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Liquid Crystal Electromechanical Elastomer: A Strong Future for Smectic A* Molecules

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ABSTRACT

Electromechanical materials are very useful as actuators when small weight, and low to moderate force are needed to manipulate small objects. The Liquid Crystal Material Research center located in Boulder, Colorado in interested in developing a novel liquid crystal based electromechanical elastomer. De Vries liquid crystals organize into layers where the director is perpendicular to the layer normal, and the optical tilt varies greatly from the x-ray tilt. In this paper we hope to exploit the properties of a rare Anti-De Vries Smectic A* molecule in which the optical to x-ray tilt is approximately one over a broad temperature range. Discussed in this paper is background on the theory of the liquid phase under investigation, and the outline of synthesis of the Smectic A* W317 analog which is used in the electromechanical elastomer material.

Subject headings: REU - Liquid Crystal Materials Research Center - Liquid Crystal Elastomer For Artifical Muscle Applications - Professor David Walba

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1. Introduction

Organic based electromechanical materials can be very useful as actuators when light weight and low current are needed to provide low to moderate force. Many materials have been developed in recent years, and currently these materials are proving useful for manipulation of lens for optical systems. Interestingly, the future applications include actuators for the robotic arms used by space and planetary probes. As of now NASA is the current leader in this field, with research being conducted at JPL's Nondestructive Evaluation and Advanced Actuators (NDEAA) center in Pasadena, California. Under the guidance of Dr. Yoseph Bar-Cohen the group has developed both red-ox and ionic based systems. The Liquid Crystal Materials Research Center located at the University of Colorado, Boulder is currently developing a novel liquid crystal elastomer based actuator system. This system could demonstrate more desirable properties such as increased force, durability, and switching time if favorable conditions are found for polymerization.

Liquid crystals of the De-Vries type are chiral molecules that organize into the Smectic A phase. In this phase the molecules can occupy the surface area of a cone with each anchored at the vertex(de Vries). When a potential difference is applied through the layers the molecules align uniformly because of the electrostatic dipoles within each molecule. In this system the optical tilt is high, but the layer shrinkage is extremely small. We hope to exploit the properties of a rare anti-De Vries type molecule which demonstrates a large electroclinic effect, meaning when a potential difference is applied parallel to the layers shrinkage occurs within them(Richardson). Herein, the theory behind the liquid crystal elastomer actuator and aspects of polymerization will be explored, and the outline for synthesis of the anti-De Vries liquid crystal analog will be explained in detail.

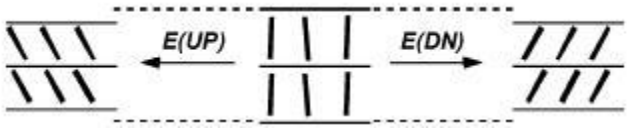

Fig. 1.— Anti-De Vries Characteristics

2. Theory

Liquid crystals are just one of the natural states of matter in nature, but have many phases of their own. In liquid crystals the molecules posses order but they are still fluid in up to three dimensions. The most known and useful phase of liquid crystals is the nematic phase. In this phase the molecules are ordered with their long axis parallel to each other. We use a vector called the director $\vec{n}$, which travels along the long axis of the molecules to describe the orientations of the molecules. Therefore, in the nematic phase the molecules are free to travel in three dimensions, but still maintain alignment with the entire long axis of the molecules pointing along the director. The molecules which show nematic phase at reasonable temperatures of 24-84 degrees C typically

have two cores with small aliphatic parts which minimize the Van Der Waals forces between. This allows the molecules to travel freely, but still have orientation because of interactions between the cores. Generally, as we increase the aliphatic terminal tail of the molecules the nematic transition temperature becomes higher and a smectic ordering of the molecules allows them to occupy their lowest free energy state(Collins).

