# UNDERSTANDING THE IMPACT OF CHAIN ALIGNMENT ON MECHANOCHEMICAL ACTIVATION

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Wei Xie

May, 2021

UNDERSTANDING THE IMPACT OF CHAIN ALIGNMENT ON MECHANOCHEMICAL ACTIVATION

Wei Xie

Thesis

Approved:

_____
Advisor
Dr. Junpeng Wang

_____
Committee Member
Dr. Yu Zhu

Accepted:

_____
Interim Director of SPSPE
Dr. Ali Dhinojwala

_____
Interim Dean of the College
Dr. Craig Menzemer

_____
Interim Director, Graduate School
Dr. Marnie Saunders

_____
Date

## ABSTRACT

Bulk activation of mechanophores embedded in polymers has been an important challenge in the field of polymer mechanochemistry, being limited to a small number of mechanophores which require low forces to activate. It has been shown before that alignment of polymer chains in these systems may correlate to enhanced activation. We hypothesized that mechanophore incorporated liquid crystalline elastomer systems may exhibit enhanced mechanochemical activation as a result of the highly aligned microstructure of these materials, and aid in expanding the scope of mechanophores applicable to bulk activation. Spiropyran (SP), a mechanophore that undergoes a reversible color change in presence of force, was embedded to a series of liquid crystalline elastomers (LCEs) and non-liquid crystal elastomers. Contrary to our expectations, we observed that SP embedded in the LCE systems showed no activation whereas some activation was visible in the SP-containing non-liquid crystal elastomers. This behavior suggests that the mesogen may have some negative impact on mechanochemical activation. Further investigation is undergoing to explore the how mesogen affects the mechanochemical activation.

ACKNOWLEDGEMENT

I am grateful for having the opportunity to have research training in Dr. Junpeng Wang's lab. First, I would like to express my deepest gratitude to Dr. Junpeng Wang, who has provided me constant instructions and support. High tribute shall go to Mr. Devavrat Sathe, for his great guidance for every stage my work. Thirdly I thank Dr. Junfeng Zhou for his selfless help and instructions in the past year. Also, I want to thank Dr. Yu Zhu for his time and guidance on this thesis and defense. Finally. I would like to express my sincere gratitude to every member in Dr. Junpeng Wang's group.

TABLE OF CONTENTS

III. RESULTS AND DISCUSSION

LIST OF FIGURES

Figure Page

# CHAPTER I

# INTRODUCTION

## 1.1 Mechanochemistry

Mechanochemistry is an attractive subject studying transformations in response to mechanical force.[1] Mechanochemistry started with inorganic materials like using ball milling to perform reactions. In recent years, research focused on mechanophores, i.e., force-sensitive functional groups, has experienced a rapid growth, with a series of mechanophores being synthesized and further studied. Since mechanophores in polymer backbones can be subjected to force along a selective direction, the study of mechanophores typically requires to be incorporated with polymer chains for force transduction. Such force responsive polymers are thought to have a potential for damage sensing, catalyst release, drug delivery, and many other applications.

In the 1930s, Staudinger first reported the reduction in the molecular weight when polystyrene was subjected to mastication. [2, 3] Then Kauzmann and Eyring further proposed that bond energy decreases under the force will result in bond breakage.[4] In 1980, Encina et al. found the peroxide linkage incorporated in polyvinyl-pyrrolidone exhibits selective scission under mechanical force and the scission rate is ten times faster than the neat poly-vinylpyrrolidone.[5] In 2005, the

Moore group introduced an azo-linkage centered poly(ethylene glycol), which shows site-specific rather than random cleavage when it is subjected to ultrasonication. This pioneering work sparked further interest in the synthesis and activation of mechanophores. [6]

## 1.2 Spiropyran as a mechanophore

Spiropyran, with the chemical structure formula shown in Figure. 1-1, is commonly made by the combination of salicylaldehyde part and indole part. Spiropyran has a weak C-O bond in the molecular structure, which can undergo a reversible spiropyran-merocyanine isomerization under external stimulus like heat, light and force.

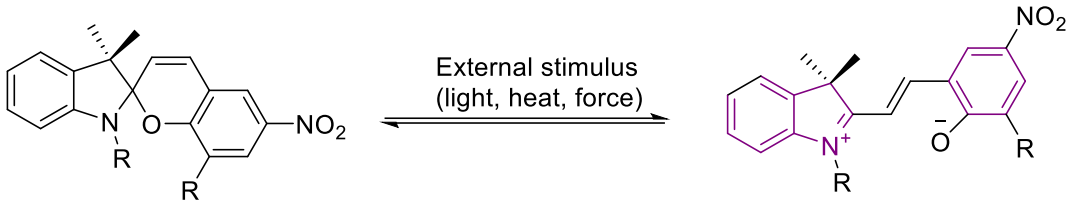



Figure. 1-1 Reversible isomerization between spiropyran (SP) and blue color merocyanine (MC)

Studies investigating temperature-responsive and photoswitchable spiropyran have been well known for a few decades. Chaude et al.[7] noticed that the reversible photo responsive reaction of spiropyran (the cleavage of C-O bond).

The photo-responsive color change of spiropyran is the result of the transformation of spiropyran to highly colored merocyanine. After shining white light placing it in dark environment, the ring-opened merocyanine will reverse back to spiropyran structure and obtain its original color.

Tipikin reported the mechanochromic properties of spiropyran upon grinding in 2001.[8] Motivated by Tipikin's observation, Moore's group from UIUC pioneered the mechanochemical study on spiropyran. In 2007, they synthesized α-bromo-α-methylpropionyloxy functionalized spiropyran as mechanophore then initiated polymerization of polymethacrylate (PMA) via single electron transfer living radical polymerization. They applied pulsed ultrasonication to the polymer solution and successfully observed mechanochromic change.[9] In 2009, they successfully demonstrated mechanochemical activation of spiropyran in bulk system.[10] Glassy spiropyran crosslinked poly (methyl acrylate) (PMMA) and elastomeric PMA were successfully prepared into dog bone shaped sample. With the applied force, spiropyran can undergo electrocyclic ring openingto form the merocyanine marked by a color change to dark red (purple) color. Therefore, utilizing this behavior of spiropyran, polymer materials with force-light responsive characteristics can be constructed by incorporating spiropyran in the center of polymer back bone through covalent bond.

The Craig group has applied single molecule force spectroscopy (SMFS) to measure the activation force of mechanophores. For spiropyran as mechanophore, the force required for the ring opening on a timescale of milliseconds is about 240 pN,[11] which is much lower compared to other mechanophores (like E-alkene gem-dichlorocyclopropane (gDCC) is about 800 pN [12]and trans-benzocyclobutene (trans-BCB) is about 1500 pN [13]).

In 2014, the Craig group introduced a spiropyran incorporated PDMS elastomer system.[14] This network enables activation of spiropyran under tensile and compressive loading of bulk samples. What made this work unique was that the PDMS elastomer system exhibited full shape recovery after removal of force and reversal of spiropyran activation within a few seconds, when placed under visible light. Furthermore, the on/off switch of color can be repeated multiple times through cyclic tensile test.

In 2019, the Silberstein group introduced spiropyran into a glassy polycarbonate.[15] 0.1% of spiropyran diol as mechanophore was mixed with 99.9% of bisphenol A, polymerized with triphosgene to yield a spiropyran- embedded polycarbonate. The activation of spiropyran was demonstrated in this stiff but ductile glassy polymer through uniaxial extensile. Notably, the activation of spiropyran occurred after yielding and continued to increase during the stress

hardening process. The spiropyran-containing polycarbonate has the potential to be applied in damage sensing.

Besides these, many other systems have been utilized for bulk activation of spiropyran. The low force of activation required spiropyran and the fact that it can be incorporated into a wide variety of systems has made it an attractive platform for development of force responsive and damage indicative polymers.

## 1.3 Spiropyran in chain-aligned polymer

In 2011, Beiermann et al. explored how orientation effects the mechanochemical reactions.[16] They incorporated spiropyran within poly (methyl acrylate) and calculated its order parameter in stretched samples, which was based on the anisotropy of fluorescence polarization, to explore how orientation effects the spiropyran- merocyanine transformation. They found that mechanophores oriented along the axis of force are more favorable to activate. Later in 2014, they further looked into the influence of alignment on mechano-chemical activation. [17]

Birefringence measurements were investigated and the results showed that when birefringence reached a plateau and maximum, polymer chains were most aligned along the force axis and spiropyran had a rapid activation.

According to the above hypothesis of promoted mechanochemical activation for aligned bulk systems, the highly aligned system has a potential to activate mechanophores more easily. However, the bulk systems from previous studies[16,17] were not inherently highly aligned enough. Limited direct evidence of the effect of orientation on mechanochemical activation. Further it is difficult to separate the effects of increasing tensile stress and alignment, since in these studies, alignment is often gradually induced when stress increases. Hence, we planned to utilize the high inherent orientational order and alignment of liquid crystalline elastomers (LCEs) and investigate its effect on spiropyran activation. If the high orientation shows enhanced activation of spiropyran, it could potentially lead to the use of such materials to enhance activation of other mechanophores which have proven difficult to activate in amorphous elastomer materials and lead to development of new classes of stress responsive and stress dissipative materials.

## 1.4 Lliquid crystalline elastomers (LCEs)

In 2016, Saed *et al*.[18] synthesized main chain LCE networks via a thiol-acrylate Michael addition reaction. The isotropic rubbery modulus, glass transition temperature, and strain at failure showed a strong dependency on cross-linker concentration and from the ranges for modulus, glass transition temperature, and

strain at failure are 0.9–3.2 MPa, 3–25 °C, and 105%–853%, respectively. They linked thermomechanical properties and actuation to a homogenous polydomain nematic LCE networks with order parameters of up to 0.80 when stretched.[19] The system combines ease of preparation with a rubbery-nematic temperature range, and strong mechanical properties. Further, they demonstrated that such systems could be used to prepare highly aligned networks with the topology frozen in by simply an additional UV photocuring step where the LCE prepared by thiol acrylate reaction (such that there are excess acrylate groups) was stretched, aligned and the excess acrylate groups photo-crosslinked. For these reasons, we choose this system as the matrix for studying the mechanochemical activation of spiropyran at first.

