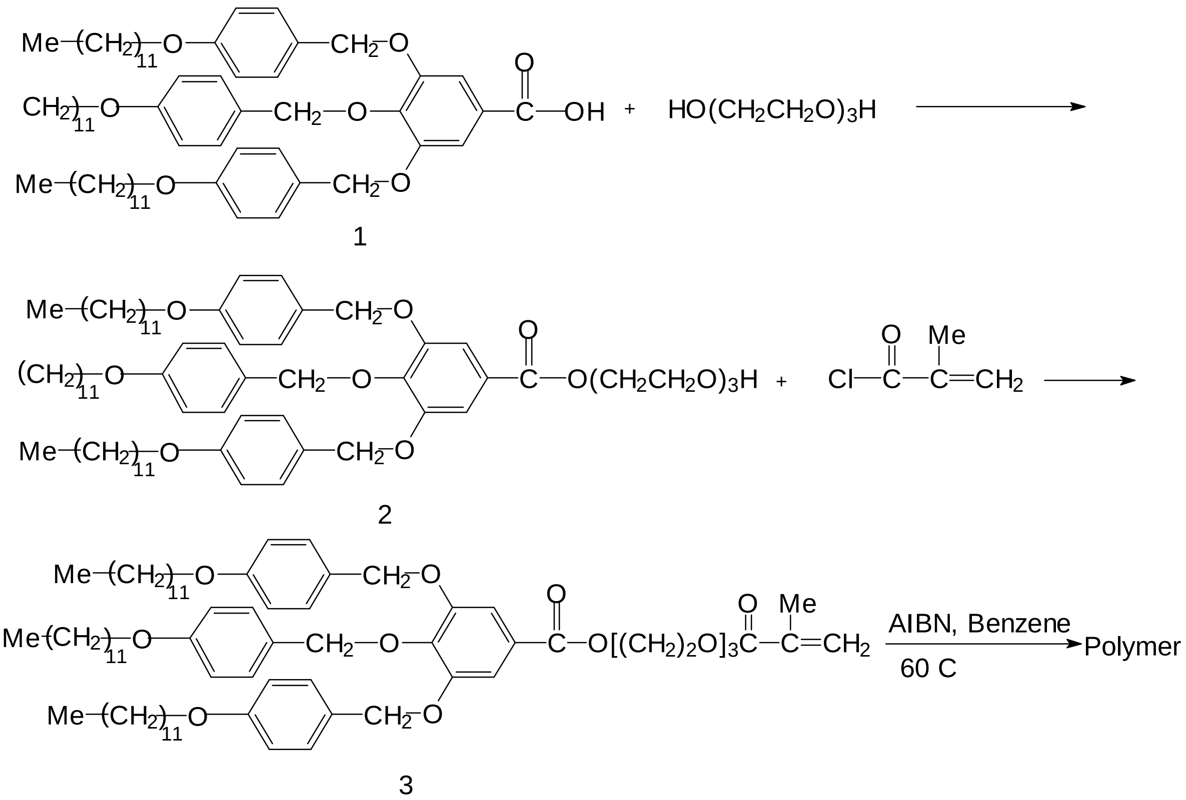


Figure 1. Synthesis of Taper-Shaped Monoesters of Oligo(ethylene oxide) with Tris(p-dodecyloxybenzyloxy)benzoic Acid Polymethacrylates

NMR studies have shown that in a magnetic field, liquid crystalline nematics tend to align parallel to the field. The rotor-like columnar structures will be studied to determine whether they will undergo rotation on exposure to a rotating magnetic field of the correct field strength. A magnetically oriented sample of poly(γ-benzyl glutamate) has been shown to undergo reorientation on rotation about some angle [20]. The movement of polymeric nematic liquids in a rotating magnetic field has been used for measurement of the twist viscosity. If the columnar mesophase undergoes rotation in a rotating magnetic field, then a nanofiber of poly(methacrylic acid) may be produced in a rotating magnetic field by hydrolyzing the polyester bonds.