The smectic phases organize into a lamellar structure with the director lying on the normal for the Smectic A phase, and the director at some temperature dependent angle from the normal for the Smectic C phase. Something interesting occurs in the Smectic C phase if the molecules are chiral - the molecules change with the direction of their tilt rotating from layer to layer - and in doing so create a helical arrangement. When Smectic C chiral molecules are placed in the cell of only a few layers they become surface stabilized via interactions with the boundaries of the cell. Because of this the helical arrangement commonly seen in Smectic C chiral is hindered and a full ferroelectric polarization can be obtained. Although the applications of the surface stabilized ferroelectric Smectic C are exciting and fruitful, the Smectic A chiral liquid crystal phase of anti-De Vries type will be especially useful for our electromechanical elastomer(Collins).

The x-ray shrinkage and optical tilt of the Smectic A* W317 is equivalent over a broad temperature range of 27.7-59.6 degrees C. With such a broad range, it is expected that layer shrinkage will be applicable for many future applications. W317 demonstrates a strong electroclinic effect, but we have made modifications to it to make it more suitable for polymerization, hence it will be eventually be given a new name. In the presence of a potential difference it basically behaves as a ridged rod, and we believe that polymerizing these units in a way that would maintain the Smectic A phase will allow for significant force and contraction of the polymer sample. In the past, various polymerizing techniques have been tried, but because order must be maintained we have chosen the thiol-ene system. This system will allow us to polymerize the units in the cell, hopefully maintaining the order. Therefore, this W317 analog will have an allyl ether tail on the single aromatic core unit, and a thiol tail on the nitro-biphenyl core unit. These units are synthesized independently and then later connected via ester linkage(Walba).

The ordering of the layers in the polymerized sample is of the greatest concern, and different approaches to the polymerization process must be explored. It is imperative that this order be maintained, and not compromised after repeated cycles of contraction. Previous samples, all of which were not polymerized in cell, showed substantial degradation of the smectic layering. The first diene compound, which the synthesis was published in chem-matter in June 2006, may have polymerized in smectic fashion, but after it was transferred to the cell and stimulated the order was lost(Walba). Hopefully the thiol-ene will allow for the order to be maintained, and also we will not have to transfer the sample to the cell which can cost a lot of ordering(Richardson).

An analog of W317 (Figure 2) with allyl ether and thiol tails will allow us to create a thiol-ene polymer with an UV light initiated reaction. Again, the greatest benefit of this system takes advantage of the low viscosity in the unpolymerized state; the sample can align into the Smectic A

state, and then polymerization can be initiated by irradiation.

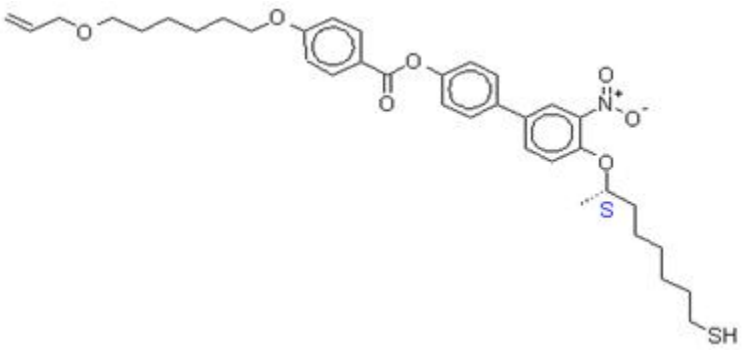

Fig. 2.— W317 Analog

3. Synthesis

The overall synthesis of W317 is outlined below(Walba). The analog has been changed at step 6, 7, and 9 in order to generate the thiol and allyl ether groups necessary for the polymer. The reagent diethyl azodicarboxylate was originally changed to diisoproply azodicarboxylate because of availability issues, but additionally it possesses enhanced basic character which is beneficial under the conditions specified for reaction 9.

