Photomechanical Effects in Ruthenium Sulfoxide Complexes

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Yuhuan Jin
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Photomechanical Effects in Ruthenium Sulfoxide Complexes

by

YUHUAN JIN

has been approved for

the Department of Chemistry and Biochemistry

and the College of Arts and Sciences by

Jeffrey J. Rack

Professor of Chemistry and Biochemistry

Robert Frank

Dean, College of Arts and Sciences
ABSTRACT

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Photomechanical Effects in Ruthenium Sulfoxide Complexes

Director of Dissertation: Jeffrey J. Rack

In order to incorporate ruthenium sulfoxide complexes into macromolecules, the complex \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) was synthesized, which has the norbornene group covalently attached to the sulfur atom through a peptide linkage. This complex was copolymerized with norbornene at specific ratios by the Ring Opening Metathesis Polymerization (ROMP) method. The obtained copolymers and \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) were characterized by UV-Visible absorption spectroscopy, \(^1\text{H}\) NMR spectroscopy and Transient Absorption spectroscopy. The copolymers yielded the same UV-Visible absorption spectrum as the ruthenium monomer, with the lowest energy MLCT absorption peak at around 370 nm for S-bonded isomer, and around 470 nm for S-bonded isomer in dichloromethane. The isomerization rate was observed to vary with the medium. For S→O isomerization, the rate constant is \(5.0 \pm 0.7 \times 10^8 \text{ s}^{-1}\) for \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) and \(2.0 \pm 0.1 \times 10^8 \text{ s}^{-1}\) for the poly-\{\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB/NB}\} 1:25 in DCE, respectively. The evidence support the conclusion that the polymer backbone affects the photoisomerization rate constant of \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) in the copolymers. Thin films were prepared from the poly-\{\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB/NB}\} copolymers to study the photomechanical effects, and the poly-\{\text{Ru}^{II}(\text{bpy})_2\text{pyS-NB/NB}\} copolymer was used as the control experiment. Under the same irradiation condition with 405nm light, the poly-\{\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB/NB}\} with ratios of 1:25, 1:40 and 1:60 exhibited reversible
phototriggered bending towards the light. The poly-{$\text{Ru}^{\text{II}}(\text{bpy})_{2}\text{pySO-NB/NB}$} with the ratio of 1:110 and the poly-{$\text{Ru}^{\text{II}}(\text{bpy})_{2}\text{pyS-NB/NB}$} did not exhibit any photomechanical response upon irradiation. The compound, [$\text{Ru}($bpy$)_{2}\text{pySO}$](AOT)$_2$ was also dissolved in a Liquid Crystal Networks system, which exhibited different responses upon irradiation with linear polarized light of different polarized directions. In order to reveal the mechanism for the photomechanical effect in the amorphous ruthenium sulfoxide incorporated copolymer systems, nanoindentation techniques were employed to study the mechanical properties of the films associated with each copolymer. The nanoindentation results indicate that the ruthenium linkaged complexes yield a more compact structure, or stiffer in comparison to the underivatized polymers. Further, the photoisomerization of the $[$Ru(bpy)$_2$pySO-NB$]^2+$ forced the polymer to form an even more compact structure. Hence, a bilayer model was developed to explain the phototriggered bending in the ruthenium sulfoxide complexes incorporated copolymer systems.
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LIST OF ABBREVIATIONS

AOT  sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate
AFM  atomic force microscope
bpy  2,2’-bipyridine
DCM  dichloromethane
DCE  1,2-dichloroethylene
LCs  liquid crystals
LCN  liquid crystal network
MLCT  metal-to-ligand charge transfer
LMCT  ligand-to-metal charge transfer
NB  norbornene
pyS-NH\textsubscript{2}  2-(pyridin-2-ylmethylsulfanyl)-ethyamine
pySO  2-(isopropylsulfinylmethyl)pyridine
pyS-C\textsubscript{18}  2-(octadecylsulfanyl methyl)pyridine
pyS-NB  Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2-(pyridin-2-ylmethylsulfanyl)-ethyl)-amide
pySO-NB  bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2-(pyridin-2-ylmethylsulfinyl)-ethyl)-amide
ROMP  ring opening metathesis polymerization
T\textsubscript{g}  glass transition temperature
SEM  scanning electron microscope
LIST OF MOLECULAR STRUCTURES

AOT

pyS-NH₂

pyS-NB

pySO-NB

pyS-C₁₈

[Ru(bpy)₂(pyS-NB)]²⁺

[Ru(bpy)₂(pySO-NB)]²⁺
poly-\{[\text{Ru}^{II}(\text{bpy})_2\text{pyS-NB}] /\text{NB}\}\}

poly-\{[\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB}] /\text{NB}\}\}
CHAPTER 1. INTRODUCTION

It is of interest from both scientific and technological points of view to prepare molecules and materials that undergo a structural change in response to external stimuli.\(^1\) The stimuli could be electrons, pH change, magnetic field, heat or light.\(^3\) Among the many different types of molecules, photochromic compounds show specific advantages, such as: light stimuli are easily controllable and nonsensitive to environment. In order to manufacture a system showing macroscopic mechanical responses based on the molecular structure changing in subnanometer scale, there are three strategies to amplify the molecular motion: the first strategy is to incorporate the photochromic molecules into liquid crystals, the phase transformation from nematic to isotropic efficiently amplifies the molecule’s motion;\(^5,16-21\) the second strategy is to align all the molecules in a crystal, the order of molecules helps to sum up the small motion of each molecule into a large motion;\(^4,22-29\) the third strategy is to incorporate the photochromic molecules into macromolecules, the large size of the macromolecules could translate the small molecular motion of the photochromic molecules into much larger motion.\(^30-32\)

The light-to-mechanical energy transduction or conversion was first realized by Agolini and Gay in 1970, when they prepared an azobenzene functionalized polyimide and studied the photogenerated stress.\(^33\) However, the photogenerated contraction was first revealed by Smets and Blauwe in 1972, who prepared functionalized spirobenzopyran crosslinked poly(ethylacrylate) exhibiting more than 2% contraction upon light irradiation.\(^34\) Following that study, photomechanical effects were studied in
many different polymers and other soft materials; with different dyes such as azobenzene and spiropyran.\textsuperscript{35-44} Thereafter, it was realized that the Liquid Crystal Network (LCN) could achieve the most contraction with photoisomerization.\textsuperscript{45} However, no sample exhibiting large scale change was indentified until the work of Ikeda and Yu in 2003.\textsuperscript{19} They prepared azobenzene functionalized mesogen crosslinked LCN film, which exhibited reversible bending upon irradiation with different wavelengths of light. This motion was due to the magnification of the nematic phase to the isotropic phase transition of the liquid crystal, which is enabled by the crosslinking of the liquid crystal monomers.\textsuperscript{18, 46} Most photomechanical studies are conducted in LCNs after Ikeda’s work. Broer and Van Oosten have developed various alignment methods for the liquid crystal to achieve faster and stronger phototriggered bending since 2004.\textsuperscript{20, 21, 47, 48} In these studies, they also characterized the photomechanical effect in LCNs films by calculating the strain difference between the top and bottom layers of the film, and estimated the performed work for the phototriggered bending.

Though most of the current photomechanical systems are based on soft materials, there are some studies based on single crystals, which employ the second strategy, using the order of the molecules in single crystal to sum up the molecular motions. The cell volume in a single crystal is changed by photoisomerization or photodimerization. The majority of the studies reports surface topology change, however, only a limited number of studies report crystal shape changing.\textsuperscript{1, 4, 22, 23, 26, 27, 49} The first well known study of crystal shape changing was reported by Irie and coworkers in 2007.\textsuperscript{23} They prepared rod-like diarylethene single crystals showing reversible bending upon light irradiation, which
was due to crystal package volume difference between the closed-ring and open-ring isomers of the diarylethene. They studied a series of diarylethene derivatives, and prepared cocrystals of diarylethene with perfluoronaphthalene, which could lift a heavy lead ball attached in the end of the crystal upon irradiation of light. Simultaneously, Bardeen and his coworkers studied a series of anthracene complexes. The single crystals of anthracene complexes exhibit shape changing by photodimerization. However, the size of those single crystals was in submicrometer scale. Besides these studies in diarylethene and anthracene single crystals, there have been only a few reports about the single crystals of azobenzene, which are in submicrometer scale and exhibit photomechanical movement upon irradiation with light.

There are just a few studies about the third strategy, which is incorporating the photochromic molecules into macromolecules and exploiting the large size of macromolecules to amplify the molecular motion. There were a few reports of reversible macroscopic photomechanical movement in amorphous polymers, which took an advantage in facilitating the fabrication of the photomechanical systems by using the third strategy. And there are just a few reports about the photomechanical studies on inorganic complexes, which are based on quinone group of the photochromes stacking with each other to form polymeric crystal material. There was no photo-mechanical study on inorganic complexes derivatized polymers except this project. The reason is that the isomerization of many inorganic photochromic compounds requires very low temperature, and the ligands exhibiting photoresponse are simple inorganic molecules
such as CO, NO, NO₂ and SO₂, \(^{53-55}\) which are hard to modify and apply in macromolecules for photo-mechanical systems.

A photo-reversible ruthenium sulfoxide compound \([\text{Ru(bpy)}_2\text{pySO}]^{2+}\) was developed previously by the Rack Group, the structure of this complex is shown in Figure 1.1.\(^9\) For \([\text{Ru(bpy)}_2(\text{pySO})]^{2+}\), the S-bonded and O-bonded lowest energy absorption maxima are 370 nm and 472 nm, respectively, and the S-bonded and O-bonded reduction potentials are 1.35 V and 0.75 V (vs. Ag/AgCl), respectively. Charge-transfer excitation of the S-isomer at 370 nm yields the O-isomer with a quantum yield (\(\Phi_{S\rightarrow O}\)) of 0.11, and an isomerization time constant (\(\tau_{S\rightarrow O}\)) of 1.5 ns in propylene carbonate. Conversely, charge-transfer excitation of the O-isomer at 470 nm yields the S-isomer with \(\Phi_{O\rightarrow S} = 0.027\) and \(\tau_{O\rightarrow S} = 6.3\) ns. Moreover, it is evident that the two isomers have distinct molecular structures. Based on this change in energy and structure, we proposed that \([\text{Ru(bpy)}_2\text{pySO}]^{2+}\) has potential application in reversible photomechanical systems.

We selected the third strategy to facilitate the development of a photomechanical system, which is incorporating the \([\text{Ru(bpy)}_2\text{pySO}]^{2+}\) complex into macromolecules. Polynorbornene was selected as the host polymer, due to its optical properties (no visible absorption) and low glass transition temperature. In order to incorporate the \([\text{Ru(bpy)}_2\text{pySO}]^{2+}\) into the polymer backbone, we designed a derivatized of the \([\text{Ru(bpy)}_2\text{pySO}]^{2+}\), which has a norbornene group covalently attached to the sulfur atom by a peptide linkage. Then this complex was copolymerized with norbornene of specific ratios to yield ruthenium complexes incorporated within copolymers. The synthesis and
characterization for both of the monomer and copolymers will be discussed in Chapter 4; the photomechanical studies for the obtained ruthenium complexes incorporated copolymers will be discussed in Chapter 5; and the mechanical properties studies by nanoindentation for the copolymers will be discussed in Chapter 6.

Figure 1.1. The molecular structure of a photoreversible complex [Ru(bpy)$_2$pySO]$^{2+}$. The structure in blue is the S-bonded isomer, and the structure in red is the O-bonded isomer.
CHAPTER 2. EXPERIMENTAL METHODS

Materials

The complexes cis-[Ru(bpy)$_2$Cl$_2$] · xH$_2$O, [Ru(bpy)$_2$(OSO)](PF$_6$)$_2$, [Ru(bpy)$_2$(pySO)] (PF$_6$)$_2$ were synthesized according to the literature procedures. The reagents [Ru(bpy)$_3$]Cl$_2$ · 6H$_2$O, 2,2'-bipyridine (bpy), m-chloroperoxybenzoic acid (m-cpba), thiosalicylic acid, triethylamine, 2-(bromomethyl)pyridine hydrobromide, 7-bromo-1-heptene, 5-bromo -1-pentene, cysteamine hydrochloride, oxalyl chloride, Bicyclo[2.2.1]hept-2-ene, 5-Norbornene-2-endo,3-exo-dicarboxylic acid, sodium hydroxide and 2nd generation Grubbs’ catalyst were purchased from Sigma Aldrich and used as received. The reagent silver hexafluorophosphate (AgPF$_6$) was purchased from Strem and used as received. All the solvents were purchased from VWR and used as received.

2-(Pyridin-2-ylmethylsulfanyl)-ethyamine (pyS-NH$_2$)

Cystamine hydrochloride (1.414g, 12.4mmol) and NaOH (1.575g, 39.4mmol) were mixed in ethanol/H$_2$O (125mL/15mL) and stirred for 15 minutes prior to the addition of 2-(Bromomethyl) pyridine hydrobromide (2.991g, 11.8mmol). The solution was refluxed and monitored by thin-layer chromatography (TLC). The solution was cooled to room temperature and volatiles were removed by rotary evaporation. The remaining residue was re-dissolved in water and extracted by chloroform. Chloroform was removed by rotary evaporation to yield a colorless liquid product. Yield: 1.7584g (88.4%). $^1$H NMR (CDCl$_3$, 300MHz): δ8.51 (d, 1H), 7.65 (t, 1H), 7.38 (d, 1H), 7.15 (t, 1H), 3.83 (s, 2H), 2.99 (t, 2H), 2.60(t, 2H).
Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2-(pyridin-2-ylmethylsulfanyl)-ethyl)-amide (pyS-NB)

Norbornene carboxylic acid (1.003g, 7.26mmol, 9:1 mixture of endo- and exo-, as determined by $^1$H NMR) was dissolved in 5mL oxalyl chloride and stirred for 2 hours. The volatiles were removed by rotary evaporation, and the residue was dissolved in 1 mL dichloromethane. Then the solution was added dropwise to a rapidly stirring dichloromethane solution (100 mL) containing pyS-NH$_2$ (1.758g, 10.5mmol) at 0 °C. The reaction was monitored by TLC. The precipitate was removed by filtering, and the filtrate was handled by rotary evaporation at 30 °C to remove the solvent. The residue was re-dissolved in H$_2$O, and HCl was added to adjusting the solution to pH 6. Chloroform was used to extract product. Solvent was removed from the organic layer by rotary evaporation and dried under vacuum to produce a near colorless/light yellow oil product. By careful mobile phase column chromatography operation with DCM/ MeOH at a ratio of 9:1, a pure endo-pyS-NB was obtained. Yield: 1.9226g (91.8%). $^1$H NMR (CD$_3$CN, 300MHz): δ8.50 (d, 1H), 7.71 (t, 1H), 7.39 (d, 1H), 7.22 (t, 1H), 6.14 (m, 1H), 5.89 (m, 1H), 3.82 (s, 2H), 3.34 (m, 2H), 3.09 (s, 1H), 2.83 (m, 2H), 2.55 (t, 2H), 1.81 (td, 1H), 1.35 (m, 3H).

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2-(Pyridin-2-ylmethylsulfinyl)-ethyl)-amide (pySO-NB)

PyS-NB (1.7358g, 6.02mmol) and 3-chloroperbenzoic acid (m-cpba) (1.2116g, 6.32mmol, 90% by NMR) were dissolved in chloroform, respectively. The m-cpba solution was added dropwise to the rapidly stirring pyS-NB solution under room
temperature. TLC was used to monitor the reaction. K$_2$CO$_3$ aqueous solution was used to wash the solution then distilled water twice. MgSO$_4$ was added to absorb residual water. All solvent was removed by rotary evaporation, the remaining residue was purified by column chromatography and dried under vacuum line overnight to yield colorless wax product. Yield: 44.9%. $^1$H NMR (CD$_3$CN, 300MHz): δ8.58 (d, 1H), 7.81 (t, 1H), 7.36 (d, 1H), 7.30 (t, 1H), 6.12 (m, 1H), 5.84 (m, 1H), 4.21 (dd, 2H), 3.52 (m, 2H), 3.08 (s, 1H), 2.91 (m, 1H), 2.83 (s, 2H), 2.71 (m, 1H), 1.80 (m, 1H), 1.27 (m, 3H).

