

**SYNTHESIS, CHARACTERIZATION AND APPLICATION OF ZIRCONIA-  
MODIFIED POLY(STYRENE-DIVINYLBENZENE) ADSORBENTS**

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**UNIVERSITI TEKNOLOGI MALAYSIA**

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF ZIRCONIA-  
MODIFIED POLY(STYRENE-DIVINYLBENZENE) ADSORBENTS

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*Dedication to my beloved father, mother, family,  
my fiancé and friends...*

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## ABSTRACT

Poly(styrene-divinyl benzene) (PS-DVB) resin is an attractive adsorbent for extraction and separation of various types of compounds due to its stability over the pH range of 1-14. However, PS-DVB resin is known to have hydrophobic surfaces that highly retain non-polar compounds while poorly retain polar compounds. To improve its use in the separation or extraction of polar compounds, PS-DVB resin must be chemically or physically bonded to hydrophilic groups to reduce its hydrophobic surface. This study explores the development of PS-DVB resins modified with acetyl chloride, chloroacetone and zirconyl chloride. The PS-DVB resin adsorbent was prepared by suspension polymerization method with polyvinyl alcohol as the suspension stabilizer at a stirring speed of 1000 rpm for 20 h. Modifications of the PS-DVB adsorbent were carried out via Friedel Crafts acylation reaction with acetyl chloride and chloroacetone using Lewis acid catalyst, Grignard reaction of the product with methyl magnesium chloride and reaction of the product with zirconium(IV) oxide chloride octahydrate. The products obtained were characterized using infrared spectroscopy, scanning electron microscopy, nitrogen adsorption analysis and thermal gravimetric analysis. The performance of the PS-DVB-based phases was evaluated by investigating its adsorption-desorption efficiency in solid phase extraction. Comparative recovery studies showed that the *p*-ethanoyl-PS-DVB and *p*-2-propanoyl-PS-DVB resins were superior compared to unmodified PS-DVB and zirconia-modified PS-DVB for solid phase extraction of the test compounds 2-chlorophenol, nitrobenzene and propiophenone.

## ABSTRAK

Poli(stirena-divinil benzena)(PS-DVB) adalah bahan penjerap yang menarik bagi kegunaan pengekstrakan dan pemisahan pelbagai jenis sebatian disebabkan PS-DVB mempunyai kestabilan pada skala pH 1-14. Walau bagaimanapun, PS-DVB mempunyai permukaan hidrofobik yang mampu menahan sebatian tidak berkutub dengan baik tetapi tidak terhadap sebatian berkutub. Untuk mempertingkatkan penggunaannya dalam pemisahan atau pengekstrakan sebatian berkutub, PS-DVB mestilah mempunyai ikatan kimia atau fizik dengan kumpulan yang dapat mengurangkan sifat hidrofobik PS-DVB. Dalam penyelidikan ini, kaedah pengubahsuaian fasa pegun PS-DVB dengan menggunakan reagen asetil klorida, kloroaseton dan zirkonil klorida telah dibangunkan. Fasa pegun PS-DVB telah disediakan melalui kaedah pempolimeran ampaiian menggunakan polivinil alkohol sebagai bahan penstabil pada kadar adukkan 1000 rpm selama 20 jam. Pengubahsuaian kimia terhadap bahan penjerap PS-DVB telah dijalankan melalui tindak balas pengakilan Friedel Crafts dengan asetil klorida dan kloroaseton menggunakan mangkin asid Lewis, tindak balas Grignard hasilnya dengan metil magnesium klorida dan tindak balas hasilnya dengan zirkonia(IV) oksida oktahidrat. Bahan penjerap yang dihasilkan dicirikan dengan menggunakan spektroskopi infra merah, mikroskopi imbasan elektron, analisis penjerapan nitrogen dan analisis gravimetri terma. Prestasi bagi fasa pegun berasaskan PS-DVB itu telah dinilai dalam kajian penjerapan-penyahjerapan melalui teknik pengekstrakan fasa pepejal. Perbandingan nilai perolehan semula analit menggunakan metanol sebagai pengelusi menunjukkan bahawa etanoil-PS-DVB dan 2-pentanoil-PS-DVB memberikan nilai perolehan semula yang tinggi berbanding fasa pegun PS-DVB tulen dan PS-DVB terubahsuai zirkonia.