However, the activation of spiropyran in thiol-acrylate LCE network in our work was unsatisfactory. To avoid probable side reactions, we changed the chemistry of preparing LCE from thiol-acrylate click chemistry to Platinum catalyzed hydrosilylation[14], which has been demonstrated to be compatible with spiropyran. The Griffin group[20,21] prepared a LCE utilizing same Platinum catalyzed hydrosilylation. We adapted their method and prepared spiropyran incorporated LCE.

# CHAPTER II

# METHODS AND EXPERIMENTS

## 2.1 Methods

Synthesis route of spiropyran was adapted from previous work by Greg O'Bryan[22].

Fabrication of LCE networks were prepared by Thiol-Acrylate Michael addition "click reaction" and Platinum catalyzed hydrosilylation chemistry according to Yakacki et al[19]. and Ren et al[21]. Dog-bode shape teflon moulds were used (dimensions 25x8.35x0.8 mm3, gauge length 5 mm, gauge width 2 mm)

NMR to identify the target synthesis molecular structures.

NMR spectroscopy was performed for all samples using Varian 300 MHz, 400 MHz and 500 MHz NMR spectrometer.

DSC to identify the thermal properties of LCEs network.

A TA hermetic aluminum pan was used. The sample was first rapidly heated to 125 °C at 10 °C /min, held for 5 mins, then cooled the sample to -50 °C at a rate of 2 °C /min followed by a final heating to 125 °C at 10 °C /min. Energy will change when the sample undergoes a physical transition, which indicated in the DSC

curve as the heat flow, we can identify the transition temperature Ti and glassy transition Tg.

Tensile test to activate the mechanophore and test the mechanical properties.

Cured samples were tested on a homemade tensile testing frame run using an Arduino Uno. Strain rate of 2% s-1 was used.

RGB analysis to identify the mechanochemical activation

Images of the sample were taken while tensile testing (1 picture /10s). The images were white balanced in Adobe Lightroom, and the color histogram tool in ImageJ FIJI was used to obtain color (RGB values) of a small section at the center. The ratios B/R, B/G, G/R were plotted vs strain.

## 2.2 EXPERIMENTS

### 2.2.1 Synthesis of spiropyran-diacrylate (6)

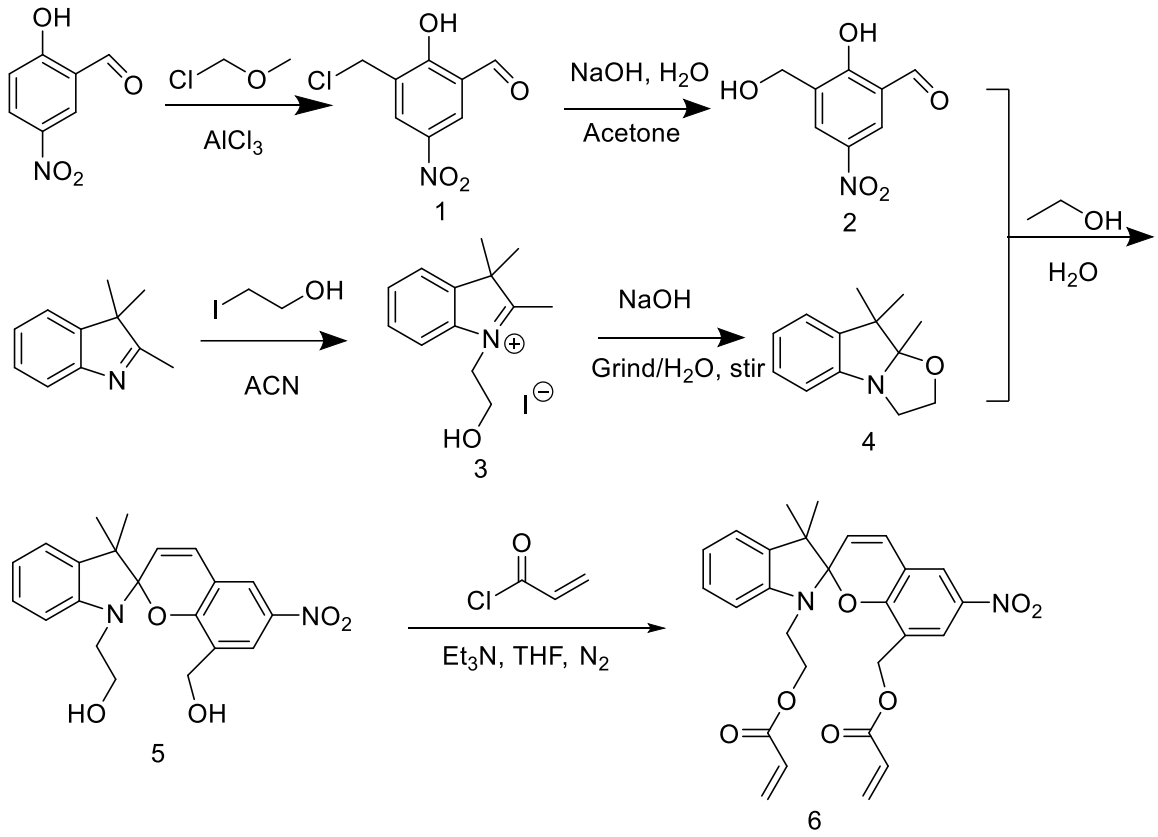



Fig. 2-1: Synthesis of Spiropyran-diacrylate (6)

A dry 3 neck round bottom flask (RBF) was prepared. 2-hydroxy-5-nitro-adehyde was dissolved in chloromethyl methyl ether in the round bottom flask, purged with nitrogen. Aluminum chloride was added and stirred at room temperature for 1 hour. The reaction was heated to 75°C, refluxed for 2.5 h. The reaction was quenched with iced water and the yellow solid residue (1) was collected. Extract the water phase with EA and evaporate the solvent. Recrystallize

from hot hexane or run a column chromatography (DCM: methanol= 97:3 as eluent).

3-Chloromethyl-5-nitro-aldehyde (1) (1 eq.) was dissolved in acetone and added to an RBF, heat to reflux for 30 minutes. 6 [M] NaOH (1.1 eq.) water solution was dropwise add to the system and refluxed for 3 hours. Saturated NH4Cl solution was added to neutralize the salt and EA was used for extraction. Mixture was filtered and chilled to participate the product (2). Recrystallize the crude yellow product with hot hexane or run a column chromatography (DCM: methanol= 97:3 as eluent).

2,3,3-trimethyl-3H-indole (1 eq.) was dissolved in acetonitrile. 2-Iodoethanol (1.25 eq.) and the solution were added into a one neck RBF. After 12 hours reflux with stirring, it was cooled down to room temperature and cold diethyl ether was added to wash it. Dark red crude product (3) was acquired after the filtration.

Green chemistry method

1-(2-Hydroxyethyl)-2,3,3-trimethyl-3H-indolium iodide (3) (1 eq.) from last step and anhydrous KOH (1.6 eq.) were added to a mortar. The mixture was grinded vigorously for about half an hour to get a yellow paste from dark red color. The paste was dissolved with petroleum ether, water was removed with $MgSO_4$. Solvent was evaporated and high vacuum was applied to dry it for next step.

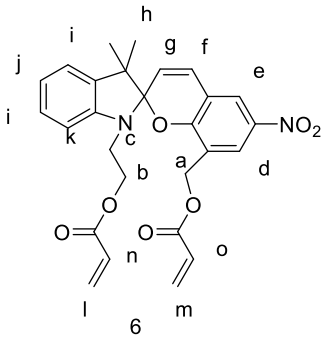
Solution method

1-(2-Hydroxyethyl)-2,3,3-trimethyl-3H-indolium iodide (3) (1 eq.) from last step and anhydrous KOH (1.6 eq.) were added to an RBF. Dissolved with water

and stirred vigorously for 1 hour. Crude product (4) was extracted with petroleum ether and water was removed with MgSO4. Solvent was evaporated and high vacuum was applied to dry it for next step.

3-hydroxymethyl-5-nitro-aldehyde (2) (1 eq.) was dissolved in ethanol and added to an RBF. Water (same volume as ethanol) and 9,9,9a-Trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a] indole (4) (1.2 eq.) from last step were added to the RBF. The RBF was heated to reflux for 5 hours. After cooling to room temperature, ethanol was rotational evaporated and water was added to the mixture. The mixture was heated to boil and filtered and this step was repeated. Crude product (5) was washed with benzene. A column chromatography (EA: Hexane= 1: 1 as eluent) was run to purify it and get dark purple solid.

Spiropyran-diol (5) (1 eq.) from last step in THF was dissolved and added to a 3-neck RBF. Triethyl amine (10eq.) was also added to the RBF, purged the RBF with $N_2$ after vacuum. Ice bath was prepared to cool the RBF. Acryloyl chloride (10 eq.) in THF solution was slowly added to the RBF by addition funnel. The reaction was stirred at room temperature for 24 hours and filtered. Solvent was evaporated and crude compound was dissolved in DCM and washed with water, 0.5 N HCl, 10% $NaHCO_3$. A column chromatography with EA: Hexane=1: 4) and prep-GPC were run to purify it.