2-(C$_n$-2sulfanylmethyl)-pyridine (pyS-C$_n$, n=8, 18)

2-(Bromomethyl) pyridine hydrobromide (0.801mmol), C$_n$-thiol (0.962mmol) and sodium hydroxide (2.12mmol) were mixed in acetonitrile and refluxed for 2 hours. The volatiles were removed by rotary evaporating, and the residue was dissolved in 50 mL H$_2$O. Chloroform was used to extract the product, and then MgSO$_4$ was added to absorb residual water. Solvent was removed by rotary evaporation to result the product. Yield: 92.3% for pyS-C8, 73.0% for pyS-C18. $^1$H NMR (CDCl$_3$, 300MHz): pyS-C8, δ8.50 (d, 1H), 7.61 (td, 1H), 7.36 (d, 1H), 7.11 (m, 1H), 3.80 (s, 2H), 2.45 (t, 2H), 1.52(m, 2H), 1.21(m, 10H), 0.84(m, 3H); PyS-C18, δ8.50(d, 1H), 7.62(td, 1H), 7.36 (d, 1H), 7.13 (m, 1H), 3.81 (s, 2H), 2.46 (t, 2H), 1.52 (t, 2H), 1.30 (m, 30H), 0.86 (t, 3H).

2- Vinylbenzyl -sulfanyl-benzoic acid (OS-VB)

Thiosalicylic acid (2.63mmol) and sodium hydroxide (6.47mmol) were mixed in 60 mL Acetone and H$_2$O (1:1 v/v) and stirred for 10 minutes. Vinyl benzyl chloride (2.61mmol) was added to the solution and refluxed under N$_2$ overnight. The reaction solution was cooled down to room temperature and the volatiles were removed by rotary
evaporation. The residue remaining was dissolved in 40mL H₂O and chloroform was used to wash away unreacted vinyl benzyl chloride. The remaining chloroform was removed by rotary evaporation. Then, HCl was added to the solution to precipitate the product and the mixture was separated by filtration to yield the product. The product was further washed with distilled water and then dried under vacuum. \(^1\)H NMR (CD₃CN, 300MHz): δ7.94 (d, 1H), 7.49 (m, 1H), 7.43 (s, 1H), 7.23 (m, 1H), 6.81 (m, 1H), 5.84 (d, 1H), 5.28 (d, 1H), 4.21 (s, 2H).

2- Vinyl benzyl-sulfinyl-benzoic acid (OSO-VB)

OS-vinyl benzyl (1.91mmol) and sodium hydroxide (1.97mmol) were dissolved in MeOH and stirred for 20 minutes. \(m\)-cpba (3.34mmol, 60% determined by NMR) was added to the solution and the solution was kept stirring further for 1 hour. All volatiles were removed by rotary evaporating. The residue was redissolved in H₂O and chloroform was used to wash the solution. Remained chloroform was removed by rotary evaporation, 0.1M HCl aqueous solution was applied to acidify the product and precipitation was formed. The mixture was filtered to yield the product, followed by washing with cold water and drying under vacuum. The product was further purified by sublimating remained m-chlorobenzoic acid at 85 °C under vacuum. \(^1\)H NMR (CD₃CN, 300MHz): δ8.15 (dd, 1H), 7.81 (dd, 1H), 7.75 (td, 1H), 7.61 (td, 1H), 7.38 (d, 1H), 7.11 (d, 2H), 6.78 (m, 1H), 5.82 (d, 1H), 5.27 (d, 1H), 4.41 (d, 1H), 3.85 (d, 1H).

\([\text{Ru(bpy)}_2(\text{pyS-NB})](\text{PF}_6)_2\) (bpy is 2,2'-bipyridine)

A mixture of \([\text{Ru(bpy)}_2\text{Cl}_2](\text{PF}_6)_2\) (0.1411g, 0.271mmol), pyS-NB (0.0948g, 0.329mmol) and AgPF₆ (0.1476g, 0.584mmol) in 50mL ethanol was refluxed under N₂.
The reaction was monitored by UV-Vis spectroscopy and the reaction was stopped when there was no future change in the visible spectrum. The final spectrum showed an absorption peak at 432 nm. The solution was cooled to room temperature and placed in the freezer to fully precipitate AgCl. The solution was filtered and all volatiles were removed by rotary evaporation. The residue was re-dissolved in 2 mL ethanol, and diethyl ether was added to induce precipitation. The orange product was obtained by filtering and dried under vacuum. Yield: 81.9%. ¹H NMR (CD₃CN, 300MHz): δ9.26 (d, 1H), 8.53 (t, 3H), 8.38 (d, 1H), 8.10 (td, 1H), 8.07 (m, 2H), 8.04 (td, 1H), 7.82 (m, 1H), 7.70 (td, 1H), 7.67 (m, 4H), 7.54 (d, 1H), 7.38 (m, 1H), 7.24 (m, 2H), 7.07 (t, 1H), 6.30 (m, 1H), 6.14 (m, 1H), 5.75 (m, 1H), 4.73 (d, 1H), 4.20 (dd, 1H), 3.54 (m, 2H), 3.04 (m, 1H), 2.85 (s, 1H), 2.78 (m, 1H), 1.78 (m, 1H), 1.30 (m, 3H), 1.14 (m, 2H).

[Ru(bpy)₂(pySO-NB)](PF₆)₂

A mixture of [Ru(bpy)₂Cl₂](PF₆)₂ (0.4095g, 0.787mmol), pySO-NB (0.2643g, 0.868mmol) and AgPF₆ (0.4178g, 1.65mmol) in 150 mL ethanol was refluxed under N₂. The reaction was monitored by UV-Vis spectroscopy and the reaction was stopped when there was no future change in the visible spectrum. The final spectrum showed an absorption peak at 363 nm. The solution was cooled to room temperature and placed in the freezer to fully precipitate AgCl. The solution was filtered and all volatiles were removed by rotary evaporation. The residue was re-dissolved in 5 mL ethanol, and then diethyl ether was added to induce precipitation. A light orange/yellow product was obtained by filtering and dried under vacuum. Yield: 88.4%. ¹H NMR (CD₃CN, 300MHz): δ 9.83 (d, 1H), 8.59 (t, 3H), 8.46 (m, 1H), 8.34 (m, 1H), 8.19 (m, 2H), 8.04 (m,
1H), 7.90 (m, 2H), 7.84 (m, 1H), 7.71 (m, 2H), 7.57 (d, 1H), 7.45 (td, 1H), 7.34 (t, 2H), 7.26 (d, 1H), 7.16 (t, 1H), 6.37 (m, 1H), 6.11 (m, 1H), 5.70 (m, 1H), 5.24 (m, 1H), 5.01 (m, 1H), 3.49 (m, 2H), 3.07 (m, 1H), 3.00 (s, 1H), 2.84 (s, 1H), 2.73 (m, 1H), 2.52 (m, 1H), 1.71 (m, 1H), 1.32 (m, 1H), 1.25 (m, 2H). Elemental Analysis: Calculated for C_{36}H_{34}N_{6}SORuP_{2}F_{12}: C (41.90%), H (8.34%), N (3.61%), S (3.18%). Found: C (42.18%), H (8.00%), N (3.67%), S (3.36%).

[Ru(bpy)$_2$(pySO-C$_n$, n=8,18)](PF$_6$)$_2$

A mixture of [Ru(bpy)$_2$Cl$_2$](PF$_6$)$_2$ (0.1009g, 0.194mmol), pyS-C$_n$ (n = 8: 0.0476g, 0.200mmol; n = 18: 0.0828g, 0.219mmol) and AgPF$_6$ (0.1112g, 0.440mmol) in 50 mL ethanol was refluxed under N$_2$. The reaction was monitored by UV-Vis spectroscopy and the reaction was stopped when there was no future change in the visible spectrum. The final spectrum showed an absorption peak at 440 nm. The solution was cooled to room temperature and placed in a freezer to fully precipitate AgCl. The solution was filtered and all volatiles were removed by rotary evaporation. The remaining solid was redissolved in 2 mL ethanol, and then diethyl ether was added to induce precipitation. An orange product was obtained by filtering and dried under vacuum. The product was mixed with m-cpba at a ratio of 1:1.2 in MeOH, stirred under room temperature. The reaction was monitored by UV-Vis spectroscopy and the reaction was stopped when there was no future change in the visible spectrum. The final spectrum showed an absorption peak at 370 nm. The solvent was removed by rotary evaporation. The remaining solid was redissolved in 2 mL ethanol, and then diethyl ether was added to induce precipitation. An yellow product was obtained by filtering and dried under vacuum. Yield: 69.3% (n = 8),
44.8% (n=18). $^1$H NMR (CD$_2$Cl$_2$, 300MHz): when n =8, δ9.99 (d, 1H), 8.52 (m, 3H), 8.36 (m, 2H), 8.21 (m, 2H), 8.06 (t, 1H), 7.90 (m, 4H), 7.55 (m, 4H), 7.23 (m, 3H), 5.01 (m, 2H), 3.43 (m, 2H), 1.39 (m, 2H), 1.14 (m, 10H), 0.84 (t, 3H); when n = 18, δ9.99 (d, 1H), 8.54 (m, 3H), 8.36 (m, 2H), 8.20 (m, 2H), 8.06 (m, 1H), 7.96, 7.87 (m, 4H), 7.69 (m, 1H), 7.56 (m, 2H), 7.41 (m, 1H), 7.24 (m, 3H), 5.01 (m, 2H), 3.41 (m, 2H), 1.41 (m, 2H), 1.15 (m, 28H), 0.87 (m, 5H).

$[\text{Ru(bpy)}_2(\text{OSO-VB})](\text{PF}_6)_2$

A mixture of $[\text{Ru(bpy)}_2\text{Cl}_2](\text{PF}_6)_2$ (0.1718g, 0.330mmol), OSO-VB (0.1069g, 0.373mmol) and AgPF$_6$ (0.1796g, 0.710mmol) in 150 mL ethanol was refluxed under N$_2$. The reaction was monitored by UV-Vis spectroscopy and the reaction was stopped when there was no future change in the visible spectrum. The final spectrum showed an absorption peak at 400 nm. The solution was cooled to room temperature and placed in the freezer to fully precipitate AgCl. The solution was filtered and washed by small amount of CH$_3$CN/EtOH mixture, and then the solvent was removed by rotary evaporation. The residue was redissolved in 5 mL ethanol, and then diethyl ether was added to induce precipitation. A red orange product was obtained by filtering and dried under vacuum. Yield: 98.1%. $^1$H NMR (CD$_3$CN, 300MHz): 9.32 (d, 1H), 8.85 (d, 1H), 8.55 (d, 1H), 8.41, 8.31 (m, 4H), 8.07 (m, 1H), 8.00, 7.87 (m, 5H), 7.50, 7.17 (m, 7H), 7.11 (d, 2H), 6.65 (m, 1H), 6.55 (d, 2H), 5.75 (d, 1H), 5.25 (d, 1H), 4.17 (d, 1H), 3.83 (d, 1H).
General polymerization procedure

The 3\textsuperscript{rd} generation Grubbs’ catalyst was synthesized from the 2\textsuperscript{nd} generation Grubbs’ catalyst, which was stirred in 3-bromopyridine for 15 minutes and then the product was precipitated by pulling the reaction mixture into cold hexane.\textsuperscript{56} The polymerization procedure was developed following Grubbs’ work.\textsuperscript{56} Ruthenium compounds and norbornene with a specified ratio were dissolved in 100 mL degassed dichloromethane to obtain a 0.1 M solution. The solution was added dropwise to a rapidly stirred and degassed dichloromethane solution containing 3\textsuperscript{rd} generation Grubbs’ catalyst (1mg/mL) at room temperature, which had been stirred for 10 minutes. After 3 hours, ethyl vinyl ether was added and the mixture was stirred for an additional 30 minutes. The solution was concentrated to 20 mL by rotary evaporation, and then added dropwise to 150 mL methanol to induce precipitation of the polymer. This procedure was repeated until the methanol solution was colorless. The product was dried overnight under vacuum at 50 °C to remove solvent that is intercalated or dissolved in the polymer. Co-poly-

\{Ru\textsuperscript{II}(bpy)\textsubscript{2}pyS-NB/NB\} \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 300MHz): \(\delta\) 9.66, 9.50, 8.54-7.21 (assigned to Ru(bpy)\textsubscript{2}pyS), 5.69, 5.44, 5.30, 5.10, 2.88, 2.52, 1.86, 1.62, 1.42, 1.08 (assigned to NB). Co-poly-{Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB/NB} \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 300MHz): \(\delta\) 9.95, 8.56-7.27 (assigned to Ru(bpy)\textsubscript{2}pySO), 5.61, 5.36, 5.22, 5.02, 2.82, 2.44, 1.80, 1.53, 1.35, 1.00 (assigned to NB). For 1:60 Ru:NB polymer, the weight average molar mass (Mw) was 1.16 x 10\textsuperscript{5} and the number average molecular weight was (Mn) was 2.12 x 10\textsuperscript{4}, yielding a polydispersity index (PDI = Mw/Mn) of 5.39.
Thin film preparation by dropcasting method

The copolymer was dissolved in dichloromethane to obtain a solution concentration of 20 mg/mL. A constant amount of the solution was layered onto a polished Teflon plate and then allowed to evaporate, yielding a polymer disk on the Teflon plate. The disk was dried by gently blowing air over the film for several minutes. The resulted film was carefully cut off the plate, and annealed at around 65 °C for 1 hour in oven. Strips of the film were then cut from the disk for further study.

Thin film preparation by spincoating

The Ru-NB/NB copolymer was dissolved in cyclohexanone to obtain a solution concentration of 5% by weight. The solution was filtered by 0.2 μm size nylon syringe filter, followed by concentrated to approximately 20% by weight under vacuum line. A 0.5 mL of the solution was dropped onto a cover glass, which was cleaned by piranha solution, and rotated with a low speed at 800 rpm for 12 seconds and 1500 rpm for 60 seconds by a spincoater KW-4A from Chemat Technology. The obtained film was further rotated at 3000 rpm for 60 seconds, followed with annealing at 65 °C in the oven overnight, to get rid of any remaining solvent.

Polymer mat preparation by electro-spinning

Poly-norbornene was refluxed with dichloromethane until fully dissolved. Ru(bpy)$_3$ was added to the polymer solution to reach a ratio of 3% by weight to the polymer. The solution was filtered through filter paper and concentrated by rotary evaporating to reach a concentration of approximately 5% by weight. Cyclohexanone was added to the solution to reach a concentration of 5% by volume, to increase the boiling
point of the solution, which helps to avoid a jam in the needle during the electrospinning process. A syringe pump was set to 0.1-0.2 mL/min to drive the injection through a 20G blunt metal needle, with a 10kV voltage applied. And a metal frame was grounded for collecting the fibers 10cm underneath the needle, the polymer fibers formed polymer matt on the metal frame. The obtained polymer matt was carefully pilled off the metal frame for further study.

**LCNs (liquid crystal networks) film preparation**

This procedure was following the strategy developed by Van Oosten,\(^2\) and the preparation work was done in Dr. Broer’s laboratory at Eindhoven University of Technology. Glass slides were cleaned by sonicating in acetone for 5 minutes, followed by UV irradiation for 30 minutes. Poly-imide resin (0.5 mL) was dropped on the glass slides and rotated at 1000 rpm for 5 seconds and at 5000 rpm for 40 seconds. The resulting films were dried on a hot plate at 100°C for 10 minutes, and annealed in an oven under Ar at 170°C ~180°C for 1.5 hours. The films were carefully rubbed on a velvet cloth in a direction parallel to one edge. Two slides with the rubbed film were stacked with opposite rubbed direction, 18μm spacers were introduced between the two slides before glued together to achieve a cell.

LCs (liquid crystals) RM 82, RM 105, RM 23 (with a ratio of 2:3:1 by weight) were mixed together in dichloromethane with 800ppm of \(t\)-butylhydroquinone as inhibitor. The molecular structures of RM 82, RM 105, RM 23 are shown in Figure 2.1. Specified ratio of Ru-complexes was loaded to this mixture. And then the solvent was removed by heating to 70°C, resulting in LCs mixture with Ru-complexes. An optical
microscope was applied to check the LC properties for the resulted mixture. Photo-initiator 819 was applied to the mixture of 1% by weight in small amount of dichloromethane, and the solvent was removed at 70 °C. A cell prepared by previous procedure was put on a hot plate set to 70 °C, the LCs mixture was applied to the cell by capillary effect. Omnicure S2000 with a 455 nm cut on filter was used to irradiate the filled cell for 300 seconds to photo-polymerize the LCs. The cell was opened and the obtained LCN film was cut off by blade razor for further study.

![Molecular structures of RM 23, RM 82 and RM 105 LC monomers.](image)

*Figure 2.1. The molecular structures of RM 23, RM 82 and RM 105 LC monomers.*
AFM (Atomic Force Microscopy)

The AFM employed for all the measurements is MFP-3D-SA from Asylum Research. The probes used for normal surface topology scanning are Olympus AC160TS from Asylum Research, with a nominal spring constant of $k=42$ N/m and frequency of 300Hz. The probes utilized for nanoindentation were Diamond like carbon coated TESP from Bruker, with a nominal spring constant of $k=42$ N/m and nominal pyramid tip shape and tip radius of ~15nm. The probes were used as received without any further treatment. The surface topology scanning was performed under tapping mode and nanoindentation is performed under contact mode in the air.