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## LIST OF SYMBOL

$A_s$	-	Internal standard peak area
$A_x$	-	Test compound peak area
BPO	-	Benzoyl Peroxide
DVB	-	Divinyl benzene
$F_s$	-	Internal standard response factor
FTIR	-	Fourier Transform Infrared
$F_x$	-	Test compound response factor
GC-FID	-	Gas Chromatography-Flame Ionization Detector
h	-	Hour
IS	-	Internal standard
KBr	-	Potassium bromide
$M_s$	-	Internal standard concentration (ppm)
$M_x$	-	Test compound concentration (ppm)
$P/P_o$		Relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure $P_o$ of the adsorbate at the temperature where the isotherm is measured
ppm	-	Parts per million
PS-DVB	-	Poly(styrene-divinyl benzene)
R.S.D.	-	Relative standard deviation
SPE	-	Solid Phase Extraction
$t_R$	-	Retention time
% R	-	Percentage of recovery
$\lambda$	-	Wavelength

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Adsorbents and Chromatography Stationary Phases**

The material on the surface of which adsorption takes place is called the adsorbent and the substance adsorbed is called the adsorbate (Gurdeep, 1974). The common surface separating the two phases, where the adsorbed molecules concentrate is referred to as the interface. The larger the surface area of the adsorbent, the more is the adsorption. Some examples of the adsorbents are charcoal, silica gel, metals, polymers and etc. The term adsorption appears to have been introduced by Kayser in 1881 to connote the condensation of gases on free surfaces, in contradistinction to gaseous absorption where the molecules of gas penetrate into the mass of the absorbing solid. Adsorption (strictly, physical adsorption) has now been internationally defined as the enrichment (i.e. positive adsorption or simply adsorption) or depletion (i.e. negative adsorption) of one or more components in an interfacial layer (Gregg and Sing, 1982).

The various forms of chromatography are classified according to the nature of the mobile and stationary phases. The mobile phase may be gaseous or liquid, while the stationary phase may be solid or liquid. For example, in gas liquid chromatography (GLC), the liquid stationary phase is dispersed on an inert solid

support. The liquid phase is held on the surface and in the pores of the support, while the mobile gas phase flows through the spaces between particles (Conder and Young, 1979).

The choice of adsorbents as the proper stationary phase is one of the most important decisions in column chromatography. The use of adsorbents of porous polymers and inorganic salt, either porous or non-porous and modified oxides, as well as surfaces of dense monomolecular polymer layers absorbed on the sufficiently developed and homogenous surface of non-porous and wide-porous adsorbent, opens extensive possibilities for selecting and controlling the nature of the adsorbent surfaces and, therefore, for controlling the selectivity of gas adsorption columns (Baiulescu and Ilie, 1975). In the last two decades, separation sciences have faced important developments. Starting with solid-phase extraction (SPE) in the 1980s, other new techniques, e.g., supercritical fluid extraction (SFE), supercritical fluid chromatography (SFC) and capillary electrochromatography (CEC) have been introduced (Liu and Pietrzyk, 2001). Besides these new analytical tools, “classical” separation techniques such as high performance liquid chromatography (HPLC) have been further developed and optimized. New inputs from synthetic chemistry and more efficient analytical tools for their characterization significantly enhanced the quality of liquid chromatography (LC) supports in terms of stability, reproducibility, selectivity and efficiency (Buchmeiser, 2001).

## 1.2 Research Background

The preparation of alternative stationary phase supports in chromatographic science is an important area that aims to develop new support materials that offer novel selectivities or overcome the shortcomings of silica supports (Shalliker *et al.*, 1997). The ideal chromatography support particle should have a high surface area on which a wide variety of chemical moieties can be irreversibly and inalterably deposited to provide useful selectivity for a number of separation problems. It should

be physically and chemically stable over a wide range of pressure, pH, temperature and solvent conditions. It should be available in a variety of particle diameters as well as pore sizes and volumes (Nawrocki *et al.*, 1993).

Microparticulate, macroporous, poly(styrene-divinyl benzene) (PS-DVB) copolymeric reversed-phase adsorbent have been used very successfully as stationary phases in HPLC (Liu and Pietrzyk, 2001). Organic beaded polymer supports based on polystyrene are almost exclusively prepared by emulsion, suspension, dispersion and precipitation polymerization techniques (Buchmeiser, 2001). However, PS-DVB resins are known to have hydrophobic surfaces that highly retain non-polar compounds while poorly retain polar compounds.