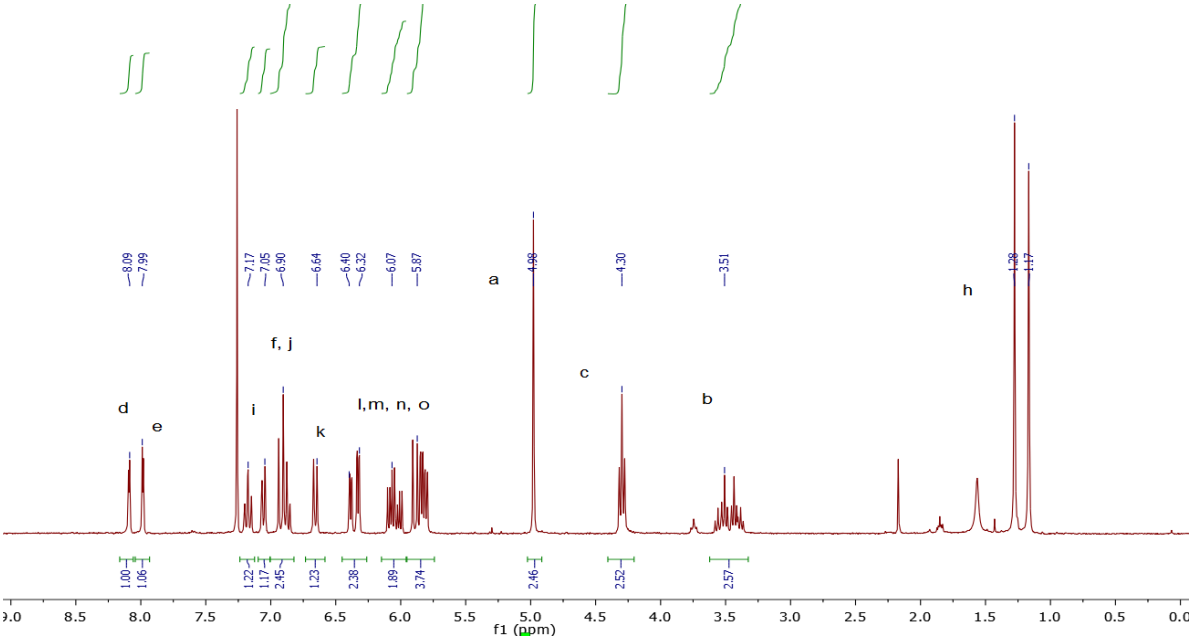
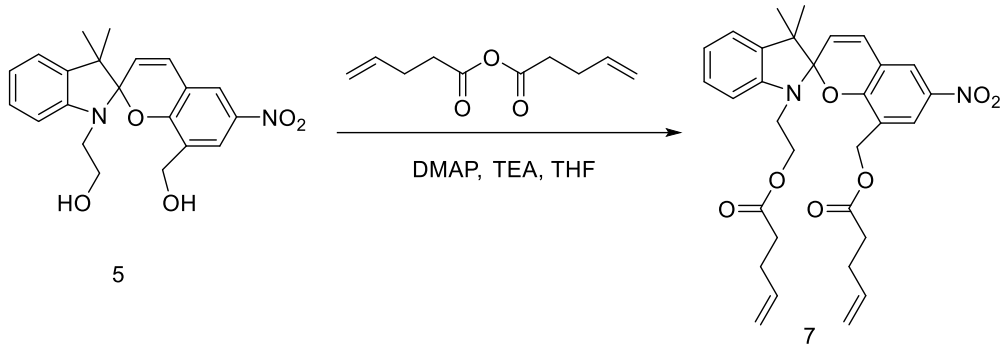




Figure. 2-2: $^{1}H$ NMR (300 MHz/ $CDCl_3$) of spiropyran-dicarylate (6)

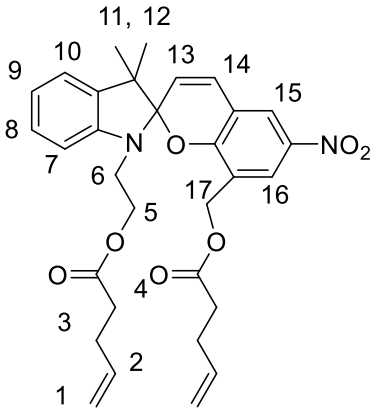
2.2.2 Synthesis of spiropyran- diene (7)




5 7

Figure. 2-3: Synthesis of spiropyran-diene (11)

Spiropyran-diol (317 mg, 0.824 mol, 1 eq) was dissolved with 7.6 mL THF in an RBF. 4-Pentenoic anhydride (330 mg, 1.813 mol 2.2 eq) and DMAP (10 mg, 0.0824 mol, 1 eq) were also added to the RBF. This reaction was allowed to stir overnight. Triethylamine (183 mg, 1.813 mmol, 2.2 eq) was added, followed by stirring for 30 min. Remove volatiles with rotary evaporator. A column chromatography (EA: HEX=25: 75) was used to get pure solid product 7 (200 mg, yield=44%).