For nanoindentation study, the spring constant of the probe is required to be calibrated. For the MFP-3D-SA system, there are three steps to calibrate the spring constant. The first step is calibration for the virtual deflection, which is a mechanical coupling of the deflection signal with the Z axis movement. Since it depends on how the light is aligned on the cantilever, it is required to be calibrated prior to each experiment when the focus position of the laser is moved. After the probe was loaded onto the AFM head, the probe was kept far away from the surface, and a single force scan was performed to yield a deflection vs Z position plot, with starting distance set to "-inf", force distance set to "inf", trigger channel set to "none". As shown in Figure 2.2 A, the data was fit for virtual deflection. Another single force scanning was performed to make sure the virtual deflection was well calibrated, which was indicated by a flat line of the plotted data. The second step is calibration for “Invols”. A clean cover glass was used as hard surface, and the probe was loaded to the surface reaching a deflection value of around 0.7 V. The
force distance was set to 3 μm, trigger channel was set to Deflection Volts, and trigger point was set to 2 volts. Then the deflection was set to -2 volts by moving the photodiode knob. By this setting, the probe would touch the surface when the deflection was 0 volts, and this would result in a nice linear region around 0 volts to fit for “Invols”. As shown in Figure 2.2 B is a resulted single force curve and the linear region is fitted to yield the “Invols”. The final step is the calibration for spring constant with thermal fitting. The deflection was set back to 0 volts by adjusting the photo diode knob. Then, the thermal data was collected until it was invariant with time. Normally, there was a high peak at lowest frequency. As shown in Figure 2.2 C, this peak was fitted for several times till a constant value is obtained for the spring constant.
Figure 2.2. A. Infinite distance deflection vs Z-sensor curve fitting for virtual deflection; B. Single force deflection vs Z-sensor curve fitting for Invols; C. Thermal fit for obtaining the spring constant.
Ultrafast Transient Absorption spectroscopy

Femtosecond transient absorption measurements were collected on an Ultrafast Systems Helios transient absorption spectrometer. A Spectra Physics Solstice laser, a one-box regenerative amplifier containing a Mai Tai femtosecond oscillator and Empower pump laser, was employed to produce 800 nm pulses at a repetition rate of 1 kHz at 3.5 W average power and a pulse width of ~100 fs. From this unit, the beam is split (50:50) with one beam directed to an optical parametric amplifier (TOPAS, Light Conversion) and the other to the Helios spectrometer (HE-vis-3200) to create the pump (472 nm; TOPAS) and probe (Helios) sources, respectively. The 800 nm probe beam passed through a CaF$_2$ plate to generate a white light continuum (~330-700 nm). The spectrum was integrated for 2 seconds for each scan. The pump and probe beams were directed through a 2 mm pathlength cuvette containing the sample where they were overlapped in space and time. The solution was vigorously stirred in the 2 mm path length cuvette during data collection. Transient absorption data were corrected by subtracting spectral background features that persisted from the previous pulse and appeared pre-pulse as well as by applying chirp correction using Surface Xplorer Pro 1.1.5 software (Ultrafast Systems).
CHAPTER 3. SAMPLE PREPARATION AND HANDLING

The project started from synthesis of a reversible, photochromic monomer. The synthesis pathway is shown in Figure 3.1. 2-(Bromomethyl) pyridine hydrobromide was allowed to react with cysteamine to obtain pyS-NH$_2$, and pyS-NH$_2$ was reacted with norbornene carboxylic acid to obtain pyS-NB. PyS-NB, the monomer ligand, was oxidized by $m$-cpba to yield pySO-NB, which was coordinated to Ru(bpy)$_2$Cl$_2$·xH$_2$O to obtain the desired Ru monomer.

The synthesis of pyS-NH$_2$ proceeds via a $S_N$1-type reaction, in contrast to the $S_N$2 pathway for the synthesis of other pyS-R ligands, such as pyS-isopropyl. The amine group is a strong electron acceptor, and it decreases the electronic density of the sulfur to be a weaker electron donor on cysteamine, comparing to the other alkyl thiol complexes. The studies of Subrata Ghosh and Gregory P. Tochtrop confirm this analysis. Since $S_N$1 reaction is favored in polar and protic solvent, a mixture of H$_2$O/EtOH was used as solvent to optimize the reaction. And strong base was introduced to help bromide leaving methyl-pyridine and to stabilize the charge on the methylene carbon.

The pyS-NH$_2$ decomposes quickly at a temperature greater than room temperature. If the reaction went longer than one hour, the reaction solution would change from colorless to yellow/brown, indicating decomposition of pyS-NH$_2$. TLC was applied to monitor the reaction process. With a mixing solution of DCM/MeOH with 9:1 ratio and 1% of TEA, the product resulted an approximate $R_f$ value of 0.3. TLC was performed in every 15 minutes, until the starting materials were consumed. For the rotary evaporation, the temperature was set to 34 °C to avoid decomposition of pyS-NH$_2$. 
Figure 3.1. The synthesis pathway for [Ru(bpy)$_2$pySO-NB](PF$_6$)$_2$ and [Ru(bpy)$_2$pyS-NB](PF$_6$)$_2$. 
For the condensation reaction, norbornene carboxylic acid was mixed with oxalyl chloride to yield norbornene carboxylic chloride as an intermediate to react with pyS-NH₂. The intermediate is very reactive and should be used immediately. There was always a large amount of HCl remaining with norbornene carboxylic chloride, so an excess amount of pyS-NH₂ was applied to the reaction. A side product pyS-NH₂·HCl precipitated out during this reaction. The pyS-NB product is colorless/light yellow oil. Since the norbornene carboxylic acid used is a mixture of –endo/-exo at a ratio of 9:1, resulted pyS-NB product with the same mixing ratio of –endo/-exo. By careful column chromatography operation with a 9:1 DCM/MeOH solvent, pure endo-pyS-NB was obtained as confirmed by ¹H proton NMR spectroscopy.

The sulfur on pyS-NB could be over-oxidized to the sulfone by excess m-cpba in chloroform at room temperature, which is different from the oxidation of pyS-isopropyl. In order to avoid the over-oxidization, the purity of mcpba used was determined by ¹H NMR, and TLC was applied to monitor the oxidation process. With DCM/MeOH solvent at a ratio of 9:1, the pyS-NB results a R_f value of approximate 0.3 and pySO-NB has a value of approximate 0.2. The mcpba in DCM solution was added dropwise to pyS-NB in DCM solution with fast stirring, with periodic checking with TLC to avoid over oxidation. The final pySO-NB product is light yellow/colorless wax.

The synthesis of [Ru(bpy)₂pyS-NB]²⁺/[Ru(bpy)₂pySO-NB]²⁺ are similar to the regular [Ru(bpy)₂pySO]²⁺ complex. However, the sulfur on [Ru(bpy)₂pyS-NB]²⁺ could not be oxidized by either m-cpba or NaIO₄ at room temperature. The large size of the norbornene group on [Ru(bpy)₂pyS-NB]²⁺ prevents the peroxide group from reaching the
sulfur atom on the Ru metal. So, the only path to synthesize \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) is from the free pySO-NB ligand, and a \(^1\)H NMR spectrum of the final \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) product shows there are multiple isomers.

For the polymerization reaction, norbornene has very low sublimation temperature, which means it requires to be handled in covered container all the time to avoid mass loss. The Ru monomer was stirred with norbornene in DCM for 10 minutes to reach a homogenous solution before addition of the Grubbs’ catalyst solution. The highest ratio of Ru monomer to norbornene is 1:20 for polymerization. Synthesis of a \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) homopolymer failed due to precipitation of \([\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) oligomer. Marcus Weck’s studies indicate that it’s hard to get a homopolymer of a charged monomer in a strong polar environment, and this is consistent with our study. J. Jeagh, an undergraduate in our lab, studied the influence of reaction time on the polymerization, and he found out that the polymerization process for the Ru monomer with norbornene is finished in 3 hours at room temperature, as initialized with 3\(^{rd}\) Grubbs’ catalyst.

For the dropcast films, the concentration of the polymer solution is critical to the film properties. The same amount of polymers was used to prepare films with constant thickness, by applying solution with larger volume of lower concentration or smaller volume of higher concentration. Too high of concentration would result in fast formation of film on the solution top surface relative to the bottom, and lead to a nontransparent film. By trying solutions with various concentrations, 20 mg/mL was found to be the best concentration to form a clear and uniform film. The film was placed in the oven at 70 °C
to evaporate any remaining solvent. The annealing step is important, as it helps the film to obtain a tight structure and results in a larger photo-mechanical movement.

For spin-coating film preparation, the correct solvent, proper concentration of solution and ideal spinning speed are required. The solution is supposed to rinse through the whole substrate surface before it dried, so a good candidate solvent would be one with a relatively high boiling point. Cyclohexanone is chosen here which has a boiling point of 160 °C, and the Ru-copolymers are very soluble in cyclohexanone. The thickness of the film depends on the concentration of the applied solution, with higher concentration is needed to obtain a thicker film. But the viscosity of the solution increases as the concentration increasing, which results in slower rinsing process and the solution could be dried before rinsing through the whole substrate surface. A too high spinning speed will spill the solution off the substrate before it rinses through the whole surface smoothly. On the other hand, a too low spinning speed will not allow the solution to rinse through the whole surface. For the poly-\{[Ru^{II}(bpy)_{2}pySO-NB]/NB\} copolymers, 0.5 mL solution with 20% by weight was loaded on a cleaned 25mmx25mm cover glass at 800 rpm for 12 seconds, followed with 1500 rpm for 60 seconds would result in a uniform film with thickness approximately 2 μm.
CHAPTER 4. CHARACTERIZATION WITH SPECTROSCOPY

\(^1\text{H} \text{ NMR spectroscopy}\)

The ligand pyS-NH\(_2\) was synthesized by connecting the sulfur on cysteamine to the methyl group of 3-bromo-methyl-pyridine. Shown in Figure 4.1A is the \(^1\text{H} \text{NMR in CDCl}_3\) for pyS-NH\(_2\). There are two identical protons on the methylene group (C7) between sulfur and pyridine, appearing as a singlet at 3.83 ppm. The amine group is a strong electron acceptor, which decreases the electronic density on the carbon adjacent to the amine and results in a downshift of the proton on this carbon. For the ethylene bridge, the protons on the carbon adjacent (C9, C10) to amine have a triplet peak at 2.99 ppm, comparing to the protons close to sulfur have a triplet at 2.60 ppm.

The ligand pyS-NB was synthesized by condensation Second-order-coupling of pyS-NH\(_2\) with norbornene carboxylic acid. Shown in Figure 4.1 B is the \(^1\text{H} \text{NMR in CD}_3\text{CN}\) for pyS-NB. The amide group further decreases the electronic density on the adjacent carbon (C7), causes the protons to shift downfield to 3.39 ppm from 2.99 ppm on pyS-NH\(_2\), and the triplet is split into a multiple peak (C10) due to the space effect of amide group. The peaks for the protons adjacent to the sulfur (C9) almost remain the same as in pyS-NH\(_2\), which remains at 2.63 ppm. And the aromatic protons (C3-6) almost have the same features as in pyS-NH\(_2\). The further assignment of the protons is determined by \(^1\text{H} \text{COSY spectra, as shown in Figure 4.2, to be discussed data.}\)

The ligand pySO-NB was synthesized by oxidizing pyS-NB with \(m\)-cpba. Shown in Figure 4.1 C is the \(^1\text{H} \text{NMR in CD}_3\text{CN}\) for pySO-NB. With the appearance of sulfoxide, the electronic density of the methylene carbon (C7) between the sulfur and
pyridine decreases, and the proton peaks shift downfield to 4.21 ppm from 3.84 ppm on pyS-NB, and are split into a doublet of doublet, as these protons are diastereotopic. The protons on the ethylene carbon (C10) adjacent to the sulfur are split into two peaks 2.91 ppm and 2.71 ppm, which are a triplet at 2.62 ppm on pyS-NB. The electronic structure of aromatic ring is affected by the sulfoxide, which is confirmed by the slightly shifted downfield for the protons peaks. The chemical shifts of the protons on the norbornene remain the same as in pyS-NB.

The complexes $[\text{Ru(bpy)}_2\text{pyS-NB}]^{2+}$ and $[\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}$ were synthesized by allowing pyS-NB and pySO-NB to react with $\text{Ru(bpy)}_2\text{Cl}_2$, respectively. Shown in Figure 4.3 A, B are the $^1\text{H NMR}$ from downfield and upfield in CD$_3$CN for $[\text{Ru(bpy)}_2\text{pyS-NB}]^{2+}$, respectively. The peaks from 9.26 to 7.07 ppm are from the aromatic protons on bipyridines, and the pyridine of pyS-NB ligand. The singlet from the methylene protons (C7) on pyS-NB is shifted downfield and split into a doublet and a doublet of doublet as diastereotopic protons, at 4.73 ppm and 4.23 ppm, as the introduce of metal center as chiral center. The protons on the ethylene carbon (C9) adjacent to the sulfur on pyS-NB was shift upfield to 1.14 ppm, while the protons on the other ethylene carbon (C10) was shift downfield from 3.39 ppm to 3.54 ppm. The protons on the norbornene group do not change upon coordination. Shown in Figure 4.3 C, D are the $^1\text{H NMR}$ from downfield and upfield in CD$_3$CN for $[\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}$, respectively. The peaks from 9.83 to 7.16 ppm are from the aromatic protons on bipyridines, and the pyridine of pySO-NB ligand. With introduce of sulfoxide as the second chiral center, the methylene protons (C7) on the pySO-NB ligand have further
complicated feature. There are two sets of multiple peaks with a ratio of approximately 1:0.9, which are related to two sets of diastereomers to the sulfoxide chiral center for the [Ru(bpy)$_2$pySO-NB]$^{2+}$. The major diastereoisomer set exhibits the methylene multiple peaks at 5.24 ppm and 4.96 ppm, whereas the minor diastereoisomer set exhibits the peaks at 5.49 ppm and 5.01 ppm, respectively. Most of the protons on the norbornene group remain the same feature, except one carbene proton (C20) is split into two sets of double multiple peaks, with a ratio of approximately 1:0.9, which is consistent with the diastereoisomers mixture from the methylene protons. And each set is split into two peaks, related to the diastereoisomers of the metal chiral center.

The polymers were also characterized by $^1$H NMR spectroscopy. For homopolynorborne, the proton peaks on the polymer are at higher field than 6.0 ppm. After copolymerization with [Ru(bpy)$_2$pySO-NB]$^{2+}$, the polymer backbone remains the same. Shown in Figure 4.4 B, C are the $^1$H NMR in CD$_2$Cl$_2$ for poly-{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB} copolymers with different Ru:NB ratio. The proton peaks for polynorbornene are identical to homo polynorborne, but the copolymers exhibit aromatic proton peaks at the region from 9.0-7.0 ppm, which confirms that the [Ru(bpy)$_2$pySO-NB]$^{2+}$ was incorporated in the polymers. By calculating the integral of the peak, the ratio of [Ru(bpy)$_2$pySO-NB]$^{2+}$ to norbornene can be estimated, though the peak signal is weak, which may result in a relative large error. For the Ru:NB 1:60 reaction mixing polymer, the ratio of Ru:NB is estimated to be 1:62, and this value is consistent with the value obtained by UV-Vis spectroscopy measurement and elemental analysis.
Figure 4.1 $^1$H NMR for ligands: A. pyS-NH$_2$ in CDCl$_3$; B. pyS-NB in CD$_3$CN; and C. pySO-NB in CD$_3$CN.
Figure 4.2. 2D $^1$H NMR Correlation spectroscopy (COSY) for pySO-NB ligand in CD$_3$CN. The blue lines represent coupling between the aromatic protons; the red lines represent the coupling between the alkene protons on the norbornene; the black line represents the coupling between the methylene protons; the purple lines represent the coupling between the ethylene protons and the green lines stand for the alkane protons on norbornene.
Figure 4.3. $^1$H NMR for $[\text{Ru(bpy)}_2\text{pyS-NB}]^{2+}$, $[\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}$ in CD$_3$CN. A, B are for $[\text{Ru(bpy)}_2\text{pyS-NB}]^{2+}$; C, D are for $[\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}$. 
Figure 4.4. $^1$H proton NMR in CD$_2$Cl$_2$ for poly-$\{[\text{Ru}^{II}\text{bpy}_2\text{pySO-NB}]$/NB$\}$ copolymers: A. Ru:NB at a ratio of 1:25; B. Ru:NB at a ratio of 1:40.
UV-Vis absorption spectroscopy

The complex [Ru(bpy)$_2$pySO]$^{2+}$ in propylene carbonate exhibits a lowest energy transition at 370nm, and is assigned to a Ru dπ → bpy π* charge transfer transition. This transition is similar to that observed in other chelating S-bonded ruthenium sulfoxide complexes, such as [Ru(bpy)$_2$OSO]$^{2+}$ (~400 nm). Irradiation with 355 nm light results in a dramatic redshift of the MLCT absorption to 472 nm. This value is similar to that of an MLCT absorption at 476 nm for the O-bonded isomer of [Ru(bpy)$_2$(py)(dmsO)]$^{2+}$, and [Ru(bpy)$_2$(pic)]$^+$ of a MLCT absorption at 483 nm (pic is 2-pyridinecarboxylate). It is concluded that the MLCT absorption at 472 nm for [Ru(bpy)$_2$pySO]$^{2+}$ is due to the O-bonded isomer.