Concurrently, we are studying the synthesis of columnar polymeric phthalocyanines which contain metals such as copper, zinc, cobalt, nickel and lead [21]. Phthalocyanines, which contain eight 11-hydroxyundecoxy chains, may be synthesized by the following process (shown in Figure 2): Catechol is alkylated by reacting it with 11-bromo-1-undecanol in dimethylsulfoxide in the presence of potassium carbonate. The resulting 1,2-di-11-hydroxyundecoxy derivative is converted to the 4,5-dibromo derivative by reaction with bromine in methylene chloride. Next the Rosenmund-Von Braun reaction yields the 4,5-dicyanide derivative which is converted to the corresponding phthalocyanine derivative by refluxing in 2-(dimethylamino)ethanol in the presence of the appropriate metal salt. Polymerizable groups may be added to the phthalocyanine system in order to keep the hexagonally arranged discotic columns frozen by polymerization. For example, we will react one equivalent of methacroyl chloride with 11-hydroxyundecoxy substituted phthalocyanine to produce the methacroyl derivative which will undergo radical polymerization.

The presence of the hydroxy terminal groups in 11-hydroxyundecoxy substituted phthalocyanine will enable us to form reversible hydrogen bonding groups at those positions. Derivatives of 2-ureido-4-pyridone are readily synthesized and dimerize strongly to form self-complementary donor-donor-acceptor-acceptor arrays [22]. The hydroxy end groups will be reacted with a cyclohexane diisocyanate followed by methylisocytosine to form one 2-ureido-4-pyridone derivative (Figure 2). The other derivative will be formed by the reaction of hydroxy-terminated polymers with the cyclohexane diisocyanate followed by methylisocytosine. At high concentrations, the 2-ureido-4-pyridone groups will form a hydrogen bond which on dilution undergoes breakage thereby allowing the molecular hook to disengage during take up of the resulting fiber bundles.