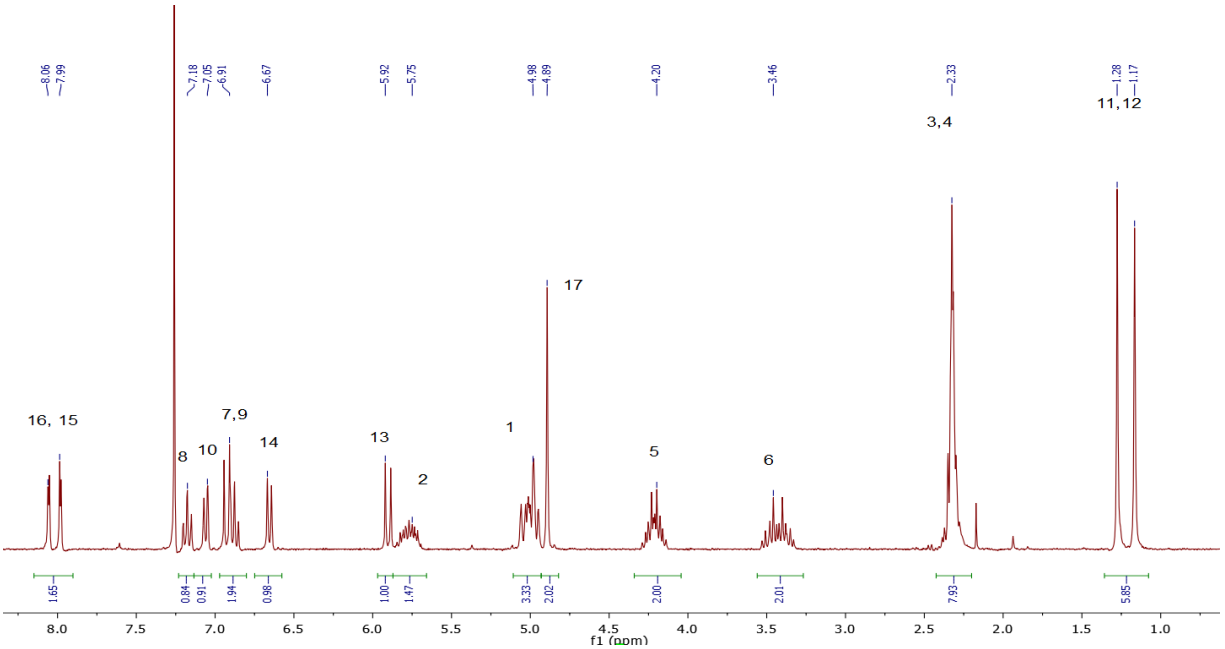



Figure. 2-4: $^{1}H$ NMR (400 MHz/ $CDCl_3$) of spiropyran-diene

## 2.2.3 Synthesis of RM 82 mesogen (11)

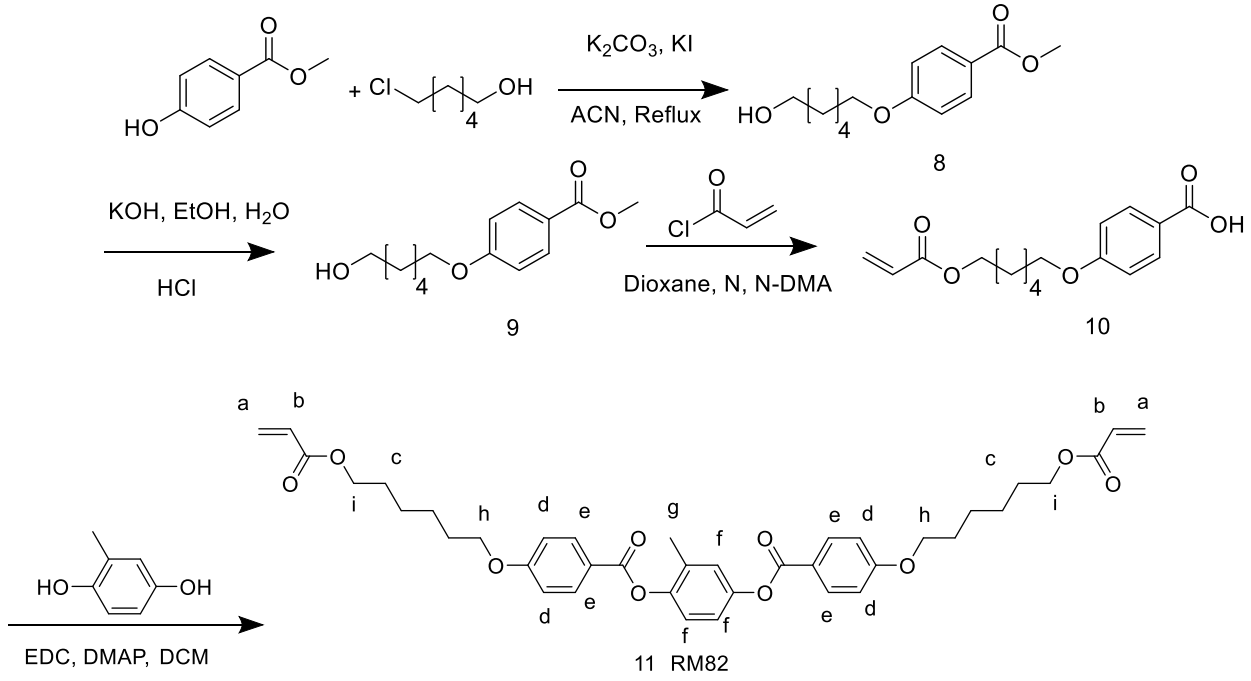


Figure. 2-5: Synthesis of RM 82 mesogen

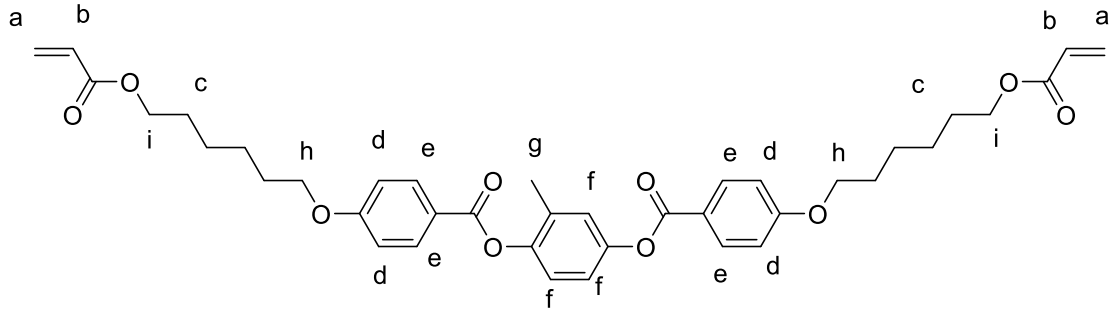
Acetonitrile was used to dissolve Methyl-(4-hydroxybenzoate) (1 eq.) and 6-bromohexanol (1.1 eq.) in an one-neck round bottom flask (RBF). $K_2CO_3$ (1.5 eq.) and KI (0.12 eq.) were added to the mixture. Heated to 90 °C and refluxed overnight. The mixture was filtered after it came to room temperature and the solvent was evaporated to get crude product 8.

Crude product 8 from last step was dissolved in ethanol in an one-neck RBF. Base (10 eq. of KOH water solution) was also added to the flask. Heated to 95 °C and refluxed for 3 hours. Removed heating and evaporated the most solvent. Crude product was washed with ether. Water phase was collected and neutralized with 2N HCl to get the white solid precipitate. The precipitate was dried to get pure product 9 for next step.

A 3-neck RBF with a condenser connected to Schlenk Line and an additional funnel were prepared. Intermediate 9 (1 eq.) from last step was added to the flask and the system was filled with N2 after vacuum. Dry dioxane (0.8 M solution) and N,N-dimethyl aniline (1.1 eq.) were added under the N2 flow. Heated to 60 °C, acryloyl chloride was dropwise added by additional funnel. The reaction took 4 hours at 60 °C under N2 atmosphere. Removed heating and added cold water to precipitate the crude product. The intermediate 10 was crystallized with hot isopropanol and dried for next step.

Intermediate 10 (2.1 eq) from last step, methyl hydroquinone (1 eq.) and 4-dimethyl aminopyridine (0.2 eq.) (DMAP) were dissolved in dry DCM. The mixture

was prepared in ice bath. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (4 eq.) (EDC) was quickly added to the system and the reaction was run at room temperature. After 18 hours reaction, DCM was added to dilute the crude product. The crude product was washed with HCl (1 N) and saturated NaHCO3. A column chromatography (EA: Hexane= 1:3 as eluent) was run and recrystallization with isopropanol was done to purify and pure product mesogen 11 was acquired.



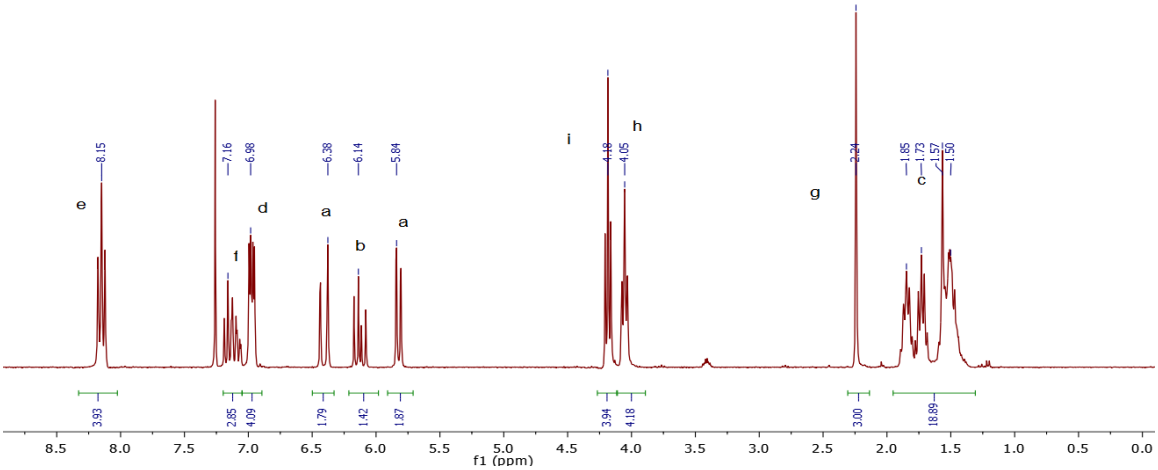




Figure. 2-6: $^{1}H$ NMR (400 MHz/ $CDCl_3$) of RM 82

2.2.4 Synthesis of 11C-diene mesogen monomer (14)

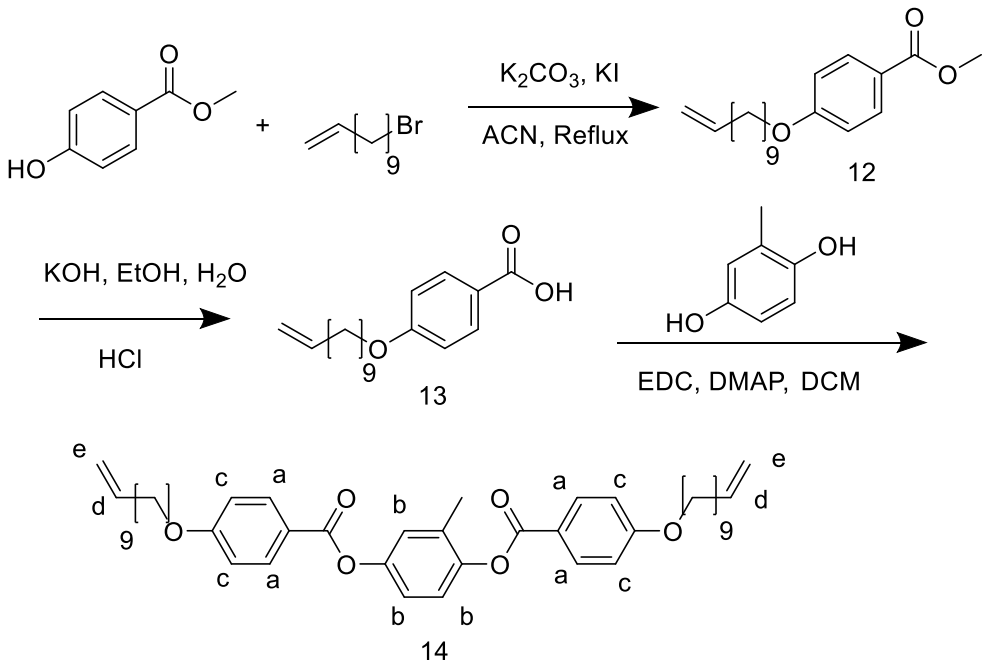


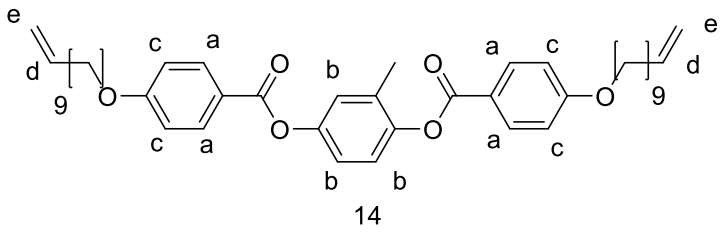

Figure. 2-7: Synthesis of 11C-diene mesogen monomer (14)

In an RBF equipped with a stir bar, Methyl 4-hydroxybenzoate (5 g, 32.85 mmol, 1.0 eq) and 11-Bromo-1-undecene (8.8 g, 37.78 mmol, 1.15 eq) were dissolved in 60 mL acetonitrile. Potassium carbonate (6.34 g, 45.95 mmol, 1.4 eq) and Potassium iodide (0.526 g, 3.285 mmol, 0.1 eq) were added to the flask. The mixture was allowed to heat to reflux overnight. After it came to room temperature filter and remove solvent with rotary evaporator, yielding white crude intermediate 12.

The intermediate 12 was dissolved in 80 mL of ethanol, adding Potassium hydride (4g, 100 mmol, 3 eq) in water (20 mL) solution. The mixture was stirred at 60°C overnight. 120 mL 1 [M] HCl solution was used to acidify the product to

precipitate. Recrystallize with hot hexane, yielding 6.0 g white crystal intermediate 13 (overall yield= 60%).