Rack and coworkers studied a series of [Ru(bpy)$_2$OSO-R]$^{2+}$ complexes, with different R group to adjust the electronic features on the sulfur atom. DFT calculations show that the d$_{xz}$ and d$_{yz}$ orbitals from Ru were stabilized significantly through a π-back bonding interaction with the sulfur of OSO ligand. By alternating the R group from benzyl to pentafluorophenyl, the lowest energy transition absorption changes from 396nm to 388nm. However, the electronic effect of sulfur was not active for the O-bonded complexes. Despite the absorption shifting for the S-bonded complexes, there is the same absorption for the O-bonded complexes.

Shown in Figure 4.5 A are the S-bonded UV-Visible absorption spectra for [Ru(bpy)$_2$pySO]$^{2+}$, [Ru(bpy)$_2$pySO-NB]$^{2+}$ and poly-[Ru(II)(bpy)$_2$pySO-NB]/NB (1:25) copolymer in DCE. The complex [Ru(bpy)$_2$pySO]$^{2+}$ exhibits a MLCT absorption maximum at 375 nm, compared to that of both [Ru(bpy)$_2$pySO-NB]$^{2+}$ and poly-
{{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}}/\text{NB}} \text{ copolymer that exhibit MLCT maxima at 367 nm. Furthermore, the alkane chain substituted pySO ligand \([\text{Ru}(\text{bpy})_2\text{pySO-C}_{18}]^{2^+}\) complexes exhibit almost the same MLCT absorption as the unsubstituted \([\text{Ru}(\text{bpy})_2\text{pySO}]^{2^+}\), while \([\text{Ru}(\text{bpy})_2\text{pySO}]^{2^+}\), \([\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2^+}\) and poly-\{\{\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}}/\text{NB}} \text{ (1:25)} \text{ copolymer exhibit almost the same MLCT maxima at 367 nm in propylene carbonate. It is observed that the MLCT absorption peak in \([\text{Ru}(\text{bpy})_2\text{pySO}]^{2^+}\) is broader than in the other two complexes. It is possible that there is unexpected O-bonded isomer in the \([\text{Ru}(\text{bpy})_2\text{pySO}]^{2^+}\), which broadens and red shifts the MLCT absorption peak.

The O-bonded complexes are formed by irradiation with 405nm light irradiation. Shown in Figure 4.5 B are the O-bonded UV-Visible absorption spectra for \([\text{Ru}(\text{bpy})_2\text{pySO}]^{2^+}\), \([\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2^+}\) and poly-\{\{\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}}/\text{NB}} \text{ copolymer in DCE. They exhibit the same MLCT absorption at 476nm, which means the electronic effect of the substituent propagated through sulfur atom is not active at O-bonded complexes. And this is consistent with the observation from the \([\text{Ru}(\text{bpy})_2\text{OSO-R}]^{+}\) complexes.\textsuperscript{62} This MLCT absorption is due to the O-bonded isomer.

The polymer chain has no effect to the electronic feature of \([\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2^+}\), which is suggested by the same UV-Visible absorption spectra for \([\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2^+}\) and poly-\{\{\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}}/\text{NB}} \text{ (1:25) copolymer. However, the photo-isomerization process is affected by the polymer chain. The quantum yield of \([\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2^+}\) \(\Phi_{S\rightarrow O}\) is 0.12 ± 0.01 in DCE, compared to the poly-
\{\{\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}}/\text{NB}} \text{ (1:25) copolymer \(\Phi_{S\rightarrow O}\) is 0.067 ± 0.01.
Figure 4.5. UV-Vis spectrum for $[\text{Ru(bpy)}_2\text{pySO}]^{2+}$, $[\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}$, poly-$\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}$ (1:25) copolymer in DCE: A. S-bonded isomers; B. O-bonded isomers.
This suggests that the polymer chain may resist the photo-isomerization in the photochrome. Compared to the diarylethene polymers, which exhibit almost the same kinetics in the monomers as in the polymers.\(^6^3\)

**Transient Absorption spectroscopy**

Transient absorption spectroscopy were collected in DCE with excitation at 370nm for \([\text{Ru(bpy)}_2\text{pySO}]^{2+}, [\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) and poly-\{[\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\} (1:25) copolymer at 395nm. The early time dynamics are almost the same for \([\text{Ru(bpy)}_2\text{pySO}]^{2+}, [\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) and poly-\{[\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\} (1:25) copolymer, which is expected since the only structure difference is on the sulfur atom. These structures should have little effect on MLCT formation. From the literature, the \(^1\text{MLCT}\) state forms from the initially Franck-Condon state in \(~40\) fs, and the relaxation from \(^1\text{MLCT}\) to \(^3\text{MLCT}\) state occurs in \(~0.5\text{-}1.3\) ps.\(^6^4\) Shown in Figure 4.6 are the TA spectra from 0 ps to 5 ps for \([\text{Ru(bpy)}_2\text{pySO}]^{2+}, [\text{Ru(bpy)}_2\text{pySO-NB}]^{2+}\) and poly-\{[\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\} (1:25) copolymer in DCE, respectively. They have almost the same feature in this time period. The 0.3 ps traces show intense peaks at \(~350\) nm and a broad absorption at \(~600\) nm. After that, the peaks decay and bleach center \(~400\) nm are growing, and blue shift to \(~370\) nm. Based on previous study, the bleach is attributed to be depletion of the ground state MLCT feature and the long wavelength broad absorption is attributed to a combination of LMCT absorption from neutral bpy to the oxidized Ru center and \(\pi^*\rightarrow\pi^*\) absorption from the reduced bpy.\(^9\)
Figure 4.6. Representative TA spectra from 0 ps to 5 ps for A. [Ru(bpy)₂pySO]²⁺, B. [Ru(bpy)₂pySO-NB]²⁺, C. poly-{[Ru(bpy)₂pySO-NB]/NB} (1:25) copolymer in dichloro-ethylene.
Shown in Figure 4.7-4.9 are the TA spectra from 5 ps to 3000 ps. The 3000 ps spectra traces are similar to the UV-Vis difference spectra of the O-bonded and S-bonded, which are a high peak at ~470 nm, a low peak at ~360nm and a bleach at ~400nm. However, the peak at longer wavelength for the 3000 ps spectra traces are ~450 nm, which are blue-shifted compare to the spectra difference of O-bonded and S-bonded. This is considered to be the solvent reorganization occurring to the O-bonded ground state, and let the 450 nm peak red shift to 470 nm on the microsecond scale. And in the 3000 ps spectra traces, the broad absorption at long wavelength relaxes back to zero, which means the complexes are on the ground state potential energy surface at this time. There are isosbestic points in all three TA spectra on this time scale, which means there only one reaction is occurring: the isomerization from $^3$MLCT$_S$ to O-bonded ground state. The isosbestic point is at ~495nm for the [Ru(bpy)$_2$pySO]$^{2+}$ and [Ru(bpy)$_2$pySO-NB]$^{2+}$, blue shifted to ~470nm for the copolymer. Given almost the same O-bonded ground state UV-Vis spectra, the $^3$MLCT excited state of the polymer complex has more blue absorption. For the poly-{$^{[\mathrm{Ru}^{\mathrm{II}}(bpy)_2pySO-NB]/NB}$} (1:25) sample, the 5 ps trace does not go through the isosbestic point, which means that the $^3$MLCT$_S$ has not been fully reached at this time. This suggests the relaxation of $^1$MLCT to $^3$MLCT is slower in the polymer complex compare to the monomer and the complex [Ru(bpy)$_2$pySO]$^{2+}$. And the difference between the 400 ps trace and the 3000 ps trace in the polymer is noticeable larger than monomer and [Ru(bpy)$_2$pySO]$^{2+}$, the isomerization rate is slowed down by the effect of the polymer backbone.
Figure 4.7. A. Representative TA spectra from 5 ps to 3000 ps for [Ru(bpy)₂pySO]²⁺; B. UV-Vis spectra including S-bonded isomer, O-bonded isomer and the difference spectrum between O-bonded and S-bonded isomers O-S for [Ru(bpy)₂pySO]²⁺.
Figure 4.8. A. Representative TA spectra from 5 ps to 3000 ps for [Ru(bpy)_2pySO-NB]^{2+};
B. UV-Vis spectra including S-bonded isomer, O-bonded isomer and the difference spectrum between O-bonded and S-bonded isomers O-S for [Ru(bpy)_2pySO-NB]^{2+} in DCE.
Figure 4.9. A. Representative TA spectra from 5 ps to 3000 ps for poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:25) copolymer; B. UV-Vis spectra including S-bonded isomer, O-bonded isomer and the difference spectrum between O-bonded and S-bonded isomers O-S for poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:25) copolymer in DCE.
As shown in Figure 4.10 are the kinetic fitting traces selected at 361nm for [Ru(bpy)$_2$pySO]$^{2+}$, 370nm for both [Ru(bpy)$_2$pySO-NB]$^{2+}$ and poly-{$[$Ru$^{II}$(bpy)$_2$pySO-NB]/NB}$ copolymer. Fitting for the first 20 to 30 ps gives bi-exponential fit, with lifetime of 0.70 ps and 3.02 ± 0.48 ps for [Ru(bpy)$_2$pySO]$^{2+}$, 0.87 ± 0.16 ps and 3.18 ± 1.6 ps for [Ru(bpy)$_2$pySO-NB]$^{2+}$, 0.71 ± 0.12 ps and 2.74 ± 0.31 ps for poly-{$[$Ru$^{II}$(bpy)$_2$pySO-NB]/NB}$ (1:25) copolymer. The 0.70–0.87 ps component is formation of the $^3$MLCT state from the $^1$MLCT state, the 2.8–3.2 ps component is formation of the $^3$MLCT$_S$ state from the thermal relaxation of $^3$MLCT state. Those three complexes have almost the same lifetime component for the formation of $^3$MLCT state and $^3$MLCT$_S$ state.

Fitting for the long duration time kinetic traces gives tri-exponential life time, which are 0.70 ± 0 ps, 3.33 ± 0.35 ps and 142.7 ± 11.3 ps for [Ru(bpy)$_2$pySO]$^{2+}$; 0.88 ± 0.12 ps, 3.77 ± 1.41 ps and 245.6 ± 34.3 ps for [Ru(bpy)$_2$pySO-NB]$^{2+}$; 0.81 ± 0.09 ps, 3.36 ± 0.31 ps and 329.8 ± 16.9 ps for poly-{$[$Ru$^{II}$(bpy)$_2$pySO-NB]/NB}$ (1:25) copolymer. The long life time component is considered to be the isomerization life time component, from the isosbestic points in the TA spectra from 5 ps to 3000 ps duration time. The two short life time components have almost the same value, but the long life time component varies from 142.7 ps to 329.8 ps.

As shown in Figure 4.11 are the kinetic fitting traces selected at 445 nm for [Ru(bpy)$_2$pySO]$^{2+}$, [Ru(bpy)$_2$pySO-NB]$^{2+}$ and poly-{$[$Ru$^{II}$(bpy)$_2$pySO-NB]/NB}$ (1:25) copolymer. The fitting result is very close to the one obtained from the fitting at 370 nm.
Figure 4.10. The fitting kinetic trace in early time period for A. [Ru(bpy)$_2$pySO]$^{2+}$ at 361 nm, B. [Ru(bpy)$_2$pySO-NB]$^{2+}$ at 370 nm, C. poly-[[Ru$^{II}$(bpy)$_2$pySO-NB]/NB] (1:25) copolymer at 370 nm. The fitting kinetic trace in long time period for D. [Ru(bpy)$_2$pySO]$^{2+}$ at 361 nm, E. [Ru(bpy)$_2$pySO-NB]$^{2+}$ at 370 nm, F. poly-[[Ru$^{II}$(bpy)$_2$pySO-NB]/NB] (1:25) copolymer at 370 nm. The black traces represent the data, the red traces represent the fit.
Figure 4.11. The fitting kinetic trace at 445 nm in early time period for A. [Ru(bpy)₃pySO]²⁺, B. [Ru(bpy)₃pySO-NB]²⁺, C. poly-{{[Ru]II(bpy)₂pySO-NB]/NB} (1:25) copolymer; in long time period for D. [Ru(bpy)₂pySO]²⁺, E. [Ru(bpy)₂pySO-NB]²⁺, F. poly-{{[Ru]II(bpy)₂pySO-NB]/NB} (1:25) copolymer. The black traces represent the data, the red traces represent the fit.
Fitting for the first 15 to 30 ps gives bi-exponential decay life time, which are 0.76 ± 0.18 ps and 2.60 ± 0.57 ps for [Ru(bpy)$_2$pySO]$^{2+}$; 0.69 ± 0.04 ps and 2.70 ± 0.17 ps for [Ru(bpy)$_2$pySO-NB]$^{2+}$; 0.93 ± 0.22 ps and 4.56 ± 1.11 ps for poly-{|Ru$^{II}$(bpy)$_2$pySO-NB|/NB} (1:25) copolymer. They are almost the same considering the error. Fitting for the long duration time kinetic traces gives tri-exponential decay life time, which are 0.70 ps, 2.95 ± 0.28 ps and 153.7 ± 4.5 ps for [Ru(bpy)$_2$pySO]$^{2+}$; 0.76 ± 0.04 ps, 3.56 ± 0.27 ps and 194.4 ± 8.3 ps for [Ru(bpy)$_2$pySO-NB]$^{2+}$; 1.07 ± 0.15 ps, 5.98 ± 1.06 ps and 414.5 ± 103.9 ps for the copolymer. The two short life time components have almost the same value, but the long life time component varies a lot. The isomerization rate constant can be determined by the followed equation (1) and (2):

$$
\Phi = \frac{k_{s\rightarrow o}}{k_{obs}} \quad \text{Equation (1)}
$$

$$
\tau_{s\rightarrow o} = \frac{1}{k_{s\rightarrow o}} \quad \text{Equation (2)}
$$

The result is listed in Table 4.1. The isomerization rate constants at wavelength 370 nm agree with the ones at 445 nm. The isomerization rate constant of [Ru(bpy)$_2$pySO]$^{2+}$ is almost one time larger than the one of [Ru(bpy)$_2$pySO-NB]$^{2+}$, and isomerization rate constant of [Ru(bpy)$_2$pySO-NB]$^{2+}$ is more than one time larger than the one of poly-{|Ru$^{II}$(bpy)$_2$pySO-NB|/NB} (1:25) copolymer. The ligand for [Ru(bpy)$_2$pySO-NB]$^{2+}$ is much longer and heavier than isopropyl in [Ru(bpy)$_2$pySO]$^{2+}$, which slows down the rotating motion during the isomerization process in [Ru(bpy)$_2$pySO-NB]$^{2+}$. The polymer backbone has every high weight, and this increases the resistance for the rotating motion in the copolymer and slows down the isomerization rate further more. And as the
isomerization rate is slower in polymer than in the monomer, indicates that the Ruthenium complex molecules perform work to the polymer backbone. And this interaction between the polymer backbones and the ruthenium complex molecules could results in amplification for the molecular structure changing of the isomerization in ruthenium complexes.

Table 4.1. The kinetics fitting result for Ru(bpy)$_2$pySO, Ru(bpy)$_2$pySO-NB, poly-{$[\text{Ru}^{II} \text{(bpy)}_2 \text{pySO-NB}] / \text{NB}$} (1:25) copolymer in DCE pumped by 370nm laser pulse.

