

## MASTER'S THESIS

### Synthesis and characterization of novel polymers: copolymers of Poly(phenyl vinyl sulfoxide) and Poly(amide sulfonamide)s

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**Synthesis and Characterization of Novel Polymers :  
Copolymers of Poly(phenyl vinyl sulfoxide)  
and  
Poly(amide sulfonamide)s**

**LAM Tsang Sing**

**A thesis submitted in partial fulfillment of the requirements**

**for the degree of**

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## Abstracts

### Synthesis and Characterization of Novel Polymers : Copolymers of Poly(phenyl vinyl sulfoxide) and Poly(amide sulfonamide)s

#### Part A : Synthesis, Characterization and Elimination Kinetics of Poly(phenyl vinyl sulfoxide) Copolymers

The uniqueness of the poly(phenyl vinyl sulfoxide) (PVSO) precursor method is that the polymers can undergo pyrolytic  $\beta$ -elimination of PhSOH molecules to give polyacetylenes. The infrared and Raman spectra showed that *trans*-polyenes were the major products, in which the reaction followed a concerted intramolecular  $E_2$  stereospecific *syn*-elimination mechanism. Because of the 'living' nature of anionic polymerization, two PVSO homopolymers and seventeen styrenic diblock copolymers were synthesized in this study. The polymers were characterized by gel permeation chromatography (GPC), infrared spectroscopy (IR), thermogravimetric analysis (TGA) and  $^1\text{H-NMR}$  spectroscopy. Partially oxidized PVSO random copolymers were prepared using either *m*-chloroperoxybenzoic acid (*m*CPBA) or hydrogen peroxide as oxidizing agent. The kinetics for the thermal elimination reactions of PVSO that led to polyenes were measured and correlated with their conjugation lengths using a UV-visible (UV-vis) spectroscopy. The measurement was carried out at constant temperatures between 65°C and 80°C, either in solid thin film or solution forms. The difference in the two set of samples was attributed to the diffusion of the elimination products from the bulk sample in film elimination; whereas in solution elimination, they were trapped in the solution and contributed to the degradation of polyenes. It

was found that the maximum molar percentage for the polyene block of the diblock copolymer to be soluble was around 33%.

The absorption spectra of the thermolyzed PVSO films and copolymer solutions, showed an overall absorption envelope interpolated with well-defined finger-like submaxima. The wavelengths of these polyene absorption submaxima remained constant irrespective to the elimination temperatures or the solubilizing blocks. The kinetic analysis showed that the thermal elimination of PVSO could be considered as a concerted non-radical chain reaction, characterized by three steps : a zero-order initiation step, followed by a first-order propagation step, and ended with a complex degradation step. The propagation rate constants  $k_p$  were shown to be independent of conjugation lengths and the extent of elimination. In the solution elimination study, the averaged activation energy for the initiation step is found to be slightly higher than that of the propagation. In other words, once the initiation step has been started, the elimination reaction will be propagated thermodynamically more favourable along the polymer chains, resulting in sequences of conjugated double bonds called polyenes.

The occurrence of secondary reactions, the presence of defects, dissolved oxygen and trapped eliminated products prevent the growth of polyene sequences to their maximum lengths. As a result, the maximum average conjugation length was 10 repeating units, corresponding to an overall absorption envelope maximum at  $\lambda_{\max} = 456.4$  nm, which was much shorter than that of Shirakawa's *trans*-polyacetylene ( $\lambda_{\max} = 700$  nm). Therefore, precursor methods can only produce shorter polyenes in analogue to polyacetylene synthesized by direct polymerization of acetylene.

**Part B :        Synthesis, Characterization and Membrane Applications of  
Poly(amide sulfonamide)s**

Stimulated by the outstanding properties of poly(amide sulfonamide)s (PASAs), which have been shown to be viable materials for reverse osmosis and pervaporation applications, two series of copolymers were synthesized in our laboratory by low temperature solution polycondensation of either the diamino monomer *N,N'*-bis(4-aminophenylsulfonyl)piperazine **3A** or *N,N'*-bis(4-aminophenylsulfonyl)-2,5-dimethylpiperazine **3B** with a mixture of terephthaloyl and isophthaloyl chloride. All of these copolymers were well characterized, and the microstructure of these copolymers was accurately elucidated in the <sup>13</sup>C-NMR study.

The effects of various feed ratios of isophthaloyl / terephthaloyl chloride on the physical properties of the copolymers were investigated. Previous pervaporation experiments on aqueous ethanol found that water permselective membranes prepared from the homopolymers of **3A** or **3B** with isophthaloyl chloride exhibited separation factors ranging from 40 to 57, but permeation flux was all below 35 g·m<sup>-2</sup>·h<sup>-1</sup>. In this part of thesis, the crystallinity of PASA copolymers was found to be trimmed down by copolymerizing diamino monomer **3A** or **3B** with increasing fraction of isophthaloyl chloride, and the expected decrease in crystallinity was verified by WAXD study.

It was envisioned that when the crystallinity of the PASA membranes decreased, permeation flux would be preferably increased at a minimum sacrifice of separation characteristics. However, experimental findings revealed that the resulting permeation flux and separation factor of pervaporation membranes derived

from various copolymers were both within the same order of magnitude. Hence, crystallinity was proved to be a secondary factor in determining the pervaporation performance of PASA membranes. To fully explore these new materials in membrane applications, one of the copolymers was selected for ultrafiltration (UF) experiments. When compared with some commercial membrane materials, the UF characteristics of PASAs were quite promising, indicating that this class of material certainly possesses the potential for further investigation.

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**Part A : Synthesis, Characterization and Elimination Kinetics of Poly(phenyl vinyl sulfoxide) Copolymers**

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