The intermediate 13 (1.3 g, 4.4 mmol, 2.2 eq), methyl hydroquinone (251 mg, 2 mmol, 1 eq.) and 4-dimethyl aminopyridine (48.9 mg, 0.4 mmol, 0.2 eq.) (DMAP) were dissolved in dry DCM. An ice bath was prepared when the mixture was prepared. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (1.53 g, 8mmol, 4 eq.) (EDC) was quickly added to the system and the reaction was run at room temperature. After 18 hours reaction, DCM was added to dilute the crude product. The crude product was washed with HCl (1 N) and saturated $NaHCO_3$. Column chromatography (EA: HEX=15: 85) and recrystallization (hot ethanol) were used to get pure product 14.



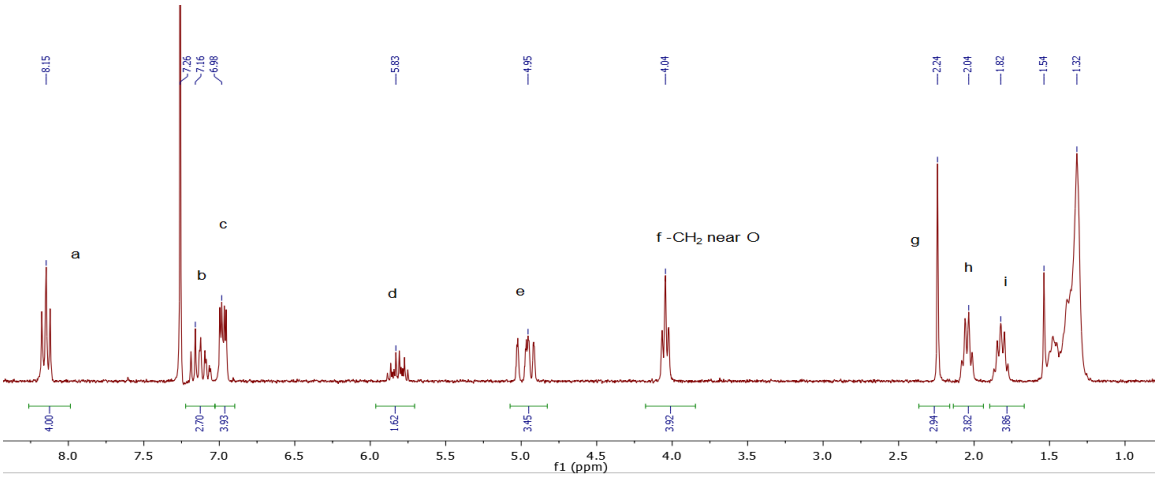




Figure. 2-8: $^1H$ NMR (400 MHz/ $CDCl_3$) of 11C-diene mesogen monomer

2.2.5 Synthesis of 11C-diene non-mesogen monomer (15)

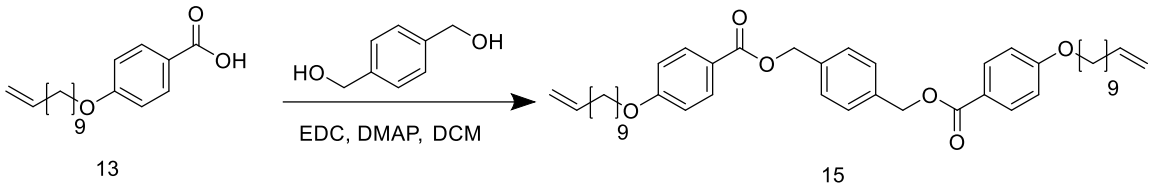
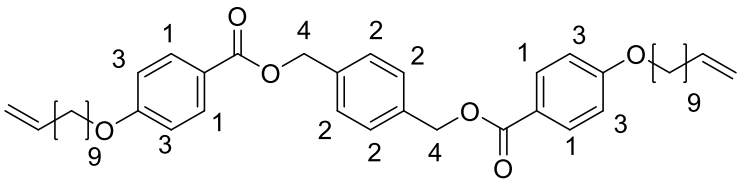



Figure. 2.9: Synthesis of 11C-diene non-mesogen monomer (15)

The intermediate 13 (4 g, 4.4 mmol, 2.2 eq), 1,4-Benzenedimethanol (251 mg, 2 mmol, 1 eq.) and 4-dimethyl aminopyridine (48.9 mg, 0.4 mmol, 0.2 eq.) (DMAP) were dissolved in dry DCM. An ice bath was prepared when the mixture was prepared. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (1.53 g, 8mmol, 4 eq.) (EDC) was quickly added to the system and the reaction was run at room temperature. After 18 hours reaction, DCM was added to dilute the crude product. The crude product was washed with HCl (1 N) and saturated $NaHCO_3$. Column chromatography (EA: HEX=15: 85) and recrystallization (hot hexane) were used to get pure product 15



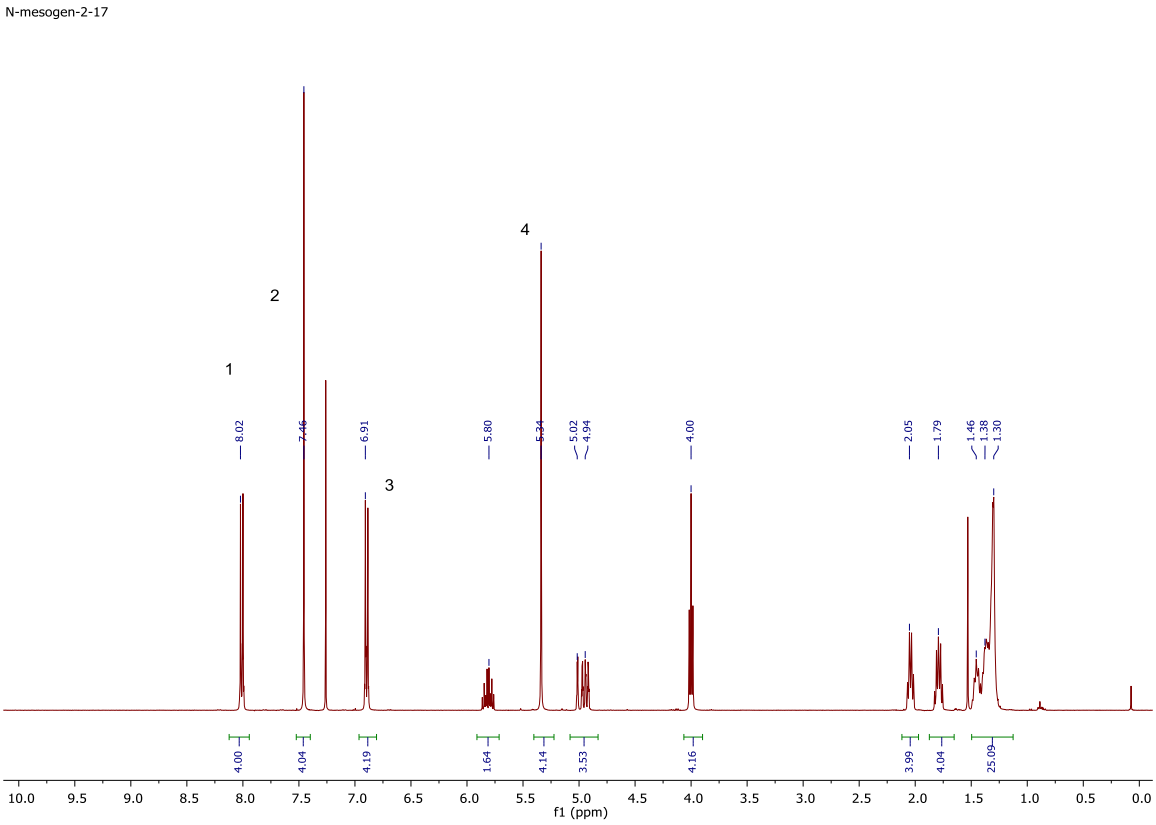



Figure. 2-10: $^{1}H$ NMR (400 MHz/ $CDCl_3$) of 11C-diene non-mesogen monomer

2.2.6 Preparation for Thiol-acrylate liquid crystalline elastomer sample

Dissolve Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) in $CHCl_3$ (20%), dissolve Butylated hydroxytoluene (BHT) in $CHCl_3$(0.001%), dissolve dipropylamine (DPA). Add spiropyran diacrylate (1% eq.) and RM 82 (1 eq.) in a vial. Add 2,2′ -(Ethylenedioxy)diethanethiol (EDDET) (0.6 eq.) with a syringe. Add PETMP (0.15 eq.) solution and BHT (0.06% eq.) solution to the vial, add enough $CHCl_3$ to dissolve the mixture. Add DPA (3% eq.) in $CHCl_3$ (50%). Pour the mixture into a polytetrafluoroethylene (PTFE) mold and cure for 24 hours at

room temperature. Remove from mold and high vacuum it to remove the solution.