<table>
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<th>Complex</th>
<th>$\Phi_{S \rightarrow O}$ (in PC)</th>
<th>$\tau_{ns}$</th>
<th>$\tau_{ns}$</th>
<th>$k_{S \rightarrow O, 370nm}$ ($10^8$ s$^{-1}$)</th>
<th>$k_{S \rightarrow O, 445nm}$ ($10^8$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_2$pySO]$^{2+}$</td>
<td>0.11</td>
<td>1.3 ± 0.1</td>
<td>1.4 ± 0.4</td>
<td>7.8 ± 0.7</td>
<td>7.2 ± 0.2</td>
</tr>
<tr>
<td>[Ru(bpy)$_2$pySO-NB]$^{2+}$</td>
<td>0.12</td>
<td>2.0 ± 0.3</td>
<td>1.6 ± 0.1</td>
<td>5.0 ± 0.7</td>
<td>6.2 ± 0.3</td>
</tr>
<tr>
<td>Poly-Ru(bpy)$_2$pySO-NB /NB</td>
<td>0.067</td>
<td>5.0 ± 0.2</td>
<td>6.2 ± 1.6</td>
<td>2.0 ± 0.1</td>
<td>1.7 ± 0.4</td>
</tr>
</tbody>
</table>
CHAPTER 5. PHOTOMECHANICAL EFFECTS IN AMORPHOUS POLYMERS AND LIQUID CRYSTALS

Background

The promise of smart materials in future nanotechnological applications is predicated on the continued evolution of responsive molecules. Due to their precise remote, temporal and spatial detecting capabilities, light-activated materials that feature macroscopic changes in structure or shape are attractive targets in emerging photomechanical applications.

Polymeric materials comprised of photochromic monomers exhibit striking changes in color as well as large strains or mechanical deformations when irradiated with light. However, the preparation of molecules and materials with these properties is non-trivial. Nevertheless, the development of such polymers is desirable due to the ease of processability, manipulation and chemical modification. Through our work with photochromic ruthenium sulfoxides, we have found evidence of dramatic photomechanical effects of polymers formed from these compounds.

New materials that simply and reliably alter their shape or structure when irradiated have value as actuators in a variety of applications. Certain examples of liquid crystalline elastomers, cross-linked polymers and crystalline materials containing photochromic monomers exhibit macroscopic deformations when irradiated. In the photochrome, light is transduced to potential energy for excited state bond rupture and formation. The photoproduct of this reaction produces a stress on the 3-dimensional structure, yielding a strain or deformation in the shape or volume of the
material. The deformation in these materials is due to the free energy differences between the excited state and ground state isomeric structures of the photochrome. Moreover, it is practiced that the photochrome is highly concentrated within the polymeric structure and that a high-level of cross-linking is present to ensure efficient propagation of the desired photomechanical effect (deformation).  

The light-mechanical energy transfer was first realized by Agolini and Gay in 1970, they prepared azobenzene functionalized polyimide and studied the photogenerated stress. The photogenerated contraction was observed by Smets and Blauwe in 1972, who prepared functionalized spirobenzopyran crosslinked poly(ethyl acrylate) exhibiting more than 2% contraction upon light irradiation. There are many different polymers studied for these photomechanical effects, with different dyes like azobenzene, spiropyran and others. There was no sample exhibiting large scale change until the work of Ikeda and Yu in 2003, who prepared azobenzene functionalized mesogen crosslinked liquid crystal network films exhibiting reversible bending upon irradiation with different wavelength of light. This motion is due to the magnification by the nematic phase to isotropic phase transition of the liquid crystal. The film bending is evidence of the photomechanical effect since then. Broer and Van Oosten developed various alignment methods for the liquid crystal to achieve faster and larger photoresponse, and measured the work performed during the bending process in bilayer model systems.

Though most of the photomechanical systems are based on soft materials, there are some works based on single crystals. The cell volume in a single crystal is changed
by photoisomerization or photodimerization, however, just few examples can exhibit crystal shape changing instead of only surface topology change.  

Irie and coworkers have studied a series of diarylethene derivatives, which undergo closed-ring and open-ring isomerization. They prepared rod-like diarylethene single crystals showing reversible bending upon light irradiation in 2007, which is due to the closed-ring and open-ring isomerization. After that, they prepared cocrystals of diarylethene with perfluoronaphthalene, which could lift a heavy lead ball attached in the end of the crystal upon irradiation of light. Simultaneously, Bardeen and his coworkers studied a series of anthroate complexes. The single crystals of Anthroate complexes exhibit shape changing by photodimerization. However, the size of those single crystals was on submicrometer scale. Besides majority of studies in diarylethene and Anthroate single crystals, there have been a few reports about the single crystals of azobenzene, which are in submicrometer scale and exhibit photomechanical movement upon irradiation with light.

Photochromic polypyridine ruthenium sulfoxide coordination complexes feature excited state $S \rightarrow O$ and $O \rightarrow S$ isomerizations when irradiated with monochromatic laser light, white light sources, or sunlight. The large quantum yields of isomerization and the picosecond isomerization time constants indicate that these complexes efficiently convert photonic energy to potential energy for selective, excited state bond rupture and bond construction. The bonding description of Ru–S and Ru–O suggests a much greater covalency for Ru–S in comparison, resulting in large differences in both Metal-to-Ligand Charge-Transfer (MLCT) absorption maxima and ground state Ru$^{3+/2+}$ reduction
potentials ($E^{\infty}$). Indeed for $[\text{Ru(bpy)}_2(\text{pySO})]^2^+\text{,}$ the S-bonded and O-bonded lowest energy absorption maxima are 370 and 472 nm, respectively, and the S- and O-bonded reduction potentials are 1.35 V and 0.75 V (vs. Ag/AgCl), respectively. Charge-transfer excitation of the S-isomer at 370 nm yields the O-isomer with a quantum yield ($\Phi_{S \rightarrow O}$) of 0.11, and an isomerization time constant ($\tau_{S \rightarrow O}$) of 1.5 ns in propylene carbonate. Conversely, charge-transfer excitation of the O-isomer at 470 nm yields the S-isomer with $\Phi_{O \rightarrow S} = 0.027$ and $\tau_{O \rightarrow S} = 6.3$ ns. Moreover, it is evident that the two isomers have distinct molecular shapes. Based on this change in energy and shape, we proposed that phototriggering between these two isomers will generate reversible changes in the shape of a macroscopic sample. On a per molecule basis, phototriggered isomerization transduces greater energy ($\sim 3 \times 10^{-19}$ J/molecule) than that released through ATP hydrolysis ($6 \times 10^{-20}$ J/molecule), which provides the energy currency for many biochemical reactions, including muscle-fiber action.

Result and discussion

Amorphous polymers

We prepared low-Tg co-polymers from norbornene and photochromic ruthenium monomers comprising a covalently attached norbornene unit as shown in Figure 3.1.(Page 32) This latter monomer is formed through reaction of 5-norbornene-2-carboxylic acid (mixture 90:10 endo:exo) and an amine-appended version of $[\text{Ru(bpy)}_2(\text{pySO})]^2^+\text{.}$ Co-polymers were formed from reaction of this monomer with norbornene in dichloromethane solution with the 3$^{\text{rd}}$ generation Grubbs catalyst. The reaction mixture was then added dropwise to a methanol solution, inducing precipitation.
The polymer was reconstituted in dichloromethane. We formed discs or films of the polymer by drop-casting method to result in a completely disordered polymeric material. Shown in Figure 5.1 is the surface structure obtained from Scanning Electronic Microscope (SEM).

![Surface structure obtained from Scanning Electronic Microscope (SEM).](image)

**Figure 5.1.** Picture of the surface structure for poly-[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB (1:40) copolymer film by SEM.

There is no appearance of obvious regular pattern, supporting the glassy and disordered character of the polymer film. Strips with approximate dimensions 1 mm x 5 mm x 0.002 mm were subsequently cut from the film with a razor blade (see diagram, Figure 5.2A-C). Laser irradiation from topside of the strip at 405 nm at room temperature yields striking changes in the polymer film (Figure 5.2D). In addition to a significant color change in accord with phototriggered S→O isomerization, the film has undergone a dramatic change in shape, actually bending towards the direction of irradiation (Figure 5.2D).
Figure 5.2 The amorphous poly-\{[Ru^{II}\text{bpy})_2pySO-NB]/NB\} (1:40) film shows reversible bending. A. Diagram depicting film dimensions (1 mm x 4.5 mm x 0.002 mm) and area of irradiation. The beam spot diameter is 5 mm. B. Diagram depicting side view of film and irradiation area. C. Image of prepared film prior to irradiation. D. Image of film in panel C after irradiation with 405 nm (100mW/cm$^2$) of the original film; E. Image of film in panel D after irradiation with 480 nm (115 mW/cm$^2$). F. Image of film in panel E after irradiation with 405 nm (100 mW/cm$^2$) of the original film. (The dashed line represents the previous position of the film.)
The dashed line represents the original position of the film prior to irradiation. As measured by Image J, the bending forms an angle of 39° and the end of the strip is 2 mm up from the original position. Continued irradiation of the film reveals no further deformation of the film. Irradiation on the topside of the film with 480 nm (corresponding to the absorption maximum of the O-isomer) from the topside shows a reversal of the film bending towards the original position (Figure 5.2E). The dashed line denotes the position of the film in frame 5.1D. The bending lowers the end of the film by 1.1 mm and forms an angle of 22° to the last position. A second irradiation with 405 nm shows a bending or curling towards the light source (Figure 5.2F), which raises the end of the film by 0.4 mm and forms an angle of 8.7° to the last position of the film. We have found that the bending can still be observed after cycling between the two wavelengths.

We can conclude that the bending of the film by light is reversible, though it does appear to attenuate with laser light irradiation. Moreover, we prepared an identical polymer with a thioether coordinated to ruthenium instead of the sulfoxide, which has almost the same absorption at 405 nm. There was very slightly deformation observed in the thioether complexes incorporated copolymer due to thermal effect. However, when the light intensity was decreased to approximately 20 mW/cm², we observed no deformation of the film as seen in Figure 5.3, while we still observed large deformation for the sulfoxide complex incorporated copolymer films under the same condition. Thus, we conclude that the reversible macroscopic deformation of the film is due to phototriggered S→O and O→S molecular isomerization of the sulfoxide in [Ru(bpy)₃pySO]²⁺ upon irradiation. It is evident from these images that photonic energy
is transduced to potential energy for bond breaking and bond making, which is subsequently converted to mechanical energy to bend the film.

Consistent with isomerization of the parent complex in solution, the film also undergoes a change in color. Shown in Figure 5.4 is a digital image of a 1 mm x 5 mm x 0.002 mm film after irradiation. The film is affixed to a paper with silicone grease to eliminate any bending of the sample. Irradiation with 370 nm light yields a red spot on the film consistent with the O-bonded isomer, which features an absorption maximum at 470 nm.

In this treatment of the sample, the first irradiation (405 nm) results in bending of the polymer film towards the light source, an observation made by others when irradiating polymer samples containing azobenzene or spirapyan photochromes.30, 47, 80

![Figure 5.3](image)

*Figure 5.3. Photographs of poly-\{[Ru^{II}(bpy)_{2}pyS-NB]/NB\} (1:60) copolymer films A. before irradiation, B. after irradiation. The irradiation was taken by 395 nm laser of ~20 mW/cm² density for 60 minutes.*

Accordingly, we conclude simply that the molecules closer to the surface nearest the light source more readily isomerizes than those deeper in the film and further from the light
source, and this could be visualized as a bilayer model. The isomerized top layer
performs work to the unchanged bottom layer and that leads to the film bending.
Following a procedure developed by van Oosten,\textsuperscript{20} the work per unit volume ($W$)
performed by the proximal or front face of the film (irradiated side) on the distal or rear
face of the film can be determined simply from $W = \frac{1}{4}(\Delta\varepsilon)^2E$, where $\Delta\varepsilon$ is the differential
strain from proximal and distal faces of the film and $E$ is the average elastic or Young’s
modulus of the polymer films. The differential strain ($\Delta\varepsilon$) is the ratio of $h/r$, where $h$ is
the thickness of the film and $r$ is the radius of a circle formed from the deformation. For
the film displayed in Figure 5.2 D, $h$ is 0.002 mm and $r$ is 1.59 mm, yielding $\Delta\varepsilon = 1.26 \times 10^{-3}$ and thus $W = 5.00 \times 10^{-4} \mu J$. This value is just for the initial bending of the film
and reflects the low glass transition temperature ($T_g$) exhibited by polynorbornene. This
treatment assumes that the elastic deformation is in one dimension, which works as the
dimension in length of the film is much larger than width and thickness. We estimate that
90\% of the incident radiation is absorbed at a depth of 0.9 \( \mu m \) of the film from Beer’s
Law assuming that the extinction coefficient of the complex in this polymer is similar to
that of the complex in solution ($\epsilon_{370} = 7240 \text{ M}^{-1} \text{ cm}^{-1}$). Accordingly, this treatment
validates the above approach in determining the differential strain.
Figure 5.4. Top-down view of 1 mm x 5 mm x 0.002 mm film of poly-{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB} (1:40) copolymer after irradiation. The film is affixed to a piece of paper with silicon glue. Irradiation with 370 nm on end turns the yellow-transparent film red.

It is reasonable to expect a relationship between the concentration or amount of photochromic ruthenium monomer comprised in the polymer and the extent of deformation. The ratio of ruthenium to norbornene (Ru:NB) is determined by elemental analysis and UV-visible spectroscopy. For the film shown in Figure 5.2, this ratio is 1:40. Shown in Table 5.1 are polymers of different ruthenium content and their respective deformation measurements. Expectedly, we find that if the Ru:NB ratio is smaller, then a smaller deformation is observed. However, at significantly small Ru:NB ratios of 1:110 or 1:300, we do not observe any macroscopic shape change in the material though there is color change as evidence of isomerization, as seen in Figure 5.5.
Figure 5.5. Photographs of poly-\{[\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\} (1:110) copolymer films A. before irradiation, B. after irradiation. C. the irradiated film compare to unirradiated one from the same plate. The irradiation was taken by 395nm laser of ~20mW/cm² density for 60 minutes.
At high concentrations of ruthenium (Ru:NB = 1:25), we find that the extent of deformation appears to decrease. While 90% of the light is absorbed in the first quarter of the film (Ru:NB = 1:25), the isomerized layer is much thinner than the film (Ru:NB = 1:40) to form an efficient bilayer bending system. Surprisingly, we are not able to form homopolymers from the \([\text{Ru(bpy)}_2(\text{pySO-NB})]^2+\) monomer, despite reports of homopolymers of poly-\([\text{M(bpy)}_2(\text{bpy-sty})]^2+\), where M is Ru or Os and bpy is 2,2'-bipyridine-4-styrene.\(^{81,82}\)

Table 5.1. Calculated works for bending the Ru-NB/NB films with different Ru-loading ratio

<table>
<thead>
<tr>
<th>NB:Ru ratio</th>
<th>h (μm)</th>
<th>r (mm)</th>
<th>Δε(10^{-3})</th>
<th>W (μJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>2</td>
<td>∞</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>12.2</td>
<td>0.16</td>
<td>1.06x10^{-5}</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td>1.59</td>
<td>1.26</td>
<td>5.00x10^{-4}</td>
</tr>
<tr>
<td>25</td>
<td>2</td>
<td>9.13</td>
<td>0.22</td>
<td>1.53x10^{-5}</td>
</tr>
</tbody>
</table>

We further characterized these polymers by gel permeation chromatography. For the polymer in Figure 5.1, we found that the weight average molar mass (Mw) was 1.16 x 10^5 and the number average molecular weight was (Mn) was 2.12 x 10^4, yielding a polydispersity index (PDI = Mw/Mn) of 5.39. By optimize the reaction condition, PDI of
the copolymer could be lowered to 3.31. While many living polymerization catalysts, such as Grubbs’ catalysts, feature PDI near 1,\textsuperscript{83} we note that the difference in molecular weight, charge and diffusion constant between the two monomers suggests that a PDI of unity is unlikely. Indeed, the molecular weight of the photochromic ruthenium monomer (1000 g/mol) greatly exceeds that of norbornene (100 g/mol). The inclusion of the $[\text{Ru(bpy)}_2(\text{pySO-NB})]^2^+$ monomer in a ring-opened norbornene polymer affects the ability of all chains to growth of equal length. However, this PDI is considerably lower than what may be observed from other methods, such as radical polymerization.