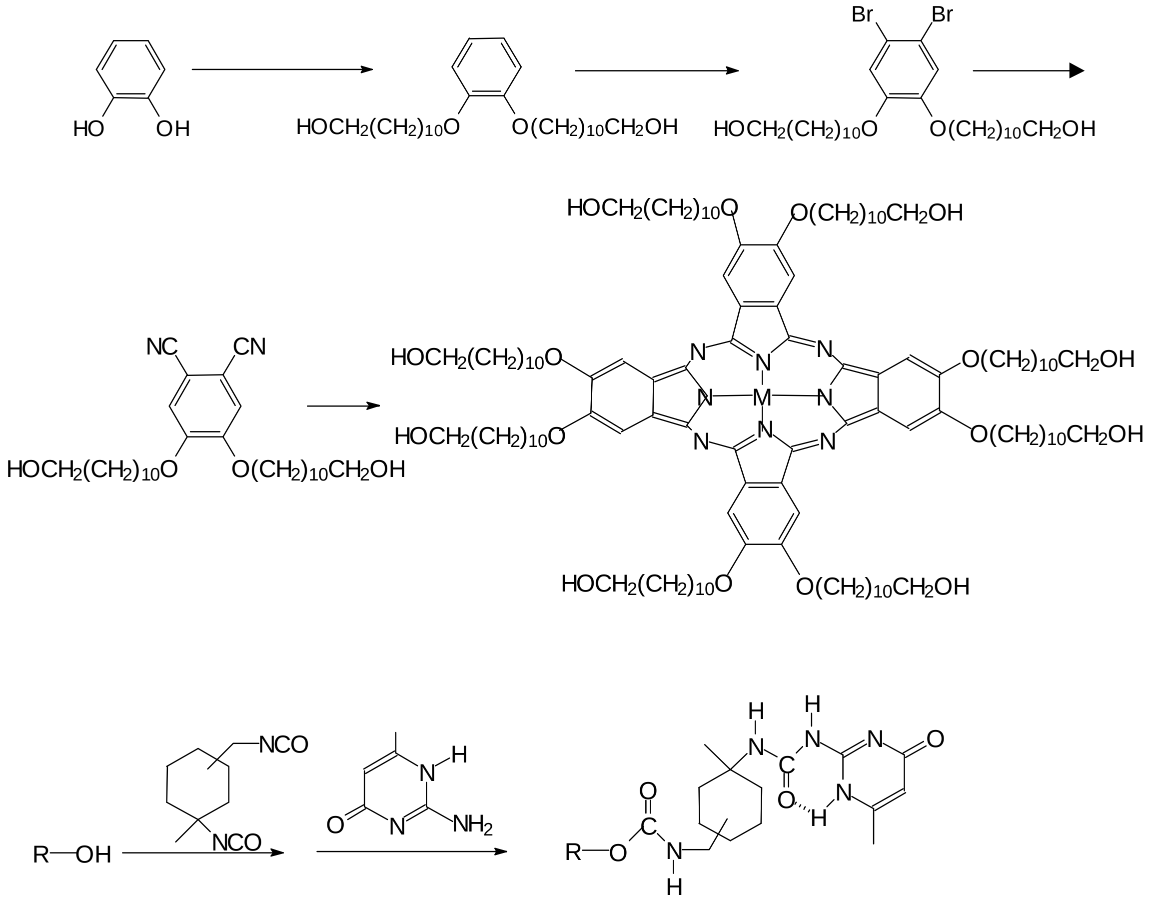


Figure 2. Synthesis of Columnar Polymeric Metal-Containing Phthalocyanines

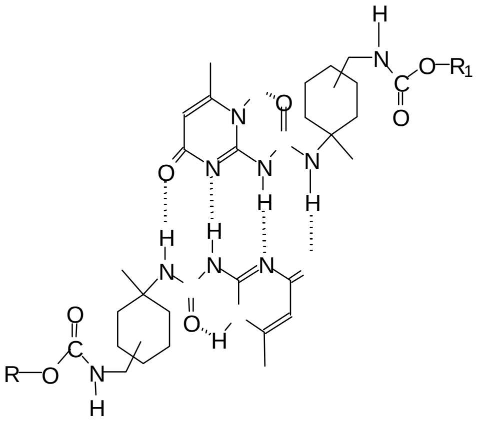


Figure 3. Hydrogen Bonding of Ureido-4-Pyrone Groups

NMR Molecular Dynamics Studies

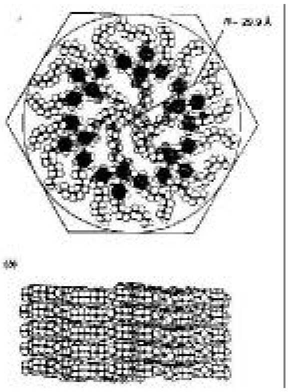
Leisen and Spiess [25,26] have used two dimensional nuclear magnetic resonance to study the rotational dynamics of substituted phthalocyaninatopolysiloxanes and (2S',3S)-2-chloro-3-methyl-pentanoyloxi-pentakis(pentyloxi)-triphenylene. The two discotic liquid crystals were both observed to undergo thermal rotation in the solid state. Thermally activated uniaxial rotation of the phthalocyanato group about the long axis of the polymer was observed to occur in the 170 to 470 K temperature range by solid-echo ^{2}H-NMR spectroscopy. (2S',3S)-2-Chloro-3-methyl-pentanoyloxi-pentakis(pentyloxi)-triphenylene was observed to undergo small-step diffusion and rotational jumps in the temperature range of 250-280 K.

Thus, it is possible to measure the rotational characteristics of the discotic molecules. This information can be supplemented with the computational results or can serve as the input data for computational studies. In order to design the discotic to engineer the structure of polymer fibers, it is important to understand the dynamics of the discotic system. Using the state of the art NMR system at Georgia Tech, unassisted and assisted dynamics (with and without external fields) are being studied to characterize the effect of external fields on the dynamics of discotic molecules (Figure 7).

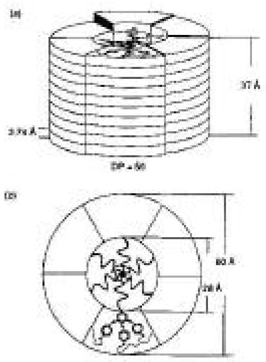
Researchers at the IBM Research Division, Zurich Research Laboratory have been able to visualize a single-molecule rotor rotating inside of a supramolecular bearing by using a scanning tunneling microscope [25]. They observed single molecules residing in one of two states separated by 0.2 nanometers, one rotating and one stationary. Energy barrier calculations for the two states demonstrated that the thermal energy at room temperature is above the energy barrier for the rotating state and below it for the immobilized state.

Structures of Discotic Columnar Liquid Crystals

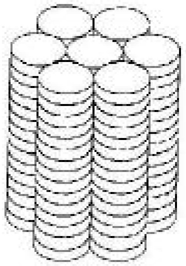
The structures of discotic columnar liquid crystals are shown schematically in Figure 4.