2.2.7 Preparation for Hydrosiloxane based LCE sample

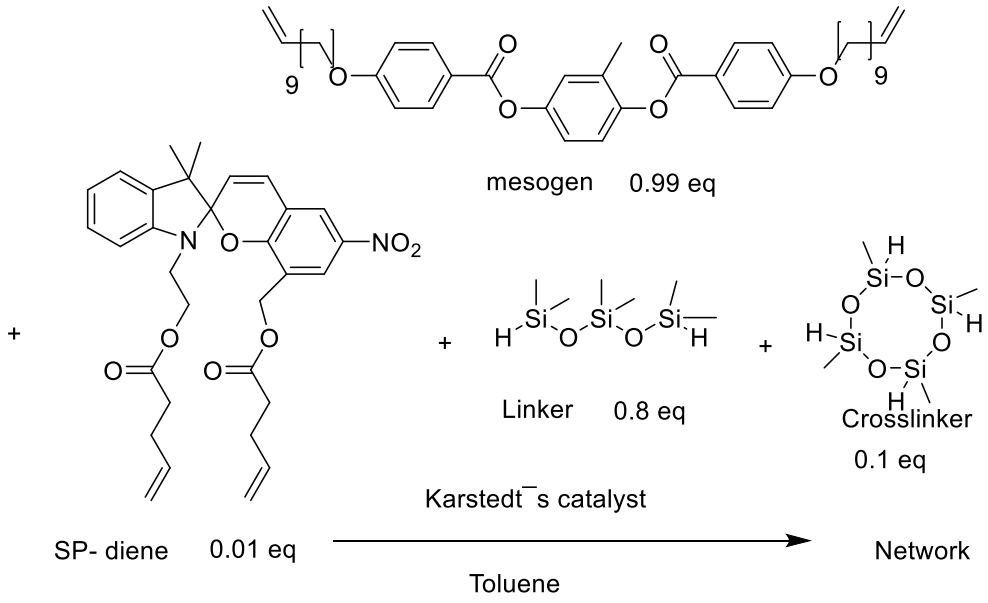



Figure. 2-11 Preparation of Hydrosiloxane based LCE sample

Diene monomer and hydrosiloxane linkers were dissolved in toluene, mixed with vortex. Karstedt's catalyst was added after mixing. Then mixture was poured to a PTFE mold. The sample was cured at room temperature for 48h. Soxhlet extraction with toluene was used to remove oligomers. The sample was evaporated under atmosphere first, then high vacuum to remove toluene.

2.2.8 Preparation for Hydrosiloxane based Non-LCE sample

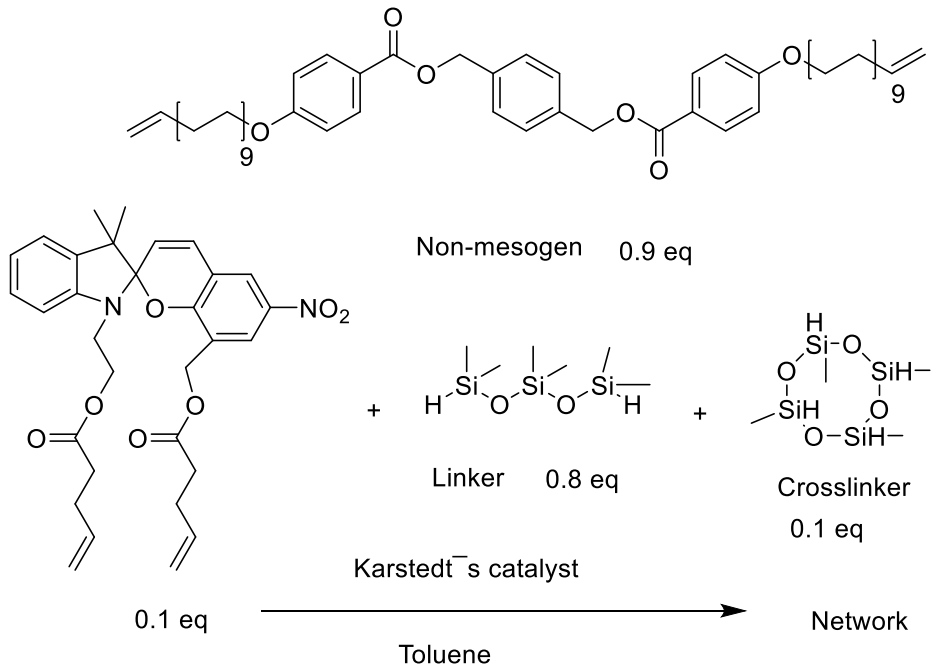



Figure. 2-12 Preparation for Hydrosiloxane based Non-LCE sample

Diene monomer and hydrosiloxane linkers were dissolved in toluene, mixed with vortex. Karstedt's catalyst was added after mixing. Then mixture was poured to a PTFE mold. The sample was cured at room temperature for 48h. Soxhlet extraction with toluene was used to remove oligomers. The sample was evaporated under atmosphere first, then high vacuum to remove toluene.

.

# CHAPTER III

# RESULTS AND DISCUSSION

## 3.1 DSC curve of spiropyran-incorporated Thiol-acrylate LCEs

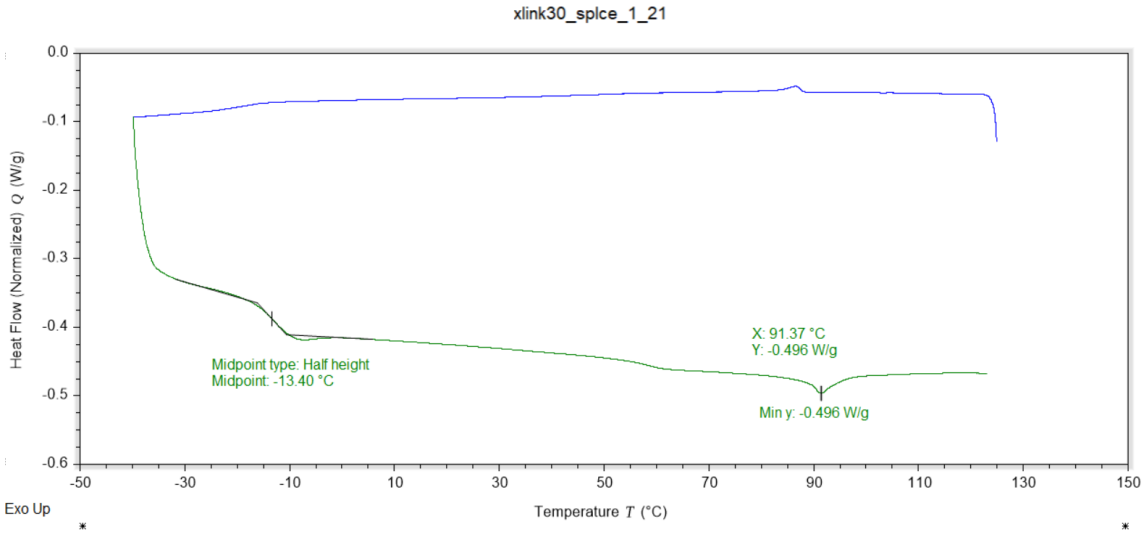



Figure. 3-1: DSC curve of spiropyran-incorporated Thiol-acrylate LCEs

From DSC curve we can see a stepwise decrease at -13.4 °C in the flow signal, which indicates $T_g$ of LCE network. At 91.37 °C we can see a valley in the flow signal, which indicates the $T_i$ of LCE network.

3.2 Stress-strain curve from tensile test of 1% SP- Thiol-Acrylate LCE

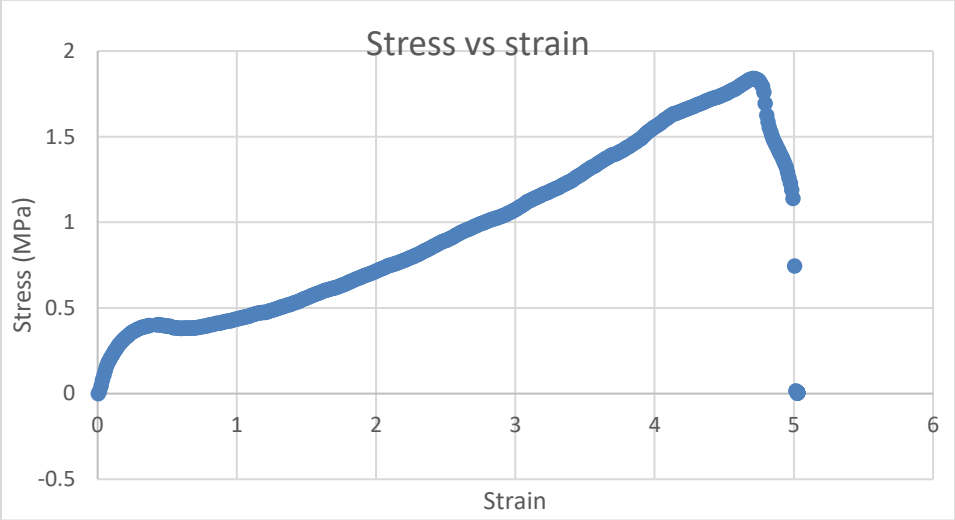



Figure. 3-2: Stress-strain curve from tensile test of 1% SP- Thiol-Acrylate LCE

From stress-strain curve we can see the curve has a plateau state at around 0.5 strain and increases linearly to around 450% strain to fail. The decrease at 0.4 indicates the yield and macroscopic orientation of LCE network, more specifically, the rotation of domains. After this plateau, the applied stress grows at an increasing rate with the strain increasing, which includes the crystalline behavior with stretching.