It is important to compare the concentration of ruthenium in this polymer featuring photomechanical effects to other examples.\textsuperscript{84} Elastomers comprised of azobenzene photochromes represent the most well studied materials that feature photomechanical bending due to a molecular isomerization. It is important to note that these materials often require modest heating ($50 – 90 \, ^\circ\text{C}$) to exceed the glass transition temperature (Tg), and often contain an azobenzene in each monomer.\textsuperscript{76, 85} In these examples, the geometry change associated with cis-trans isomerization triggers the orientational order of the elastomer (smectic vs. nematic),\textsuperscript{73, 86} though there are recent reports of photomechanical effects in glassy polymers.\textsuperscript{76, 87} In contrast, for the disordered, atactic ruthenium polymers discussed here, we observe similar strains and deformations with polymers that contain only 2-4\% (by mole) of the photoactive monomer, indicating an efficient conversion of photonic energy to mechanical energy on the macroscopic scale.
In aggregate, the data show that the macroscopic deformation observed in these films following laser irradiation is due to the molecular rearrangement displayed by the ruthenium sulfoxide photochrome. Within the concentrations of the photochrome explored, we find that a critical concentration is required to observe a macroscopic deformation and that this deformation increases with an increase in the concentration of the photochrome. Thus, to explain the reactivity of these polymers, we envision deformations on three dimensional scales.\(^{32}\) On the molecule scale, the S→O isomerization produces a space change. It is manifest that the peptide linkage between the sulfoxide and the norbornene efficiently amplifies the molecular volume change and backbone deformation following phototriggered isomerization of the sulfoxide, permitting the polymer to bend or otherwise deform, which is on the “domain level”, roughly at nanoscale. At the microscale, there are likely domains of the polymer structure which act cooperatively with one another and in concert with the molecular motions to further amplify the deformation. We propose that the polymer structure is supramolecular in nature and that the polymer folds around the photochrome in a specific fashion in order to facilitate energy transduction and distortion of the film following irradiation. The inability to form homopolymers from the ruthenated norbornene monomer argues against a block co-polymer structure. At the macroscale, these effects collaborate to produce an observable macroscopic photomechanical effect from an excited state isomerization of a bound sulfoxide ligand, which can be explain by bilayer model, as shown in Figure 5.6. Given light irradiation from the topside of the film, the light intensity reduces as penetrating the film by the absorption of photochrome. Part of the film isomerized and
the volume of which is decreased while another part remains the same, resulting bilayer system with a top layer and bottom layer. The contraction of the top layer then performs work to the bottom layer and results in bending the film towards the light.

*Figure 5.6.* A scheme shows the bilayer model mechanism for the photomechanical effect.
**Liquid crystal networks (LCNs)**

We used the liquid crystal mixture of RM 82, RM 105 and RM 23 as hosts to load with the ruthenium sulfoxide complexes for photomechanical study. The RM 82, RM 105 and RM 23 liquid crystals mixture system was developed by Van Oosten for the photomechanical study with azobenzene photochromes. The structures of the liquid crystals are shown in Figure 2.1 (Page 27). The liquid crystal monomer RM 23 has a benzonitrile end group, leading to a higher polarity than the liquid crystal monomer RM 105. While RM 82 has acrylate on both ends to act as crosslinker. The aim of developing photochromic LCNs requires a good mixing of the liquid crystals (LCs) with the photochrome. A problem is that LCN is forming 2-D sheets and, to a first approximation, the photochrome can be thought to be a sphere. As a result, it is difficult to mix these two geometric shapes. Good mixing could be obtained by adjusting the ratio of RM 23 to RM105 for the polarity matching. However, a high ratio of RM105 to RM23 would narrow the temperature range of nematic phase for the LCs system, or even eliminate the nematic phase. The elasticity of the resulted LCNs is determined by the concentration of the crosslinker RM 82. A too high elasticity would result in difficulty of film bending.

We prepared different component ratio of RM liquid crystals with different loading of ruthenium sulfoxide complexes. Ruthenium sulfoxide complexes are charged ionic complexes, so it is required to increase the ratio of RM 23 to match the high polarity of the Ru complexes. A mixing ratio of 3:1:2 by weight was used for RM 105 : RM 23 : RM 82, to reach a high polarity LC system with a broad nematic phase temperature range. The LCs were dissolved in DCM with [Ru(bpy)₂pySO](PF₆)₂.
[Ru(bpy)$_2$pySO-Cn, n=6,8,18](PF$_6$)$_2$, [Ru(bpy)$_2$pySO](AOT)$_2$. After stirring for 10 minutes, the solvent was removed by heating on a hot plate at 65°C. Interestingly, [Ru(bpy)$_2$pySO](PF$_6$)$_2$ and [Ru(bpy)$_2$pySO-C$n$, n=6,8](PF$_6$)$_2$ precipitated once the solvent was removed, while [Ru(bpy)$_2$pySO-C$_{18}$(PF$_6$)$_2$ and [Ru(bpy)$_2$pySO](AOT)$_2$ were homogeneously mixed with the LCs. It is supposed that the long alkane chain of -C$_{18}$ and AOT are hydrophobic or decrease the polarity of the ruthenium sulfoxide complexes. The LCs mixture with [Ru(bpy)$_2$pySO-C$_{18}$(PF$_6$)$_2$ and [Ru(bpy)$_2$pySO](AOT)$_2$ were then applied onto a glass slide for polarized optical microscope study. A hotstage (Linkam) was used for controlling the temperature. For the LCs mixture with 1.5% [Ru(bpy)$_2$pySO-C$_{18}$(PF$_6$)$_2$ loading by weight reached nematic phase at 36°C and the isotropic phase at 68°C. Shown in Figure 5.7 A-C are the photographs taken by polarized optical microscope at 62°C. The special pattern in 5.7 B-C is due to the nematic phase of the liquid crystal. This pattern appears and alternates between parallel and perpendicular cross polarized light, which is due to the dichroism property of liquid crystal. There are clusters shown in all of the pictures, and the clusters existed even when the sample was heated above the isotropic phase temperature. It can be concluded that the [Ru(bpy)$_2$pySO-C$_{18}$(PF$_6$)$_2$ is not dissolved in the LCs mixture, though the LCs mixture exhibits nematic phase feature. For the LCs mixture with 1.5% [Ru(bpy)$_2$pySO](AOT)$_2$ loading by weight reached nematic phase at 42°C and the isotropic phase at 70°C.
Figure 5.7. Polarized microscope pictures for LCs mixture loaded with: A. [Ru(bpy)$_2$pySO-C$_{18}$](PF$_6$)$_2$, single polarized, B. perpendicular cross polarized, C. parallel cross polarized, D. [Ru(bpy)$_2$pySO](AOT)$_2$, single polarized, E. perpendicular cross polarized, F. parallel polarized. All pictures are taken at nematic phase.
As shown in Figure 5.7 D-F are the photographs taken by polarized optical microscope at 62°C. It appears homogeneously in Figure 5.7 D, which is a picture under single polarized light. The nematic feature appears in Figure 5.7 E-F, which are photographs under parallel and cross polarized light. While in Figure E there are some dark area exhibiting features different to LC nematic patterns, they are gone in Figure F. Given the 1.5% by weight loading ratio, this feature cannot be the precipitation of the ruthenium complex. Moreover, the changing between parallel and crossed polarized light supports that those area are well aligned. By increasing the loading of [Ru(bpy)$_2$pySO](AOT)$_2$ the dark area increases. However, for an increased loading of 3% by weight, the LCs mixture did not show any nematic phase feature.

The obtained LCs mixture with [Ru(bpy)$_2$pySO](AOT)$_2$ was mixed with photoinitiator 819, and then loaded into a 30μm thickness cell with rubbed polyimide coating and photopolymerized to result in an aligned LCNs film. The loading operation was taken at 70°C to melt the LCs and loaded by capillary effect, then the temperature was slowly decreased to 65°C to reach the nematic phase. The small valleys on the rubbed polyimide surface force the LCs to align in the rubbed direction, and therefore LCs in the cell would be uniformly aligned. The aligned nematic phase was annealed to result in a LCNs film by photopolymerization, with a mercury lamp having 455 nm cut on filter. The photopolymerization was done in 2 minutes at 65°C. The pictures of the cell were taken under cross polarized light, as shown in Figure 5.8 A-B.
Figure 5.8. A photopolymerized LCNs cell loaded with [Ru(bpy)$_2$pySO](AOT)$_2$. A. photograph from perpendicular cross polarized light, B. photograph from parallel cross polarized light, C, polarized UV-Vis absorption spectrum.
It is perpendicular cross polarized light in Figure 5.8 A, and it is parallel cross polarized light in Figure 5.8 B. The dichroism feature of the film is clear from these two pictures, and the homogeneous color supports a uniform feature in the film. Another cell was fulfilled with the same LCs mixture without ruthenium complex, and photopolymerized under the same condition to result in LCNs film as control. The cells were carefully opened by a razor blade, and the LCNs films were still layered on the bottom glass slides. Polarized UV-Visible spectrum were taken for the LCNs with [Ru(bpy)$_2$pySO](AOT)$_2$, and the LCNs without ruthenium complexes was used as blank, as shown in Figure 5.8 C. There are broad absorption peaks from 350 nm to 450 nm in both parallel and perpendicular polarized direction. We proposed that the [Ru(bpy)$_2$pySO]$^{2+}$ was partially isomerized during the photopolymerization process, there was light with wavelength shorter than 450nm passed through the filter due to the very high intensity of the mercury lamp. The absorption peaks are significantly higher in parallel than in perpendicular polarized direction.

The order parameters in the LCNs can be calculated from the polarized absorption. The dichroic ratio R and the order parameter S are given by the following equation, respectively:

\[
R = \frac{A_{\text{para}}}{A_{\text{perp}}} \tag{5.1}
\]

\[
S = \frac{(R - 1)}{(R + 2)} \tag{5.2}
\]

Where $A_{\text{para}}$ and $A_{\text{perp}}$ are the absorption measured with light parallel and perpendicular to the rubbing direction of the LCNs, respectively. We took the absorption value at 370 nm, which is the absorption maximum for the ruthenium sulfoxide complex.
The calculated dichroic ratio is 1.54, and the order parameter is 0.15. This LCN is in high order, even compared to the azobenzene LCN, which has an order parameter of 1.41.\textsuperscript{89}

The LCNs were then cut from the glass slide into strips for photo-mechanical study. The film strips are approximate 1mm x 6mm x 30μm. As shown in Figure 5.9, the film was hold by a tweezer. A 405nm laser light with about 100mW/cm\textsuperscript{2} intensity was directed onto the film from right side. A bending angle of 33° was formed towards the direction of light. Interestingly, the bending amplitude is related to the polarized direction of the laser light. The response reached the maximum by rotating the polarized direction of the laser light. From the polarized UV-Visible spectra, it is shown that the film reaches maximum light absorption when the polarized direction is parallel to the alignment direction, and reaches minimum light absorption when it is perpendicular. In the perpendicular situation, the absorbed light could not support enough energy to drive the film bending. And the LCNs without ruthenium complexes exhibited no response to the same irradiating condition.

The bending mechanism of the LCNs film is similar to the amorphous polymer film, which could be explained by the bilayer model. When the 405nm light progresses through the film, [Ru(bpy)\textsubscript{2}pySO\textsuperscript{2+} on the top part isomerizes and destroys the nematic phase of the liquid crystal. This nematic to isotropic phase change causes a volume decrease in the vertical direction, while the bottom part remains the same. The contraction of the top layer leads to work performing on the bottom layer and then the film bends towards the light.
Figure 5.9. LCNs with [Ru(bpy)$_2$pySO](AOT)$_2$ film shows bending towards the irradiation of 405 nm light: A. the film before irradiation, B. the film after irradiation.

Summary

The aim of converting photonic energy into mechanical energy has been implemented by the photoisomerization of ruthenium sulfoxide complex, in both amorphous polymer and LCNs systems. Compared to most of the LCNs system studied, the preparation of amorphous polymer is much easier and of lower cost. And, both the amorphous and LCNs systems need much lower concentration of ruthenium complexes loading in comparison to azobenzene dyes. This gives credit to the ruthenium sulfoxide as a dye for photomechanical. The bending mechanism of LCNs is well studied and known as nematic to isotropic phase transition. While the details for the properties changing in amorphous polymer are unclear. The next chapter will take studies on the mechanical properties changing in the amorphous polymer.
CHAPTER 6. NANOINDENTATION STUDY IN THE COPOLYMER FILMS

Background

The mechanism of the photomechanical effect is different for the LCNs and amorphous polymers. There are two separate thoughts, while most of the studies in photomechanical effects are focus on the LCNs.\textsuperscript{18-21, 48, 89, 90} We proposed that there are domain structure, in the amorphous ruthenium sulfoxide complexes incorporated copolymers polymers, and this supramolecular structure can be altered by the photoisomerization of the ruthenium complexes to result in the macroscopic film bending.\textsuperscript{91} From SEM study, there is no long range crystalline or semicrystalline structure observed in the copolymer films, which introduces a challenge to examine the domain structure hypothesis. However, the structure change should affect the mechanical properties of the copolymers, since the more compact structure will result in the higher Young’s modulus and hardness for the copolymers. It is of interest to study the mechanical properties change in nanoscale for those copolymers, to indentify the hypothesis of domain structure in the amorphous copolymer films.

AFM has proven to be a useful tool in detecting both the morphology and mechanical properties of materials on the nanoscale.\textsuperscript{92-97} In 1989, an AFM-like instrument was first introduced to measure the mechanical properties on a surface by Burnham and Coloton.\textsuperscript{98} Since then, AFM has been applied to various materials like metal,\textsuperscript{99-102} crystals,\textsuperscript{103-106} biomaterials\textsuperscript{107-110} and polymers,\textsuperscript{111-116} by the means of force-displacement curves. However, the nanoindentation studies obtained by AFM instrument were treated as semi-quantitive in the early stages, due to the uncertainty in the spring
constant and Z axis position. In the later time, it was realized that the exact Z axis position could be obtained by calibration from the deflection vs Z axis movement plot, and the Z axis values after calibration would be consistent within 1%. In the early stage, the spring constant of the probe cantilever was taken from the nominal value of the manufactures, which may vary 100% between probes. Cleveland and coworkers developed a nondestructive method to determine the exact spring constant for probe cantilevers, by attaching a known mass small object onto the end of the cantilevers to characterize the change of resonance frequency. There are a number of methods to determine the exact spring constant value. The Dynamic Thermal Analysis method developed by Hutter and Bechhoefer is popularly employed in commercial AFM systems, which uses Brownian motion of the cantilever and equipartition theorem to obtain the spring constant. This method was well calibrated by Proksch and Cleveland and, compared to other methods, resulted in consistent spring constant values.

Another challenge to obtaining reliable results in mechanical properties from the nanoindentation technique is applying the appropriate modeling method in data analysis. The first widely applied method is the Hertz model, which is based on interaction of two elastic sphere particles. The fundamental assumption in Hertz model is that the surface is continuous and frictionless; furthermore, the strains in the contact area are sufficiently small to follow the linear theory of elasticity. Most of the time, the fundamental condition could not be reached for Hertz model. And there have been many different approaches developed to correct the contact area calculation of the Hertz model. Oliver and Pharr studied the unloading curves of a series of different materials by a pyramid
shape probe, and realized that the unloading curves could be described by a power function instead of linear function.\textsuperscript{129} And it has been one of the most popular methods for obtaining mechanical properties of surface by the nanoindentation techniques, since 1992.\textsuperscript{116, 117, 130-133}

**Oliver-Pharr Model**

Penetrating the surface with an indenter tip with a loading force $F_{\text{max}}$ on the tip, results in a penetration depth of $h_{\text{max}}$, as shown in Figure 6.1. When the tip reaches the maximum depth, the sample surface conformed to the tip shape at depth $h_{c}$, and this depth to the initial surface is $h_{s}$. During the unloading process, the tip has direct contact with the surface through $h_{t}$, and left unrecoverable depth $h_{f}$. The $h_{s}$ could be given by:

$$h_{s} = \varepsilon \frac{F_{\text{max}}}{S_{\text{max}}}$$  \hspace{1cm} (6.1)

Where $\varepsilon$ is a constant and $S$ is elastic unloading stiffness. The $\varepsilon$ depends on the geometry of the indenter, and a value of 0.75 was recommended for the pyramid indenter based on empirical observation. $S$ is given by:

$$S = \frac{d_{F}}{d_{h}}$$  \hspace{1cm} (6.2)

The unloading curve follows a power law, which is described by:

$$F = BE^{*}(h - h_{f})^{m}$$  \hspace{1cm} (6.3)

Where $B$ and $m$ are constants, $BE^{*}$ and $m$ could be deduced from the fitting of force vs displacement curve. The power constant $m$ is related to the efficient indenter shape.
Figure 6.1. The schematic graph shows the indentation parameters when the indenter reached the maximum depth and unloaded from the sample surface. $F_{\text{max}}$ is the loading force applied on the tip, $h_{\text{max}}$ is the maximum penetration depth, $h_s$ is the sink in depth at the maximum penetration depth, $h_c$ is the depth where the tip conformed with the surface, $h_f$ is the unrecoverable depth after tip unloading and $A$ is the cross section area of the tip-sample contact area and the initial surface area.
For an ideal pyramid tip, the value of $m$ is 1.5. But normally the actual value of $m$ varies from 1.2~1.8. After the identification of Equation 6.3, $S_{\text{max}}$ could be calculated by Equation 6.2.