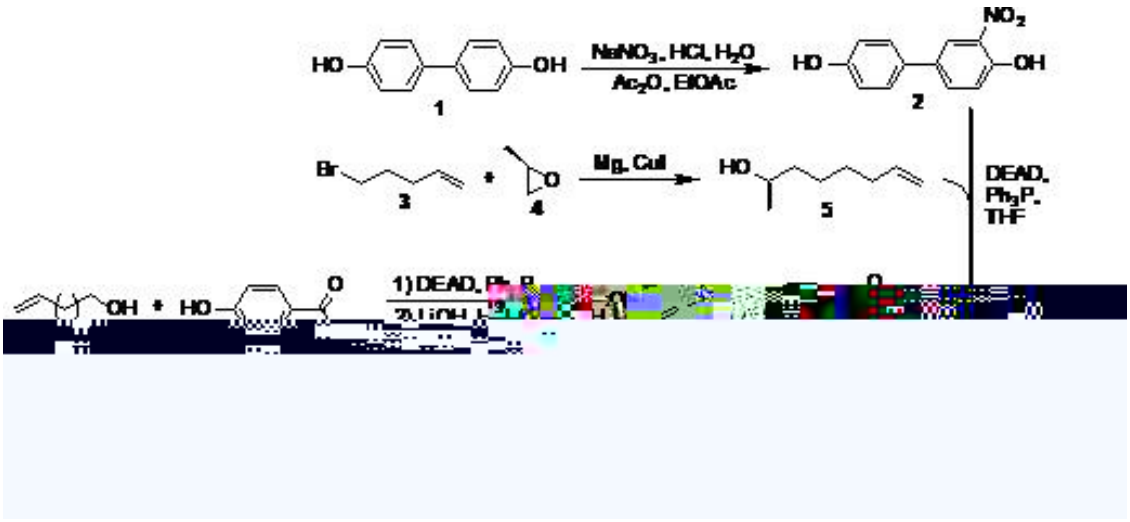

Fig. 3.— Synthesis of W317

The core, 3-nitro-biphenyl-4,4'-diol, is the first molecule in the sequence, and vitally important to the structure of the W317 analog. Because it has a strong electron withdrawing group on the 3 position of the right core, it possesses a DπA system, and hence strong polarization. It is easily

synthesized by electrophilic substitution with the generation of a nitro cation by hydrochloric acid and sodium nitrate - instead of the common nitric acid and sulfuric acid. The modified nitration achieves the same effect with safer reagents, and less of the 3, 3' side product. The reaction takes place in two phases; the aqueous phase is where the nitro cation is generated, and the organic ethyl acetate phase is where the biphenyl-diol is concentrated. A few drops of acetic anhydride helps to emulsify the layers, and in about two hours the clear reaction mixture turns a dark brown. The organic phase is then separated, and the aqueous phase is washed with ethyl acetate to remove any miscible solvent. It was then dried in magnesium sulfate, which captures any remaining water molecules in an exothermic reaction. Ice was used when needed; however, this depended on the quality of the separation. The red brown liquid was concentrated by a rotary evaporator, and then purified by flash chromatography with a mixture of 4:1 hexane-ethyl acetate.

The first tail, R-Oct-7-en-2-ol, was prepared via a Grignard reaction, and will eventually be joined to the 3-nitro-biphenyl-4,4'-diol. The Grignard reagent was synthesized from Mg metal and 5-bromo-1-pentene with iodine crystals acting as an activator. The contents were allowed to react for 2 hours, and then Copper (I) iodine was added. The copper forms bonds with two of the Grignard reagents, and changes them from a basic to nucleophilic character. Then, the chiral center, (R)-propylene oxide was added, and the reaction proceeded fast and exothermically. After 5 hours the reaction was quenched with saturated ammonium chloride solution. The remnent copper forms a water soluble ligand with the ammonia, and was easily removed in the aqueous layer. The rest was extracted with ether, and allowed to dry over calcium chloride. I reported a 64 percent yield, but this could be higher if one skillfully adds the volatile propylene oxide to the exothermic reaction chamber. The clear liquid was concentrated by a rotary evaporator, and then purified by flash chromatography with a mixture of 4:1 hexane-ethyl acetate.