3.3 Photos (upper) and RGB analysis (lower) of 1% SP- Thiol-Acrylate LCE

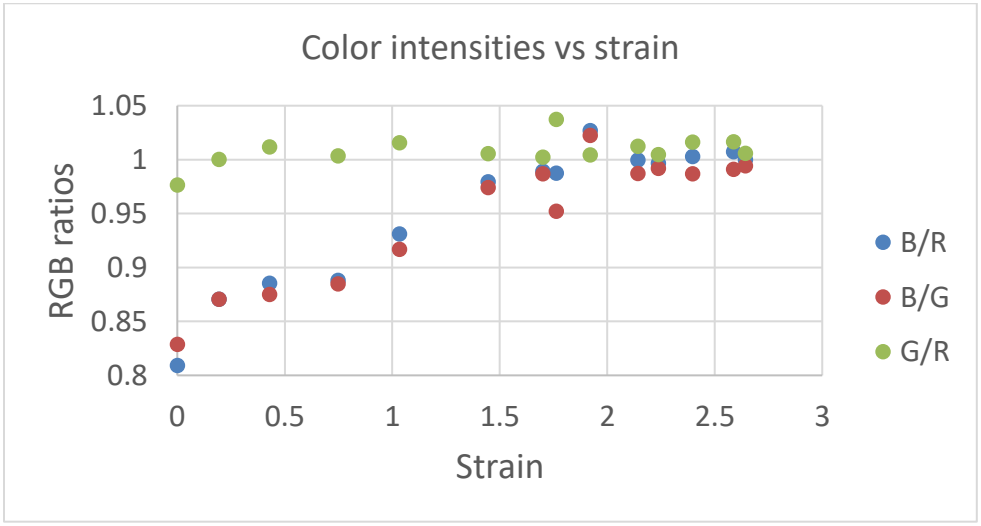



Figure. 3-3: Photos (upper) and RGB analysis (lower) of 1% SP- Thiol-Acrylate LCE

If mechanochemical activation is present, the B/G and B/R color ratios would increase above 1. However, here they appear increase initially and plateau around 1. The initial increase was attributed to the material becoming transparent as the LCE undergoes alignment under stress and the color ratios begin to reach

that of the neutral background. Thus, it was concluded that no activation was seen. Further, no color change was observed with the naked eyes.

Why this SP incorporated thiol-acrylate LCE not mechanochemically activable is still unclear. We assumed that some unknown side reactions and insufficient mechanical properties of network might be the probable reasons. To eliminate the probable negative factors, we decided to prepare siloxane-based LCE network, which exhibits a higher stress strain[21] at failure and employees Platinum catalyzed hydrosilylation chemistry that is compatible with spiropyran.[14]

To further examine the availability of spiropyran-diene and feasible mechanochemical activation of SP contained siloxane-based network, we prepared SP contained PDMS according to Craig's previous work[14]. Significant blue color was observed when SP contained PDMS sample was stretched (Figure. 3-4), which proved the purity of spiropyran-diene we prepared and compatibility between Platinum catalyzed hydrosilylation chemistry and spiropyran.

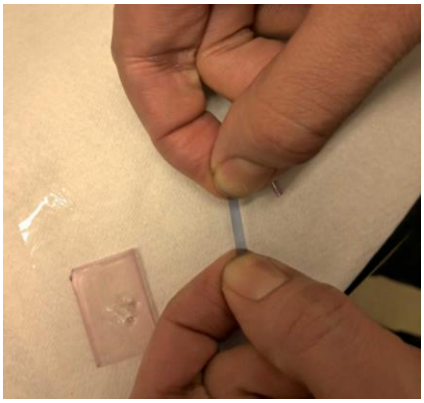


Figure.3-4: Activation of SP contained PDMS sample

## 3.4 DSC curve of 1% SP- Hydrosiloxane LCE

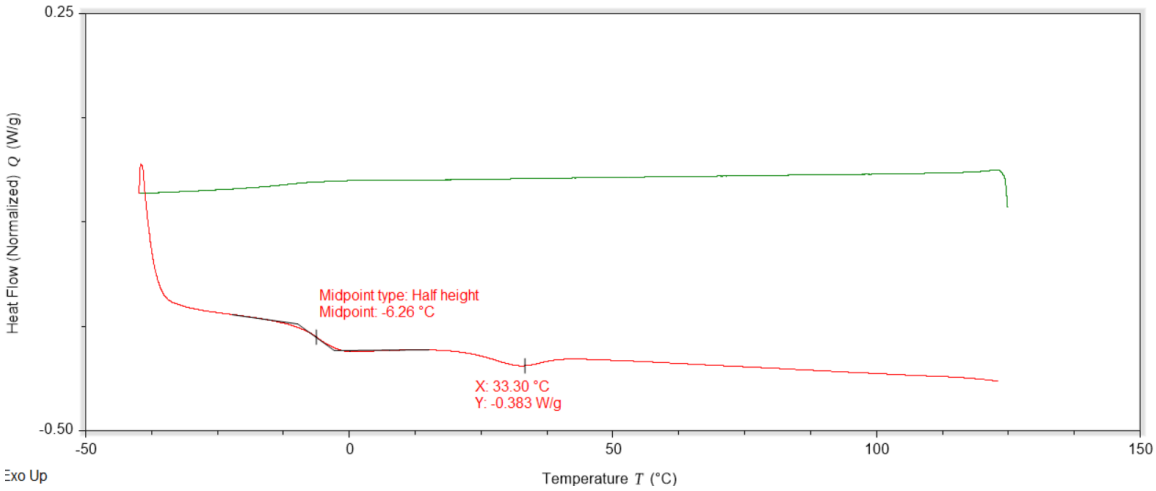



Figure. 3-5: DSC curve of 1% SP- Hydrosiloxane LCE

From DSC curve we can see a stepwise decrease at -6.26 °C in the flow signal, which indicates $T_g$ of LCE network. At 33.30 °C we can see a valley in the flow signal, which indicates the $T_i$ of LCE network.

3.5 Stress-strain curve from tensile test of 1% SP- Hydrosiloxane LCE

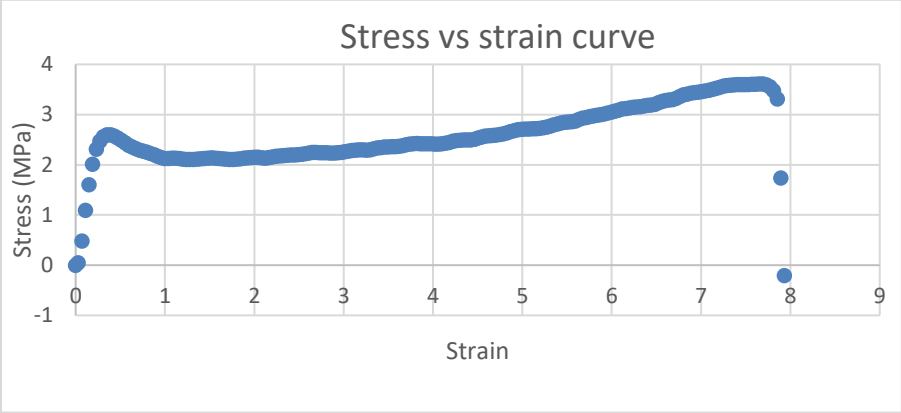
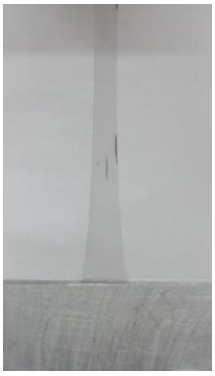
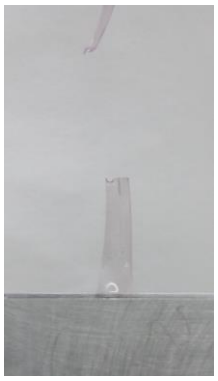



Figure. 3-6: Stress-strain curve from tensile test of 1% SP- Hydrosiloxane LCE

The sample yield at around 30% strain and fail at around 760% strain, which shows a better stress strain at failure, but the activation still unsatisfactory.

3.6 Photos (upper) and RGB analysis (lower) of 1% SP- Hydrosiloxane LCE

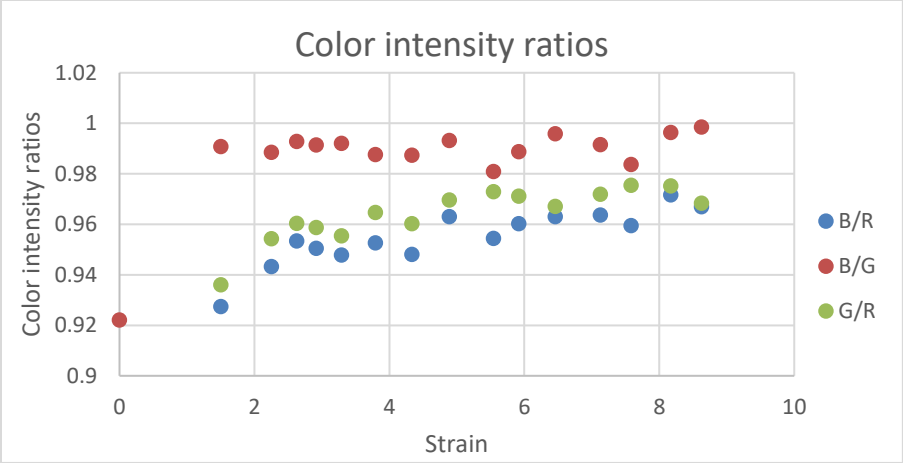



Figure. 3-7: Photos (upper) and RGB analysis (lower) of 1% SP-Hydrosiloxane LCE

All ratios are around 1 and unsatisfactory mechanochemical activation was achieved.

The mechano-chromophore spiropyran we synthesized was proved to be activatable according to the right structure from NMR and successful SP-PDMS sample. But 1% SP- Hydrosiloxane LCE was still unsatisfactory to be activated, we had to rethink about our idea and check if the liquid crystal mesogen in LCE system has negative effect on mechanochemical activation. So we modified the structure of mesogenic monomer 14 to non-mesogenic monomer 15 in order to eliminate the liquid crystal behavior. The results of SP- Hydrosiloxane N-LCE follow below.