The contact depth of the tip and the sample at maximum penetration depth is:

$$h_c = h_{\text{max}} - h_s \quad (6.4)$$

By introducing Equation 6.1 into Equation 6.4, it turns into:

$$h_c = h_{\text{max}} - \varepsilon \frac{F_{\text{max}}}{S_{\text{max}}} \quad (6.5)$$

The cross sectional area of the indenter and the surface is a function of the contact depth. For a pyramid indenter, the area function is:

$$A = 3\sqrt{3} \tan^2 \theta \cdot h_c^2 \quad (6.6)$$

Once the contact area is determined, the hardness $H$ and effective Young’s modulus $E^*$ is estimated by Equation (6.7) and Equation (6.8):

$$H = \frac{F_{\text{max}}}{A} \quad (6.7)$$

$$E^* = \frac{1}{2\beta} \sqrt{\frac{\pi}{A}} S_{\text{max}} \quad (6.8)$$

where $\beta$ is taken as a dimensionless unity. The effective Young’s modulus is a combination of the sample modulus and the tip modulus, it is defined by Equation (6.9):

$$\frac{1}{E''} = \frac{1 - \nu_{\text{sample}}^2}{E_{\text{sample}}} + \frac{1 - \nu_{\text{tip}}^2}{E_{\text{tip}}} \quad (6.9)$$
where $\nu$ is the Poisson ratio. The Poisson ratio could be measured for bulk materials, but it is relatively difficult in nanoscale. However, the Young’s modulus of the tip is much larger than the sample. $E_{\text{tip}}$ can be neglected, as it would just result in an error of less than 1%. In this work, the effective Young’s modulus is used instead of the sample Young’s modulus for abbreviation.

**Factors Affecting Nanoindentation Measurement by AFM**

In a typical AFM system, the photodiode detector records the deflection from the back of the probe cantilever, and the deflection signal is converted into displacement of the probe cantilever. By knowing the spring constant of the cantilever, the measured force can be translated from the cantilever displacement by Hook’s law. Though the nominal spring constant is supplied for the probe by manufacturers, the exact value varies even up to 100%. For a reliable measurement, calibration for spring constant of the probe is required. Meanwhile, we need to select indenting probe with appropriate shape and spring constant.

The deflection signal varies during the piezomovement of the Z axis in the AFM systems. For the AFM instrument we used, the noise is several nanometers and linearly related to the Z axis piezomovement. This noise can be reduced to below 1% by a linear fitting of the deflection signal vs Z axis piezomovement, as shown in Figure 2.2 A (Chapter 2, page 30). The cantilever displacement is obtained from the voltage change at the photodiode detector, and a calibration is required to convert the voltage change into cantilever displacement of nanometer unit. For this calibration, a hard sample is needed, which is much stiffer than the cantilever to make sure no indenting occurs. We selected
silicon glass here. There is linear relation between the deflection signal and the Z axis movement around the range when the probe touches the sample surface. Once we fit the plot of deflection vs Z axis movement, we can get an accurate conversion from the voltage change into cantilever displacement. This calibration is required each time when the probe is reloaded or the laser beam is realigned. Otherwise an error of up to 30% can occur. After the calibration of deflection, the spring constant of the cantilever could be obtained by thermal noise methods, which uses Brownian motion of the cantilever and deduces the spring constant from the equipartition theorem. A corrected thermal noise method was developed by Cleveland and coworkers and applied to this work, which brought the spring constant value within 10% with other spring constant calibration methods. Regardless of the variation of the calibration values, this work was done by the same probe, which makes comparison of the results reliable.

For nanoindentation experiment, the spring constant of the cantilever should be close but larger than the sample. A softer cantilever will not allow indenting occurs, and too stiff of a cantilever will not result in a sensitive experiment. The sample modulus is calculated based on the contact area. A probe with regular shape tip is required to calculate the contact area at specific contact depth. And the tip with wider angle is preferred to the narrow ones, which could increase the contact area and improve the accuracy of the experiment. The Bruker TESPD probe was used in this work, with a spring constant value of 42 N/m and pyramid shape and about 22° at apex.
**Result and Discussion**

We prepared thin films for nanoindentation study by spincoating a cyclohexanone solution of ruthenium derivatized copolymers onto a cleaned glass cover slip. (25mm x 25mm) The copolymers used in this study were poly-\{[Ru^{II}(bpy)_{2}pySO-NB]/NB\} (1:25), poly-\{[Ru^{II}(bpy)_{2}pySO-NB]/NB\} (1:40), poly-\{[Ru^{II}(bpy)_{2}pySO-NB]/NB\} (1:110), poly-\{[Ru^{II}(bpy)_{2}-pyS-NB]/NB\} (1:40) and polynorbornene homopolymer (poly-NB). The obtained thin films were annealed at 65 °C in an oven overnight, to eliminate solvent dissolved in polymers. The thickness of the films is estimated to be ~3 μm varying between samples, by AFM measurement, which was done by surface topology scanning over artificial scratches and the edges of the films. The nanoindentation experiment was done under contact mode. A maximum loading force of approximate 9 μN was applied on the probe to penetrate into the film with a constant velocity 2 μm/s. Once the probe reached the maximum depth, it was held at that position for 5 s to allow the pressed area to reach a stable state before removing the tip from the film surface at the same constant velocity 2 μm/s. The real-time load-displacement data was recorded, for the analysis of the mechanical properties of the films. For each sample, the indentation experiment was performed at least 7 times in a randomly selected area and the average values were taken in the end.

Shown in Figure 6.2 are the surface topology images for a poly-\{[Ru^{II}(bpy)_{2}pySO-NB]/NB\} (1:40) copolymer film after indentation studies. In Figure 6.2 A, there are white spots randomly distributed in a 40 x 40μm area. The white spots are the residual indenting imprints for each individual experiment.
Figure 6.2. A. The image of surface topology after nanoindentation for poly-
{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB} (1:40) copolymer film, B. 3D graph for one of those
indenting imprints.

For elastoplastic materials, due to the plastic deformation, a non-recoverable residual
imprint would be left after the removing of the load. The space between each spots is
larger than 1.5 μm to make sure that each indenting experiment is independent to each
other. In Figure 6.2 B is the 3D profile image for one of the indenting imprints, the shape
of the residual imprint fits the shape of the AFM probe used. The size of the residual
imprint is about 0.5x0.5 μm by area, and 65 nm by depth from a cross line measurement.
The depth of the residual imprint is much lower than the indenting depth with an
approximate value of 200 nm. The indenting depth is less than 20% of the films thickness,
which results in a negligible influence from the substrate.\textsuperscript{134} For elastoplastic materials, there are both elastic and plastic deformations during the indenting process. The plastic deformation is nonrecoverable, while the elastic deformation is recovered immediately after the loading is removed.\textsuperscript{117} The resulting in residue depth is smaller than the maximum penetration depth.

Shown in Figure 6.3 is a selected force vs indentation curve for poly-\{[Ru\textsuperscript{II}(bpy)$_2$pySO-NB]/NB\} (1:40) film. The black line is for the approaching process, red line is for the retracting process and the blue line is for the dewelling process. There are complicated interactions involved during the approaching process, like surface breaking. It is reasonable not to select the approaching trace to study the mechanical properties for the samples.\textsuperscript{114} The instrumental indenter holds the indenter tip at the same height for a period of time, to allow the pressed sample reaching a stable state. For the indentation experiments by AFM, a dewelling process is applied instead of this holding process, where the Z piezo voltage of the AFM is maintained at a constant. This approach results in a roughly constant force applied on the cantilever, and drives the tip deeper into the sample. However, this process is gentle and allows the pressed sample surface reaching a relative stable state. During the unloading process, the elastic deformation is recovered while the plastic deformation remains. The tip is separated from the sample surface when the elastic deformation is fully recovered, which occurs at the depth of the indenting residual. From the unloading curve, it is observed that the loading force on the cantilever reaches zero at indentation depth of approximate 70 nm, where the probe is separated from the sample surface. This depth value is consistent with the
topology scanning result of the residual imprints. The elastic deformation is the dominant factor during the unloading process, and most of the nanoindentation studies are based on the analysis of the unloading process.\textsuperscript{114, 130, 135}

![Image](image.png)

\textit{Figure 6.3}. A selected force vs indentation curve for poly-\{[[Ru\textsuperscript{II}(bpy)]\textsubscript{2}pySO-NB]/NB\} (1:40). The black line is for the approaching process, the red line is for the retract process, and the blue line is for the dwelling process.

The recorded force vs indentation curves from these nanoindentation studies are shown in Figure 6.4. The black lines represent poly-\{[[Ru\textsuperscript{II}(bpy)]\textsubscript{2}pySO-NB]/NB\} (1:25), the orange lines represent poly-\{[[Ru\textsuperscript{II}(bpy)]\textsubscript{2}pySO-NB]/NB\} (1:40), the brown lines represent poly-\{[[Ru\textsuperscript{II}(bpy)]\textsubscript{2}pyS-NB]/NB\} (1:40), the green lines represent poly-\{[[Ru\textsuperscript{II}(bpy)]\textsubscript{2}pySO-NB]/NB\} (1:150), and the gray lines represent poly-NB.
Figure 6.4. The force vs indentation curves for poly-\{[\textrm{Ru}^{II}\textrm{(bpy)_{2}}\textrm{pySO-NB}]\} (1:25) (black lines), poly-\{[\textrm{Ru}^{II}\textrm{(bpy)_{2}}\textrm{pySO-NB}]\} (1:40) (orange lines), poly-\{[\textrm{Ru}^{II}\textrm{(bpy)_{2}}\textrm{pySO-NB}]\} (1:150) (green lines), poly-\{[\textrm{Ru}^{II}\textrm{(bpy)_{2}}\textrm{pyS-NB}]\} (1:40) (brown lines) and poly-NB (gray lines).

The plot shows that the maximum penetration depth decreases, as the loading concentration of the ruthenium sulfoxide complexes increased from pure poly-NB to \{[\textrm{Ru}^{II}\textrm{(bpy)_{2}}\textrm{pySO-NB}]\} (1:25). Even for a very low loading as 1:150 of Ru:NB, there is a significant change in the hardness of the materials. Surprisingly, there is significant difference between the poly-\{[\textrm{Ru}^{II}\textrm{(bpy)_{2}}\textrm{pySO-NB}]\} (1:40) and \{[\textrm{Ru}^{II}\textrm{(bpy)_{2}}\textrm{pyS-NB}]\} (1:40) samples, though they have the same ruthenium complexes concentration and similar molecular structure. The depth of the residual imprint follows the same order as the maximum penetration depth for the samples.
The mechanical parameters were determined by carefully fitting the force vs indentation curves with Oliver-Pharr model. (Detail fitting results are shown in Appendix A) The Young’s moduli are 140±11 MPa, 240±9 MPa, 503±16 MPa, 677±10 MPa and 336±9 MPa respectively for poly-NB, poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:150), poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:40), poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:25) and poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-S-NB}]/\text{NB}\}\) (1:40). In the same order, the stiffness values are 54±6 N/m, 73±4 N/m, 83±3 N/m, 78±1 N/m and 57±2 N/m respectively; while the hardness values are 84±7 MPa, 134±6 MPa, 477±23 MPa, 983±28 MPa and 459±30 MPa respectively. The Young’s modulus of poly-NB is consistent with the value obtained by Dynamic Mechanical Analysis (DMA). Poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:25) sample has the highest Young’s modulus and hardness value, which means that poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:25) has the most compact structure and is the most difficult to be distorted. For plastic materials, the Young’s modulus is not proportional to hardness as for metal materials. Compared to the poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:40) sample, the Young’s modulus of poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:25) is approximate 30% higher, but the hardness is 100% higher. With a ruthenium complex loading of 1:150 to norbornene, the poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:150) is almost double the value for pure poly-NB. However, the stiffness of poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:25) is slightly lower than poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:40). All of the ruthenium sulfoxide loaded polymers exhibit similar stiffness values, while both of the pure poly-NB and poly-\(\{[\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}]/\text{NB}\}\) (1:25) feature coincidently similar values. It is natural to
come to a conclusion that the ruthenium sulfoxide complexes introduce a significant structure change to the polymers.

The mechanical properties of the polymer films were changed, by irradiating with approximate 65 mW/cm$^2$ 405 nm light for 60 s. As shown in Figure 6.8 is the force vs indentation curves for poly-{$\{\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}\}/\text{NB}$} (1:40) copolymer film before and after irradiation.

![Figure 6.5. The force vs indentation curves for poly-{$\{\text{Ru}^\text{II}(\text{bpy})_2\text{pySO-NB}\}/\text{NB}$} (1:40) film before and after irradiating with 65mW/cm$^2$ 405nm laser light for 60s.](image)

We found that both the maximum penetration depth and the residual imprint depth are smaller after irradiation. The \([\text{Ru}(\text{bpy})_2\text{pySO}]^{2+}\) photochrome undergoes isomerization from S-bonded isomer to O-bonded isomer upon irradiation of 405nm light. This molecular structure changing could induce a bending towards the light for the
[Ru(bpy)$_2$pySO]$^{2+}$ incorporated copolymer films. And the shifting of the force curves is a result of this isomerization. However, there is no significant shifting for other samples including poly-{{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB}} (1:25) and poly-{{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB}} (1:150), though there were isomerization occurring which could be identified by the color change. By carefully fitting with Oliver-Pharr model, the mechanical parameters were obtained. (Fitting detail results are shown in Appendix A) The values of Young’s modulus are 133±11 MPa, 244±10 MPa, 713±19 MPa, 705±15 MPa and 318±9 MPa, respectively, for poly-NB, poly-{{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB}} (1:150), poly-{{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB}} (1:40), poly-{{[Ru$^{II}$(bpy)$_2$pySO-NB]/NB}} (1:25) and poly-{{[Ru$^{II}$(bpy)$_2$pyS-NB]/NB}} (1:40). In the same order, the stiffness values are 48±7 N/m, 74±3 N/m, 104±3 N/m, 81±1 N/m and 51±6 N/m respectively, while the hardness values are 98±15 MPa, 135±3 MPa, 988±36 MPa, 614±50 MPa, and 502±92 MPa respectively.

A comparison of the mechanical parameters for the samples before and after irradiation with 405 nm light are shown in Figure 6.6 - 6.8, where blue columns represent the value before irradiation and the red columns represent the value after irradiation.
Figure 6.6. The fitting results of Young’s modulus for the nanoindentation experiments by Oliver-Pharr model. The blue columns represent the original samples; the red columns represent the samples after irradiation with 405 nm light.
Figure 6.7. The fitting results of stiffness for the nanoindentation experiments by Oliver-Pharr model. The blue columns represent the original samples; the red columns represent the samples after irradiation with 405 nm light.
Figure 6.8. The fitting results of hardness for the nanoindentation experiments by Oliver-Pharr model. The blue columns represent the original samples; the red columns represent the samples after irradiation with 405 nm light.

The Young’s modulus for poly-\{[\text{Ru}^{II}(bpy)_2\text{pySO-NB}]/\text{NB}\} (1:40) increases more than 30% after irradiation, as shown in Figure 6.7. While the Young’s modulus for poly-\{[\text{Ru}^{II}(bpy)_2\text{pySO-NB}]/\text{NB}\} (1:25) slightly increases after irradiation. Overall, the Young’s modulus increases for the polymers with incorporation of ruthenium sulfoxide complexes, which undergo isomerization with irradiation. While the Young’s modulus is decreased slightly for poly-NB and poly-\{[\text{Ru}^{II}(bpy)_2\text{pyS-NB}]/\text{NB}\} (1:40), which could not undergo isomerization. However, the change in poly-NB, poly-\{[\text{Ru}^{II}(bpy)_2\text{pySO-NB}]/\text{NB}\} (1:150) and poly-\{[\text{Ru}^{II}(bpy)_2\text{pyS-NB}]/\text{NB}\} (1:40) is negligible considering the error bar. The change of stiffness is similar to Young’s modulus, as Shown in Figure
6.8. The poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:40) exhibits the largest increase of approximate 25% for the stiffness. The poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:25) exhibits a slight increase for the stiffness, while poly-NB and poly-\{[Ru^{II}(bpy)_2pyS-NB]/NB\} (1:40) exhibit slight decrease. The poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:40) sample is the only sample exhibiting changes before and after irradiation. The hardness exhibits the most change for the poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:40) sample, while the hardness of this sample is still much lower than poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:25) sample even after irradiation, as shown in Figure 6.9. The hardness changes before and after irradiation are negligible for poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:25) and poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:150) samples. However, there might be hardness increasing in poly-NB and poly-\{[Ru^{II}(bpy)_2pyS-NB]/NB\} (1:40).