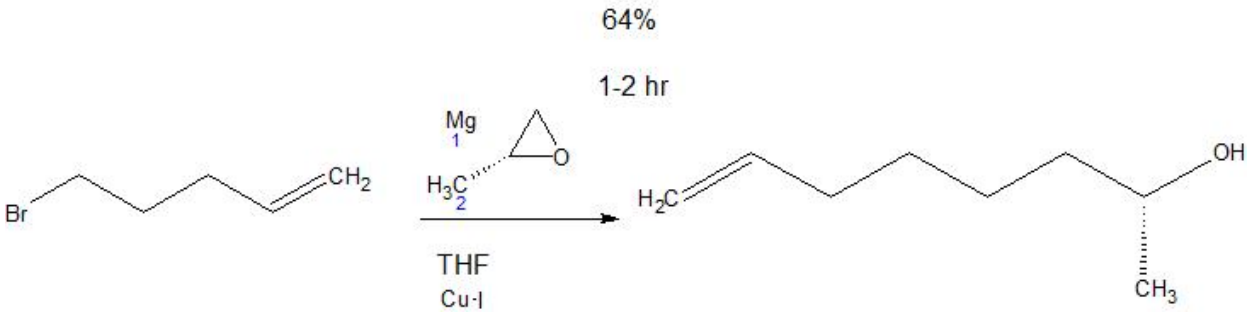

Fig. 4.— Synthesis of Chiral Tail

The Mitsunobu reaction was is the next step in the sequence outlined in figure 3. This high yielding reaction is extremely useful. It is commonly used to join carboxylic acids and alcohols, but because our phenol is acidic by the electron withdrawing effects of the nitro group, the reaction works in high yield even to join phenols and alcohols. When completed, the dark red liquid was concentrated by a rotary evaporator, and then purified by flash chromatography with chloroform.

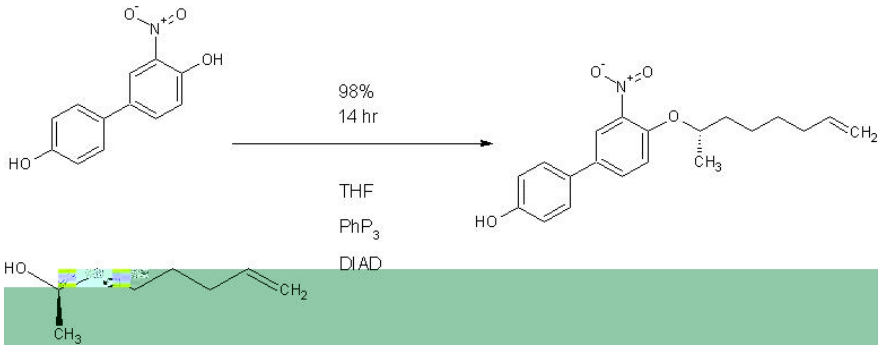

Fig. 5.— Mitsunobu Couping

In step 3 (below) you can see the bonding of an electron pair from the nitrogen to the hydrogen on the carboxylic acid (molecule 4). However, in our case molecule 4 would be a phenol ring, and in addition ours contains a nitro group which makes the molecule acidic enough to give its hydrogen to the diazo compound allowing the reaction to progress. The yield of the compound (S)-4'-(1-Methyl-hept-6-enyloxy)-3'-nitro-biphenyl-4-ol was surprisingly high at 98 percent. This can be justified because the nitro group is only bonded on one side of the ring, and gives acidic properties to the closest hydrogen, and therefore only one side reacts with the chiral alcohol(Hughes).