Although silica and modified silicas are the most widely used and most useful chromatographic supports, it is well known that silica and bonded silicas are not stable outside the range of pH 2 to approximately 8 (Wehrli *et al.*, 1978). Above pH 8, silica is subjected to attack by alkali and it dissolves. Below approximately pH 2, the siloxane linkages which hold bonded phases to silica are subjected to hydrolytic attack and are slowly removed from the surface (Glajeh *et al.*, 1987). The dissolution of silica and removal of bonded phase is accelerated at high temperature and leads to changes in retention, selectivity and peak shape, loss of column bed integrity, and contamination of product in preparative chromatography. The typical commercial alkyl silane bonded silica phase is seldom used at more than 20-30°C higher than room temperature because of its instability at high temperature (McNeff *et al.*, 2000).

Another interesting development is in the synthesis and application of zirconia stationary phases. The surface area of zirconia is low when compared to the silica supports typically used as chromatographic supports. However, it is important to recognize when considering the surface area data that true density of monoclinic zirconia is approximately 5.8 gmL<sup>-1</sup> whereas the density of commercial silica is 2.3 gmL<sup>-1</sup>. Cubic zirconia is reported to have the highest density 6.27 gmL<sup>-1</sup> (Nawrocki *et al.*, 1993). Due to its higher density, the surface area of zirconia is comparable to that of silica in terms of surface area per unit volume.

### 1.3 Statement of Hypothesis

PS-DVB resins have a hydrophobic surface. To extend its applicability in extraction or chromatographic performance, the PS-DVB resins should have a chemical bonding or hydrophilic groups to decrease and mask its hydrophobic surface. Chemical modification on the PS-DVB resins can be carried out by the Friedel Craft acylation reaction and Grignard reaction. Zirconia can be then introduced onto the PS-DVB resin. Zirconia-modified PS-DVB resin is expected to have lower hydrophobic surface and more stable compared with unmodified PS-DVB resin.

### 1.4 Research Aim

The aim of this study is to synthesize new adsorbents based on PS-DVB resins and study the performance of the adsorbents by physiochemical methods.

### 1.5 Research Objectives

- i. To synthesize PS-DVB adsorbent using the suspension polymerization method.
- ii. To modified PS-DVB adsorbents using three steps or reactions:
  - (a) Friedel Crafts acylation reaction of PS-DVB with acetyl chloride and chloroacetone using Lewis acid catalyst;
  - (b) Grignard reaction of the product (a) with methyl magnesium chloride;and

- (c) reaction of the product (b) with zirconium(IV) oxide chloride octahydrate.
- iii. To characterize and study the performance of the new adsorbents by physiochemical methods.

## **1.6 Scope of Study**

A complete reaction scheme is given in Figure 1.1. In this research, PS-DVB resins were synthesized using the suspension polymerization method. Optimization of the suspension polymerization method was carried out by studying the effect of reaction time, effect of stabilizer and effect of seeding polymerization. The physical properties of the PS-DVB resins were studied by fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetry analysis, and nitrogen adsorption analysis. Batch of PS-DVB resins which exhibit the most suitable adsorbent properties such as high surface area, minimum pore size was chosen to be modified. Comparison of the physical properties of both native and modified PS-DVB phases was carried out and the performance of the modified PS-DVB phases was evaluated by investigating its adsorption-desorption efficiency in solid phase extraction.