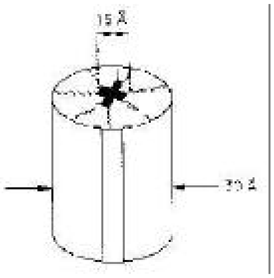
Supramolecular Cylinders



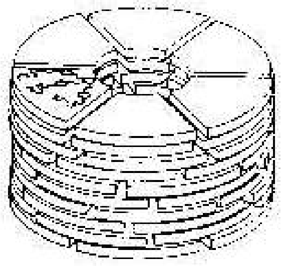
Self-Assembled Supramolecular Cylinders



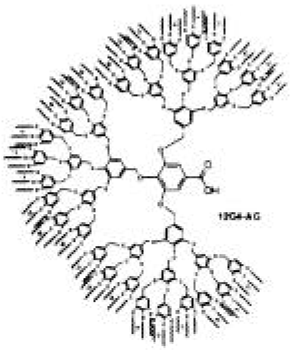
Hexagonal Columnar Mesophase



Phthalocyanine Columnar Phase

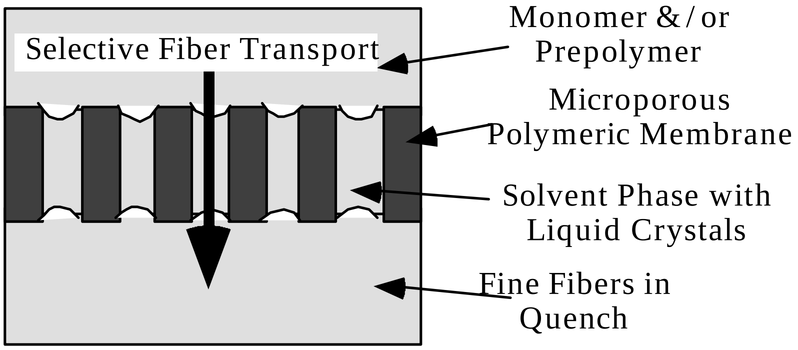


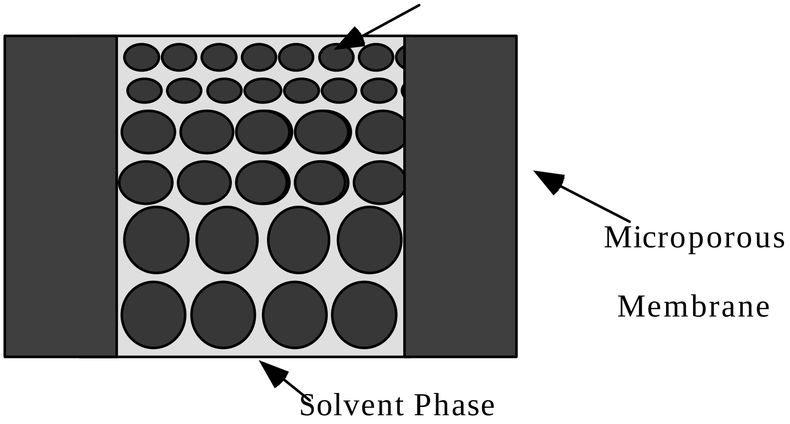
Self-Assembled Columnar Phase



Monodendron Building Blocks

Figure 4. Discotic Columnar Liquid Crystals





nano-technology (6) ultra-fine fiber production with discotics of increasing sizes

For spinning fine fibers from supplied polymer solutions, the molecular weight is

polymerization and spinning are carried out in sequence in the discotic membrane system, the molecular weight of the polymer can be made very high by using chain

superior fiber properties depending on the processing conditions.

REFERENCE

1. K. Eric Drexler, “Nanosystems: Molecular machinery, manufacturing, and Computation; Wiley-Interscience, NY, 1992.
2. Rohrer, H., “Nanoworld: Chances and Challenges”, Microelectron Eng, 32, 5(1996).
3. Randall, J., Frazier, G., Seabaugh, A., Broekaert, T., “Potential Nanoelectronic Integrated Circuit Technologies”, Microelectron Eng, 32, 15 (1996).
4. Anon, “Nano-engineered Materials Produce Passive Electronic Devices with Improved Performance”, Mater Technol, 12, 47(1997).