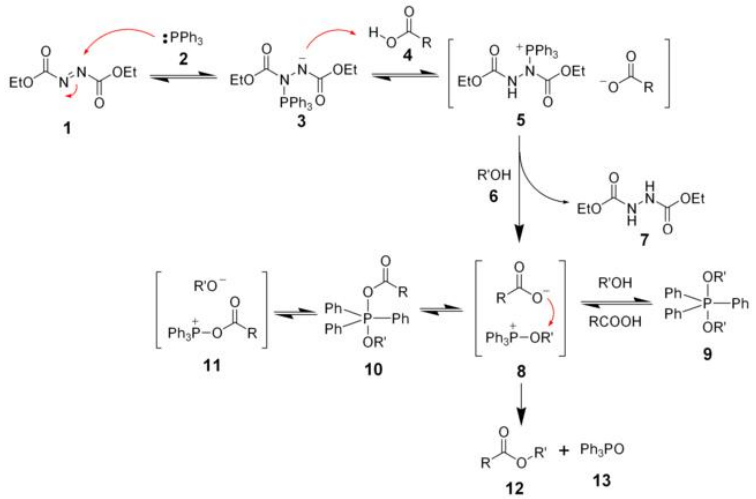

Fig. 6.— Mitsunobu Reaction Mechanism

Next the molecule, (S)-4'-(1-Methyl-hept-6-enyloxy)-3'-nitro-biphenyl-4-ol, was subjected to 9-BBN, which attacks and bonds to the double bond in the chiral tail. The product of this was then saturated with MCPBA, which gives the effect of anti-markovnikov oxidation. The step is very time consuming, and the yields are very low at around 30 percent. This is mostly due to the fact that the reagents are very sensitive to air and do not last long once the bottles are opened. The yellow liquid was then concentrated by a rotary evaporator, and then purified by flash chromatography with a mixture of 9:1 hexane-ethyl acetate.

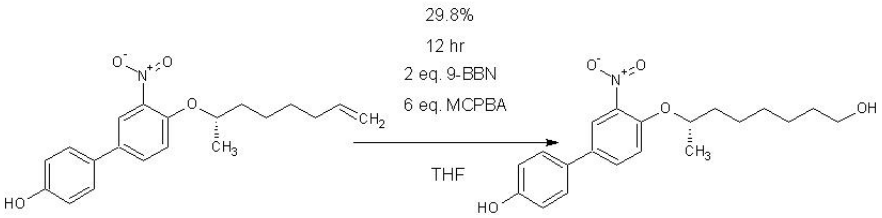

Fig. 7.— Oxidation with 9-BBN

The left half of molecule was the next part synthesized. The two part synthesis consisted of a Mitsunobu reaction between Methyl 4-hydroxy benzoate and 1,6-dibromohexane, and finaly, a Williamson Ether synthesis that couples the important allyl ether group onto the tail of the single aromatic core (left core). Sodium hydride is used for the second reaction to drive the reaction forward and produce the product, methyl 4-[6-(ethenyloxy)hexyl]benzoate. The first liquid was concentrated by a rotary evaporator and purified by flash chromatography with a mixture of 10:1 hexane-ethyl acetate. After this purified compound was subjected to the Williamson Ether systhesis, the crude product was then purified agin by flash chromatography in chloroform.