## a) Preparation of PS-DVB resin

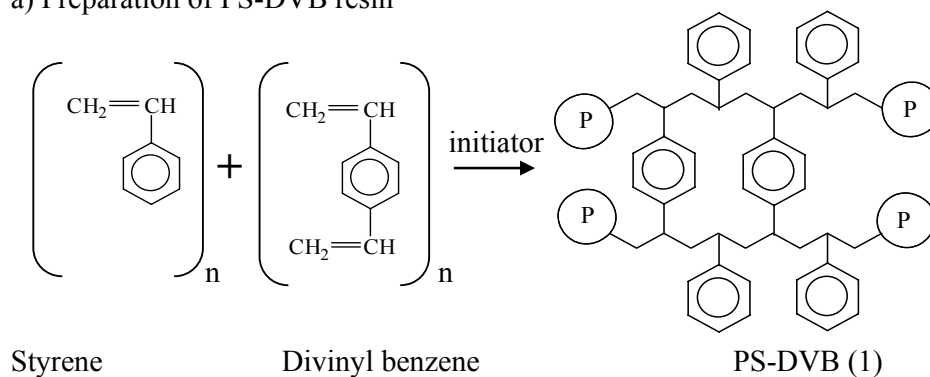
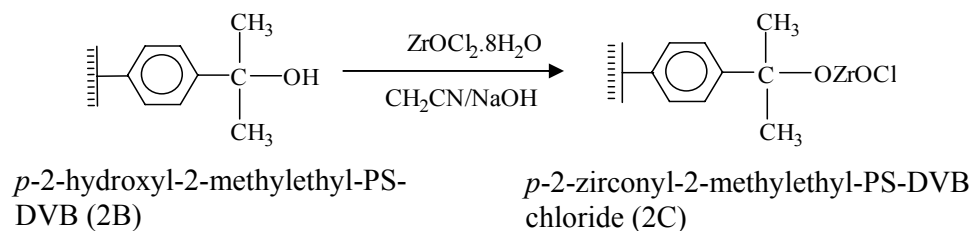
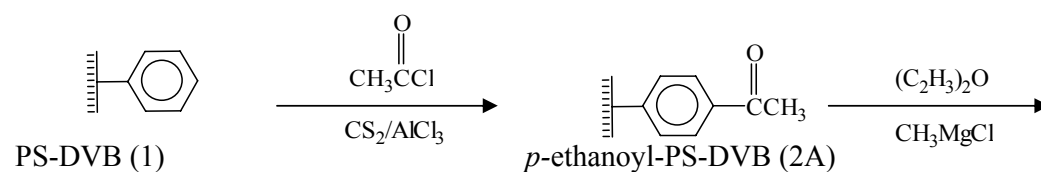
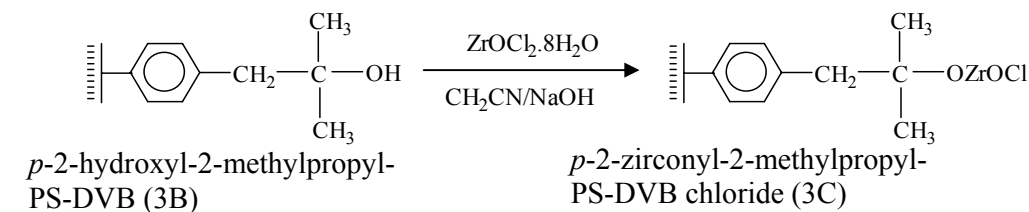
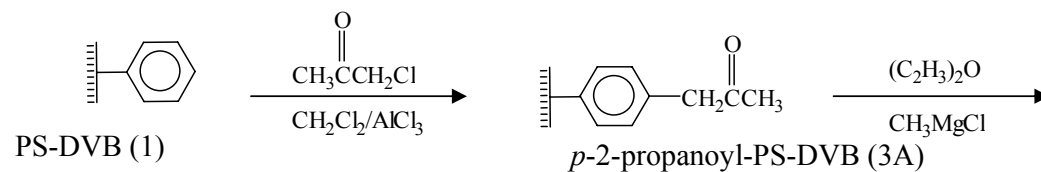
b) Preparation of *p*-2-zirconyl-2-methylethyl-PS-DVB chloride (2C)c) Preparation of *p*-2-zirconyl-2-methylpropyl-PS-DVB chloride

Figure 1.1 A complete reaction scheme



## **1.7 Outline of the Thesis**

This thesis consists of six chapters. Chapter 1 presents general background of this study, research aim, research objectives and scope. Chapter 2 compiles the literature reviews and theoretical background on PS-DVB and Zirconia, modification of PS-DVB and its application as an adsorbent for solid phase extraction (SPE). The procedures for characterization and application of the synthesized materials are presented in Chapter 3. Chapter 4 reports the results and discusses the preparation of PS-DVB, and modification of PS-DVB. It also describes the characterization and application of unmodified and modified PS-DVB as adsorbents in the solid phase extraction analysis. The concluding Chapter 5 summarizes this thesis by presenting the overall conclusions and suggestions for future study.

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