3.7 DSC curve of Non-liquid crystal monomer (upper) and 1% SP- Hydrosiloxane N-LCE (lower)

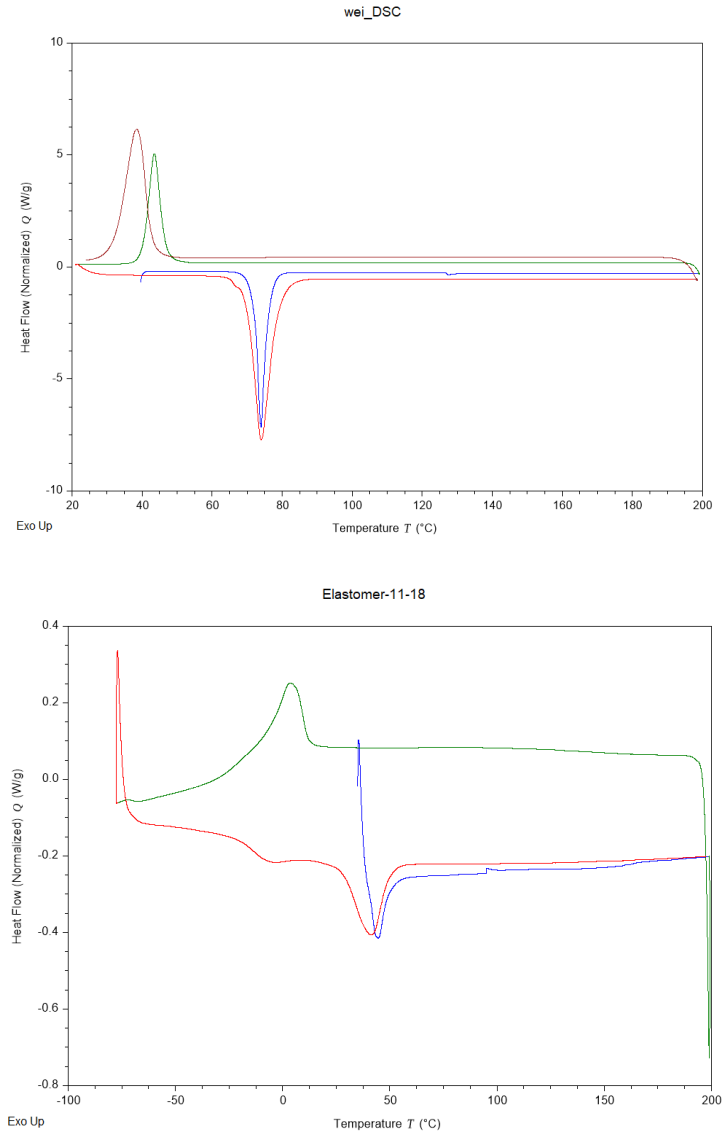



Figure. 3-8: DSC curve of Non-liquid crystal monomer (upper) and 1% SP-Hydrosiloxane N-LCE (lower)

The non-liquid crystal monomer(upper) showed a Tm at 75°C. No $T_i$ was observed, which indicates the success of eliminating liquid-crystal behavior.

For 1% non-liquid crystal hydrosiloxane elastomer, it showed a $T_g$ peak at -15°C and a $T_m$ peak at 45°C, no $T_i$ was observed, which is consistent with the monomer.

3.8 Stress strain curve (upper) and photos (lower) of 1% SP- Hydrosiloxane N-LCE

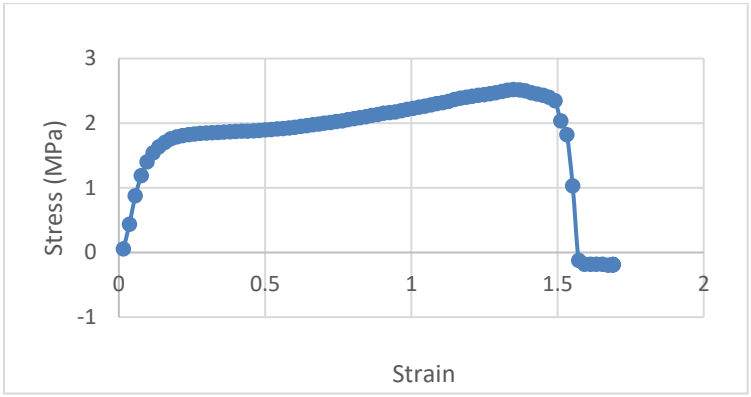



Figure. 3-9: Stress strain curve (upper) and photos (lower) of 1% SP-Hydrosiloxane N-LCE

The sample yields at around 20% and fail at 150%. The stress-strain at failure is worse than 1% SP- Hydrosiloxane LCE. No mechanochemical activation was observed.

We also tried to prepare 10% SP- Hydrosiloxane N-LCE, surprisingly the preliminary result showed eye visible mechanochemical activation (Figure. 3-10). In the future we would prepare different content SP-Hydrosiloxane LCE sample and SP- Hydrosiloxane N-LCE sample and explore how the alignment and SP-content would affect the mechanochemical activation.

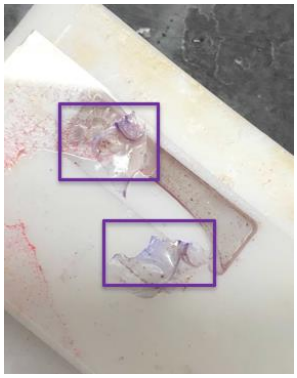


Figure. 3-10: Preliminary activation of 10% SP- Hydrosiloxane N-LCE

# CHAPTER IV

# CONCLUSIONS

Reasonably pure mechanophore spiropyran was synthesized and functionalized to SP-diacrylate and SP-diene forms. Acrylate mesogenic monomer RM 82, alkene mesogenic and non-mesogenic monomer were successfully prepared as well. Using thiol-acrylate Michael addition and Platinum catalyzed hydrosilylation, a series of spiropyran incorporated networks were fabricated. Unlike our initial idea that highly aligned spiropyran incorporated LCE would exhibit enhanced mechanochemical activation, the two SP-contained LCE networks both showed unsatisfactory mechanochemical activation. However, compared to highly aligned SP-contained LCE networks, not highly aligned PDMS elastomer system and preliminary result from 10% SP-contained Non-liquid crystalline elastomer network both showed some visible mechanochemical activation, which suggests highly aligned mesogen fabricated LCE network may have some negative effect on mechanochemical activation. Further investigation is undergoing to explore how the mechanophore content and chain alignment would affect the mechanochemical activation.

REFERENCES


1. Takacs, L. *Chem. Soc. Rev.* **2013**, *42* (18), 7649–7659.
2. Li, J.; Nagamani, C.; Moore, J. S. *Acc. Chem. Res.* **2015**, *48* (8), 2181–2190.
3. Staudinger, H.; Bondy, H. F. Isoprene and Rubber. XIX. Ber. Dtsch. Chem. Ges. B 1930, 63, 734−736.
4. Kauzman, W.; Eyring, H. *J. Am. Chem. Soc.* **1940**, *62* (11), 3113–3125.
5. Encina, M., Lissi, E., Sarasu ´a, M., Gargallo, L., and Radic, D. (1980). J*. Polym. Sci. Polym. Lett. Ed.* 18, 757–760.
6. Berkowski, K. L.; Potisek, S. L.; Hickenboth, C. R.; Moore, J. S. *Macromolecules* **2005**, 8975–8978.
7. Chaude, O. Cahiers Phys. 50, 17 (1954)0 51, 6 (1954); 52, 3 (1954).
8. Tipikin, D. S. Mechanochromism of organic compounds by the example of spiropyran. Russ. *J. Phys. Chem*. 75, 1720–1722 (2001)
9. Potisek, S. L.; Davis, D. A.; Sottos, N. R.; White, S. R.; Moore, J. S. *J. Am. Chem. Soc.* **2007**, *129* (45), 13808–13809.
10. Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martínez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, *459* (7243), 68–72.

11. Gossweiler, G. R.; Kouznetsova, T. B.; Craig, S. L. *J. Am. Chem. Soc.* **2015**, *137* (19), 6148–6151.
12. Wang, J.; Kouznetsova, T. B.; Kean, Z. S.; Fan, L.; Mar, B. D.; Martínez, T. J.; Craig, S. L. *J. Am. Chem. Soc.* **2014**, *136* (43), 15162–15165.
13. Wang, J.; Kouznetsova, T. B.; Niu, Z.; Ong, M. T.; Klukovich, H. M.; Rheingold, A. L.; Martinez, T. J.; Craig, S. L. *Nat. Chem.* **2015**, *7* (4), 323–327.
14. Gossweiler, G. R.; Hewage, G. B.; Soriano, G.; Wang, Q.; Welshofer, G. W.; Zhao, X.; Craig, S. L. *ACS Macro Lett.* **2014**, *3* (3), 216–219.
15. Vidavsky, Y.; Yang, S. J.; Abel, B. A.; Agami, I.; Diesendruck, C. E.; Coates, G. W.; Silberstein, M. N. *J. Am. Chem. Soc.* 2019, 141 (25), 10060–10067.
16. Beiermann, B. A.; Kramer, S. L. B.; Moore, J. S.; White, S. R.; Sottos, N. R.; *ACS Macro Letters* 2012 1 (1), 163-166.
17. Beiermann, B. A.; Kramer, S. L. B.; May, P. A.; Moore, J. S.; White, S. R.; Sottos, N. R. *Adv. Funct. Mater.* 2014, 24, 1529.
18. Saed, M. O.; Torbati, A. H.; Starr, C. A.; Visvanathan, R.; Clark, N. A.; Yakacki, C. M. J. Polym. Sci. Part B Polym. Phys. 2017, 55 (2), 157–168.
19. Yakacki, C. M.; Saed, M.; Nair, D. P.; Gong, T.; Reed, S. M.; Bowman, C. N. RSC Adv. 2015, 5 (25), 18997–19001.
20. Ren, W.; Griffin, A. C. Phys. Status Solidi B 2012, 249, 1379– 1385.
21. Ren, W (2007). Structure-property Relations of Siloxane-based Main Chain Liquid Crystalline Elastomers and Related Linear Polymers. URI: http://hdl.handle.net/1853/16248

22. O’Bryan, G.; Wong, B. M.; McElhanon, J. R. ACS Appl. Mater. Interfaces 2010, 2 (6), 1594–1600.