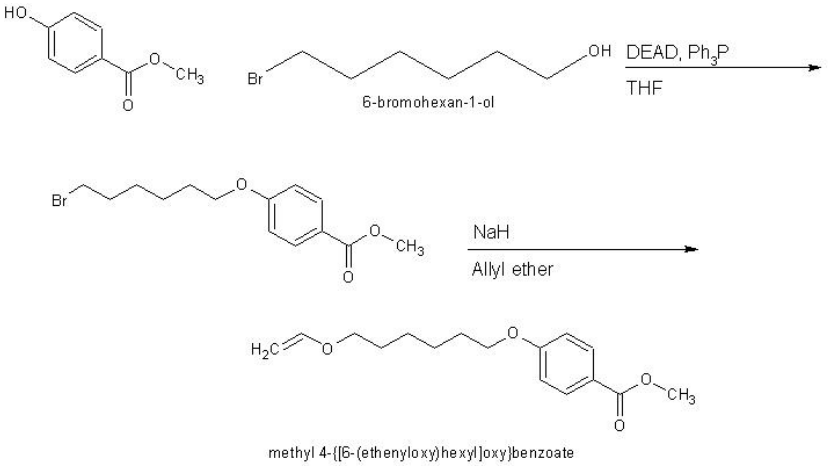

Fig. 8.— Left Core Synthesis

If I had more time, such as a full semester, the next reaction I would have done would be the

sulfanation of (S)-4'-(1-Methyl-hept-6-enyloxy)-3'-nitro-biphenyl-4-ol. This reaction replaces the primary alcohol group at the end of the tail on the double aromatic core with a thiol group. The first step is to add bromine in place of the hydroxyl with hydrobromic acid, then thiourea attacks the adjacent carbon causing the bromine to leave. Finally, base attacks the sulfonylurea group and the molecule leaves as urea.

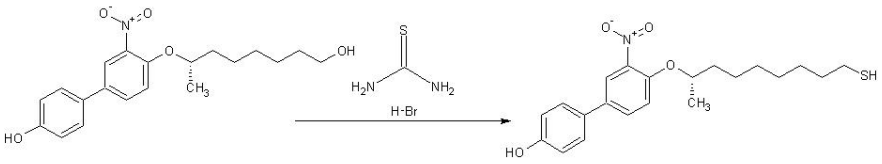

Fig. 9.— Addition of thiol via thiourea

The final step to synthesize the W317 analog is to couple the two halfs together with DCC mediated coupling.

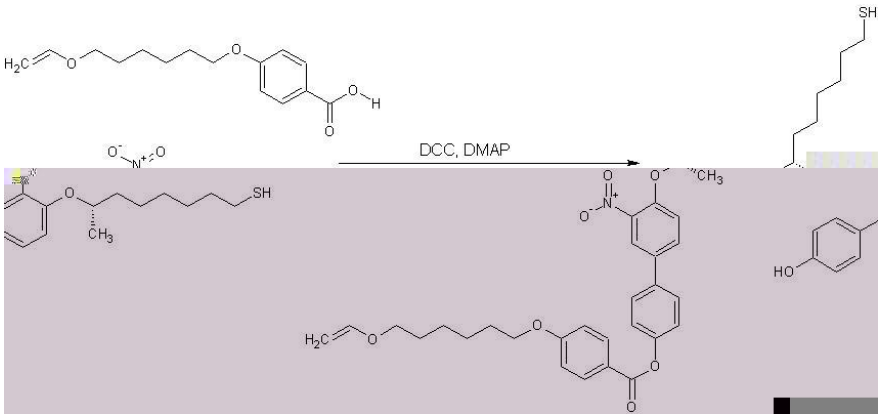

Fig. 10.— DCC mediated coupling

4. Polymerization

The thiol-ene polymerization is a widely used and understood photocuring system. Samples subjected to light in the ultra violet wavelength are excited causing a free radical reaction between a terminal sp^2 hybridized carbon, and a thiol group. Reaction rate is increased when the sp^2 carbon is close to an electron donating group, commonly an ether group.

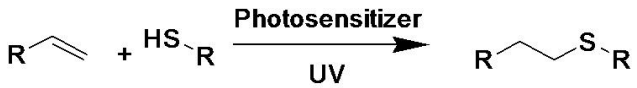

Fig. 11.— Thiol-ene System

5. Conclusion

Once appropriate conditions are found for polymerization, layer shrinkage should theoretically lead to shrinkage in the polymer sample. Synthesis of the W317 analog is currently under way and results will be forthcoming. Characterization will begin immediately after synthesis is complete.

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