5. Govindaraj, A., Sen, R., Nagaraju, B. V., Rao, C. N. R., “Carbon Nanospheres and Tubes Obtained by Pyrolysis of Hydrocarbons”, Philos Mag Lett, 76, 363(1977).
6. Bandow, S., Rao, A. M., Williams, K. A., Thess, A., Smalley, R. E., Eklund, P.C., “Purification of Single-wall Carbon Nanotubes by Microfiltration”, J Phys Chem B, 101, 8839(1997).
7. Ebbesen, T. W., “Carbon Nanotubes”, Phys Today, 49, 26(1996).
8. Peigney, A., Laurent, Ch., Dobigeon, F., Roussert, A., “Carbon Nanotubes Grown in Situ by a Novel Catalytic Method”, J Mater Res, 12, 613(1997).
9. Robertson, D. H., Dunlap, B. I., Brenner, D. W., Mintmire, J. W., White, C. T., “Fullerene/tubule Based Hollow Carbon Nano-Gears”, Mater Res Soc Symp Proc 349, 282(1994).
10. Averback, R.S., Zhu, H., Tao, R., Hofler, H., “Sintering of Nanocrystalline Materials: Experiments and Computer Simulations”, Proc of TNS Annu Meet, 203 (1996).
11. Tuzen, R. E., Noid, D. W., Sumpter, B. G., Otaigbe, J. U., “Molecular Dynamics Simulation of Polymer Flow in Nano-Channels”, Polym Mater Sci Eng Proc ACS Div Polym Mater Sci Eng, 76, 585(1997).
12. Tuzen, R. E., Noid, D. W., Sumpter, B. G., Merkle, R., “Dynamics of He/C60 Fluid Flow Inside carbon Nanotubes”, Nanotechnology, 8, 112(1997).
13. Dare-Edwards, M. P., “Novel family of Traction Fluids Deriving from Molecular Design”,, J Synth Lubr, 8, 197(1991).
14. Allen, M. P., Tildesley, D. J., Computer Simulation of Liquid, Clarendon Press, Oxford, 1987.
15. Pinches, M. R. S., Tildsey, D. J., Smith, W., “Large Scale Molecular Dynamics on Parallel Computers Using the Link-Cell Algorithm”, Molecular Simulation, 6, 51 (1991).
16. Brown, D., Clarke, J. H. R., Okuda, M., Yamazaki, T., “A Large Scale Molecular Dynamics Study of Chain Configurations in the N=100 Alkane Liquid”, J Chem Phys, 104, 2078(1996).
17. McKechnie, J. I., Haward, R. N., Brown, D., Clarke, J. H. R., “Effect of Chain Configurational Properties on the Stress-Strain Behavior of Glassy Linear Polymers”, Macromolecules, 26, 198(1993).
18. Haile, J. M., Molecular Dynamics Simulations, Wiley Interscience, 1992.
19. Percec, V., Heck, J., Tomazos, D., Falkenberg, F., Blackwell, H., and Ungar, G., “Self-assembly of Taper-shaped Monoesters of Oligo(ethylene oxide) with 3,4,5-Tris(p-dodecyloxybenzyloxy)benzoic Acid and of Their Polymethacrylates into Tubular Supramolecular Architectures Displaying a Columnar Mesophase”, J. Chem. Soc. Perkin Tran., **1**, 2799 (1993).
20. Noel, C. in “Polymeric Liquid Crystals”, Blumstein, A., ed., Plenum Press, New York, pp. 46-50, 1985.
21. Van de Pol, J.F., Neeleman, E., van Miltenburg, J.C., Zwikker, J.W., Nolte, R.J.M., and Drenth, W., “A Polymer with the Mesomorphic Order of Liquid Crystalline Phthalocyanines”, Macromolecules, **23**, 155 (1990).
22. Sijbesma, R.P., Beijer, F.H., Brunsveld, L., Folmer,B.J.B., Hirschberg, J.H.K.J., Lange, R.F.M., Lowe, J.K.L., and Meijer, E.W., “Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding”, Science, **278**, 1601 (1997).
23. Web document: http://www.lci.espci.fr/VO/activities/phthalo/VO-Pc-meso.html.
24. Percec, V., Chu, P., Johansson, G., Schlueter, J.C., Ronda, J.C., and Ungar, G., ACS Polym. Prep., 37(1), 68 (1996).
25. Schwiegk, S., Werth, M., Leisen, J., Wegner, G., and Spiess, H.W., “Rotational Dynamics of Substituted Phthalocyaninatopolysiloxanes as Measured by 2D Solid-State NMR Spectroscopy”, Acta Polymer, 44, 31 (1993).

26. Leisen, J., Werth, M., Boeffel, C., and Spiess, H.W., “Molecular Dynamics at the Glass Transition: One Dimensional and Two Dimensional Nuclear Magnetic Resonance Studies of a Glass-Forming Discotic Liquid Crystal”, J. Chem. Phys., 97(5), 1 (1992).
27. Gimzewski et. al., Science, **218**, 531-533 (1998).

Figure 7: NMR plot for a candidate discotic molecule