These mechanical parameter changes are consistent with the photomechanical studies on different samples. By irradiation with 405 nm light, the prepared film strips exhibited the most photo-triggered movement for the poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:40) copolymer, and much less for the poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:25) copolymer. When the concentration of ruthenium sulfoxide was diluted to 1:110 of Ru:NB, there was isomerization without photomechanical movement. It is proposed that there are not enough ruthenium complex molecules performing work to result in film bending. And there was no photomechanical effect for poly-NB and poly-\{[Ru^{II}(bpy)_2pyS-NB]/NB\} (1:40) copolymer neither, because there was no isomerization occurring. Both of the Young’s modulus and hardness increased significantly for the poly-\{[Ru^{II}(bpy)_2pySO-NB]/NB\} (1:40) copolymer samples after isomerization, which
reveals that the poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:40) copolymer has more compact structure after isomerization. As proposed in Chapter 5, the polymer structure exhibits domains and that the polymer folds around the photochrome in a specific fashion in order to facilitate energy transduction and distortion of the film following irradiation. The S→O isomerization produces a space change and leads to a deformation of the polymer backbone. It is manifest that the peptide linkage between the sulfoxide and the norbornene efficiently amplifies the molecular volume change and backbone deformation following phototiggered isomerization of the sulfoxide, permitting the supramolecular structure to reorganize and reach a more compact structure. And this reorganization yields the film bending towards to the light. While in the poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:25) copolymer samples, the polymer structure is already very compact, and it is harder for the isomerization to yield a more compact structure. It is possible that this leads to the less photomechanical effect in the poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:25) copolymer films compare to the poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:40) copolymer samples.

**Adhesion Force Analysis**

Adhesion force could describe the interaction between the probe and the sample surface. It is a combination of van der Waals force, electrostatic force, capillary force and the force due to chemical bonds.\textsuperscript{137} The adhesion force can be measured by finding the critical point, at which the cantilever force overcomes the adhesion force and pulls the probe from the surface during the retracting process. As shown in Figure 6.9, there is a retracting force curve trace for poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:40) copolymer film, which is exhibiting negative peak feature and the value of the negative peak represents
the adhesion force. The value of adhesion force is affected by both of the contacting area and the sample properties under the same measuring environment.

![Force vs Z distance curve](image)

*Figure 6.9.* A typical force vs Z distance curve for poly-{{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB}} (1:40) copolymer film. The height of the negative peak is the value of adhesion force.

The measured average values for all the samples are shown in Figure 6.10. The blue columns represent the adhesion force before irradiation and the red columns represent the adhesion force after irradiation. It is observed that all of the ruthenium complexes incorporated polymers exhibiting larger adhesion force than pure poly-NB, though the poly-NB sample has the largest contact area due to the deepest penetration. The ruthenium complexes are composed of ruthenium complexes cation with plus two
charges and two anions with minus one charge. It is observed the presence of the ruthenium complexes enhances the electrostatic force and increases the adhesion force in the polymers.

![Figure 6.10. The fitting results of measured adhesion force. The black columns represent the original samples; the red columns represent the samples after irradiation with 405 nm light.](image)

The highest adhesion force was observed for the poly-\{[Ru^{II}(bpy)_{2}PyS-NB]/NB\} (1:40) copolymer sample, which could due to the larger contact area comparing to the poly-\{[Ru^{II}(bpy)_{2}PySO-NB]/NB\} (1:40). And the slightly lower adhesion force in poly-\{[Ru^{II}(bpy)_{2}PySO-NB]/NB\} (1:25) compared to poly-\{[Ru^{II}(bpy)_{2}PySO-NB]/NB\} (1:40), suggests that the factor of smaller contact area overcomes the factor of higher ruthenium complexes concentration, while the poly-\{[Ru^{II}(bpy)_{2}PySO-NB]/NB\} (1:40) obtains
much greater adhesion force comparing to the poly-\{[\text{Ru}^{\text{II}}\text{(bpy)}_2\text{pySO-NB}]/\text{NB}\} (1:150). It is possible that the charge distribution starts to reach a relative invariable saturation in the poly-\{[\text{Ru}^{\text{II}}\text{(bpy)}_2\text{pySO-NB}]/\text{NB}\} (1:40). And it is sufficient to mention that it is impossible to obtain the copolymer with higher ratio than 1:25 of Ru:NB without any precipitation during the polymerization process. It is not surprised that none of the samples exhibit significant changing within the error after irradiation, because there is no new charge’s generating or losing to alter the electrostatic force, which is the domain interaction contributing to adhesion force here.

**Comparison of Different Cantilever-like Mechanical Systems**

All the self-actuated mechanical deformation is transferred by elastic wave, and the velocity of elastic wave is determined by \sqrt{(E/\rho)}. The fastest response time (inertial time) is the duration time for the elastic wave transferring through the smallest dimension, where is the thickness (L) for the cantilever systems.\(^{138}\) The inertial time \(\tau_i\) is determined by \(L/\sqrt{(E/\rho)}\), which should be shorter than the time scale of the mechanical motion. It is of interest to compare different photomechanical systems and a similar cantilever mechanical system in the nature (Venus flytrap). As shown in Table 6.1, the characterization for Ru-NB copolymers, azobenzene LCNs, diarylethene single crystal and Venus flytrap. The velocity of the elastic wave varies from 5.0-8.4x10\(^5\) mm/s in the ruthenium sulfoxide complexes incorporated copolymers, 10x10\(^5\) mm/s in azobenzene LCNs to 25x10\(^5\) mm/s in diarylethene single crystal and 10\(^5\) mm/s in Venus flytrap. They are within approximately the same magnitude. The inertial times for these systems are approximately within the magnitude of 10\(^{-9}\) s, except the one for Venus flytrap (10\(^{-4}\)s).
The azobenzene LCNs system and diarylethene single crystal system have almost the same velocity of elastic wave, but 1000 times difference in the motion time scale, which is approximately 0.01 s in azobenzene LCNs,\textsuperscript{139} and 2.5x10\textsuperscript{-5} s in diarylethene single crystal.\textsuperscript{23} And the ruthenium sulfoxide incorporated copolymers systems have much shorter inertial time than Venus flytrap, but the motion time is even longer. However, the generation mechanism of the elastic wave is different in these systems. Venus flytrap uses water diffusion between tissue cells to generate elastic waves, and all the other systems are using photoisomerzation to generate elastic wave. In solution, the isomerization could be finished within 10 ps in diarylethene,\textsuperscript{140} about the same in azobenzene and approximately 170 ps in ruthenium sulfoxide complexes.\textsuperscript{141} It is reasonable that ruthenium sulfoxide complexes incorporated copolymer systems have longer motion time scale than diarylethene and azobenzene systems. However, the reason of much shorter motion time scale in diarylethene than in azobenzene is unclear. The rates in solid states should be much different in solid state, the answer may be clear to us if we can know the isomerization rate in solid states.

**Summary**

The mechanical properties of the polymers are enhanced by the incorporating of ruthenium complexes, which is suggested by higher Young’s modulus and hardness. However, the difference between the ruthenium sulfoxide and thioether linkaged complexes incorporated polymers suggests that ruthenium sulfoxide complexes play an important role in the polymer structure for the copolymers. After photoisomerization, the poly-[\text{Ru}^{II}(bpy)_{2}pySO-NB]/NB (1:40) sample exhibits more than 30% percent increase
of the Young’s modulus, as well as an increase in the hardness and stiffness increasing. Essentially, this means a more compact structure in the poly-\{\text{Ru}^{II}(\text{bpy})_2\text{pySO-NB}/\text{NB}\} (1:40) sample after isomerization. And this structure change results in the polymer film contracting and bending towards to the light as noticed in Chapter 5.

Table 6.1. Comparison for ruthenium sulfoxide complex incorporated copolymers and other photomechanical systems with natural mechanical system

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<th>L (mm)</th>
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<th>E (Pa)</th>
<th>$\sqrt{E/\rho}$ (mm/s)</th>
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<td>$4.0 \times 10^{-9}$</td>
<td>$2.4 \times 10^8$</td>
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<td>$2.8 \times 10^{-9}$</td>
<td>$5.0 \times 10^8$</td>
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<td>$6.8 \times 10^8$</td>
<td>$8.4 \times 10^5$</td>
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<td>Azo-LCN</td>
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<td>$9 \sim 11 \times 10^{-9}$</td>
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<td>$110 \times 10^8$</td>
<td>$25 \times 10^5$</td>
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<tr>
<td>Venus flytrap</td>
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<td>$10^5$</td>
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CHAPTER 7. SUMMARY AND FUTURE CONSIDERATION

Summary

A two color, photochromic Ruthenium sulfoxide complex was modified by introducing a norbornene group on the sulfur atom through a condensation reaction. This monomer was copolymerized with norbornene to yield different poly-\{[\text{Ru}^{	ext{II}}(\text{bpy})_2\text{pySO-NB}]\}/NB\} copolymers with different ratios of Ru to NB. The monomer and copolymers were characterized by $^1$H NMR spectroscopy, UV-Visible absorption spectroscopy and TA spectroscopy. For the $[\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2+}$ complex, the chemical shift and splitting in one alkene proton reveals that the norbornene group is in close proximity to one aromatic ring of the bipyridine, which is coordinated to the ruthenium metal center. For the copolymers, the appearance of aromatic peaks from $[\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2+}$ supports that the $[\text{Ru}(\text{bpy})_2\text{pySO-NB}]^{2+}$ was successfully incorporated into the polymer. There is no difference between the monomer and copolymers in the UV-Visible absorption spectrum. Both samples undergo isomerization with irradiation of light. However, by ultrafast transient absorption spectroscopy, the $\text{S} \leftrightarrow \text{O}$ isomerization was found to be significantly slower in the copolymers: the rate constant changed from 2.0 ns in the monomer to 5.0 ns in the copolymer (Ru:NB 1:25) in the same solvent. This slowing down indicates that the $\text{S} \leftrightarrow \text{O}$ isomerization is affected by the polymer backbones.

Thin films were prepared with the ruthenium complexes derivatized copolymers. The copolymer films were amorphous or disordered in structure, which was characterized by SEM. Upon irradiation with 405nm light to trigger the $\text{S} \leftrightarrow \text{O}$ isomerization, the ruthenium sulfoxide copolymer films exhibited the photo-mechanical motion, which was
bending towards the light. And the deformation could be alternated with irradiation with 472nm light, which caused the O→S isomerization. However, the photomechanical motion was not observed in dilute Ru:NB concentration (1:110), nor in ruthenium thioether copolymer, which is not photochromic. The work required for bending was calculated for different Ru:NB ratio copolymers, and poly-\{[Ru^{II}(bpy)_{2}pySO-NB]/NB\} (1:40) copolymer showed the greatest amount of work of 3.47x10^{-4} μJ, to result in a largest bending scale. The work needed for bending is much less than the potential energy difference between the S-bonded and O-bonded isomers of the ruthenium sulfoxide complex molecules in the film, which means this photo-mechanical system has the potential to perform more work to the external environment.

Ruthenium sulfoxide complexes were also applied to the LCNs systems for photomechanical study. [Ru(bpy)_{2}pySO](AOT)_{2} was found to have a good mixing with RMs LC monomers. [Ru(bpy)_{2}pySO](AOT)_{2} of 1.5% by weight was loaded to a liquid crystal mixture of RM105:RM23:RM82 with a ratio by weight 3:1:2. Then the mixture was loaded into a cell with rubbed polyimide coating by capillary effect, and the LCs were photopolymerized at nematic phase to result in aligned LCNs film. The resulted ruthenium complexes loaded LCNs film exhibited dichroism property. By polarized UV-Visible spectroscopy, the LCNs exhibited different absorption along parallel and perpendicular directions, indicating that the [Ru(bpy)_{2}pySO](AOT)_{2} molecules were aligned in specific direction in the LCNs film. The LCNs film had different response upon irradiation with 405nm light along different direction, due to the different
absorption coefficient along different direction for the ruthenium sulfoxide complex in the LCNs film.

Nanoindentation study was employed for the ruthenium complexes incorporated copolymers by AFM. It was observed that both hardness and Young’s modulus of polynorbornene increased by the incorporation of ruthenium complexes, even with a very low ratio of Ru:NB 1:150. The different Young’s modulus and hardness in poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pyS-NB]/NB} (1:40) and poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:40) samples suggest that the ruthenium sulfoxide complex affects the polymer backbone differently to the ruthenium thioether complex. The mechanical properties are positive related to the concentration of the ruthenium complexes concentration in the copolymer. After irradiation with 405nm light to trigger the S→O isomerization, the young’s modulus increased as much as 35% in the poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:40) copolymer sample, and there was significant increase for the hardness. The increasing in Young’s modulus and hardness reveals that there is a more compact structure in poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:40) copolymer sample after isomerization. However, the increasing of Young’s modulus and hardness is not significant neither in poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:150) nor in poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:25) samples. And both the Young’s modulus and hardness are still of the highest value in the poly-{[Ru\textsuperscript{II}(bpy)\textsubscript{2}pySO-NB]/NB} (1:25) sample. It is proposed that the structure change of the polymer requires enough concentration of ruthenium sulfoxide complex to supply work in solid polymer films.
An understanding in the mechanism of the photomechanical effect was developed. The ruthenium sulfoxide complex molecules interact with the polymer backbone, and result in a supramolecular structure of polymer backbones folding around the ruthenium sulfoxide complex molecules in the copolymer films. Upon irradiation with 405nm light, the S→O isomerization occurs and there is structure change in the ruthenium sulfoxide complex molecules. And the peptide linkage between the sulfoxide and the norbornene efficiently amplifies the molecular volume change and backbone deformation following phototriggered isomerization of the sulfoxide, which causes a reorganization of the supramolecular structure when the concentration of the ruthenium sulfoxide complex is high enough. This reorganization results in a more compact structure in solid state. During the irradiation process, the light intensity is decreasing as the light going through the film, due to the absorption of the ruthenium sulfoxide complex. The ruthenium sulfoxide complex molecules are isomerized the most on the top surface layer, and the least on the bottom layer. The top layer achieves a more compact structure and of course a volume decreasing, while the bottom layer remains the same. In the end, the top layer performs work on the bottom layer to result in the film bending towards the light.

Future Consideration

There are two aspects under consideration for the future study. The first part is improving the photomechanical system to achieve a faster and stronger response; the second part is developing better understanding of the photomechanical effect for the ruthenium sulfoxide complexes.
The [Ru(bpy)$_2$pySO]$^{2+}$ has a quantum yield of approximately 0.12 in propylene carbonate solution, which is lower than azobenzene and diarylethene complexes. If we can use a complex which has similar structure but much higher quantum yield, like [Ru(bpy)$_2$pyEtSO]$^{2+}$, the response time could be shorter. We selected polynorbornene as polymer backbone for the current photomechanical system, because that polynorbornene has low Tg to allow relative easy deformation. There are many other polymers exhibiting low Tg and little absorption at above 370 nm, like polycyclooctane, which are potential candidates for the photomechanical systems. Besides modification of the materials, it is possible to achieve a better photomechanical response by optimizing the thickness corresponded to the concentration of the ruthenium sulfoxide in the film.

Though we can well explain the photomechanical effect with a bilayer model, there are still some details missing. First, the photoisomerization of the ruthenium sulfoxide complexes results in a more compact polymer structure, this is revealed by the nanoindentation study. It is proposed that the polymer backbone is folding around the ruthenium sulfoxide molecules and achieving a lowest energy state. After photoisomerization, the structure change of the ruthenium sulfoxide molecules requires the polymer backbone reorganizing to achieve another lowest energy state, which has less volume in the solid state. This hypothesis may be verified by a theoretical stimulation. Second, there is a huge gap between the inertial time and the motion time scale. The inertial time for poly-{$\{[\text{Ru}^{II}(\text{bpy})_{2}\text{pySO-NB}]_{\text{NB}}\}$} (1:40) is $2.8 \times 10^{-9}$ second, but the motion time scale is approximately 1 second. It is important to know the actual isomerization rate in the polymer films, which may fill the gap between the inertial time
and the motion time scale. It is possible to study the kinetics of the photoisomerization by TA spectroscopy in a homogenous solid film.
REFERENCES


APPENDIX A: THE NANOINDENTATION FITTING RESULTS

*Table A.1.* The nanoindentation fitting result for poly-NB polymer film

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No.1-7 are results before irradiated by 405nm laser light, No.8-14 are results after irradiated with 405nm laser light.
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No.1-8 are results before irradiated by 405nm laser light, No.9-16 are results after irradiated with 405nm laser light.
Table A.5. The nanoindentation fitting result for poly-\{[\text{Ru}^{II}(bpy)_2pyS-NB]/NB\} (1:40) copolymer film

<table>
<thead>
<tr>
<th>No</th>
<th>Ec (MPa)</th>
<th>Stiffness (N/m)</th>
<th>Hardness (MPa)</th>
<th>Adhesion Force (nN)</th>
<th>M</th>
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Table A.5: continued

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<th>Hardness (MPa)</th>
<th>Adhesion Force(nN)</th>
<th>M</th>
</tr>
</thead>
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No.1-10 are results before irradiated by 405nm laser light, No.11-20 are results after irradiated by 405nm laser light.