



**UNIVERSITI PUTRA MALAYSIA**

***PREPARATION, CHARACTERIZATION AND REACTIVITY RATIOS OF  
COPOLYMERS 3-(TRIMETHOXYSILYL)PROPYLEMETHACRYLATE  
AND TRIS (METHOXYETHOXY) VINYLSILANE WITH  
N-VINYLPYRROLIDONE AND ACRYLAMIDE***

**AMEEN HADI MOHAMMED**

**FS 2017 9**



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By

**AMEEN HADI MOHAMMED**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

**March 2017**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

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**March 2017**

**Chairman : Professor Mansor Hj. Ahmad, PhD**  
**Faculty : Science**

The incorporation of two different monomers, having different physical and/or chemical properties, in the same polymer molecule in varying proportions leads to the formation of new materials with great scientific and commercial importance. The basic requirements for polymeric materials in some areas of medical applications are that they are hydrophilic, soft and oxygen-permeable. The aims of this work are to prepare and characterize four series of copolymers at low conversion, to determine the reactivity relationships of these copolymers, and to prepared and study properties of hydrogels that can be of some interest for medical purposes.

Vinylsilane monomers (3-(trimethoxysilyl)propyl methacrylate (TMSPM) and tris (methoxyethoxy)vinyl silane (TMEVS)), N-vinyl pyrrolidone (NVP) and acrylamide (AM), were used to prepare the copolymers. TMSPM-co-NVP, TMEVS-co-NVP, TMSPM-co-AM and TMEVS-co-AM with different compositions were synthesized by free radical polymerization at low conversion using benzoyl peroxide (BPO) as initiator. The copolymers were characterized by Fourier Transform Infrared (FTIR) and Proton Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ), and their compositions were determined by elemental analysis. The monomer reactivity ratios were calculated by linearization methods proposed by Fineman-Ross and Kelen-Tudos, the intersection method proposed by Mayo-Lewis, and nonlinear method proposed by curve fitting procedure. The derived reactivity ratios ( $r_1, r_2$ ) for TMSPM-co-NVP, TMEVS-co-NVP, TMSPM-co-AM and TMEVS-co-AM were: (3.722, 0.097), (0.504, 0.328), (1.872, 0.801) and (0.240, 1.242), respectively. The microstructure of copolymers and sequence distribution of monomers in the copolymers were calculated by statistical method based on the average reactivity ratios and found that results are in agreement with ( $r_1, r_2$ ) values. No study has been reported on the copolymerization and reactivity relationships of hydrophobic monomers (TMSPM, TMEVS) with hydrophilic monomers (NVP, AM).

Four series of TMSPM-co-NVP xerogels were prepared by bulk polymerization to ~100% conversion using BPO as initiator: (i) TMSPM/NVP copolymers covering a wide range of composition (10-90% NVP), (ii) TMSPM/NVP copolymers covering a wide range of composition (10-90% NVP), but all comprising a fixed content (1% w/w) of ethylene glycol dimethacrylate (EGDMA) as cross-linking agent, (iii) TMSPM30/NVP70 copolymers containing different concentrations (0-2%) of EGDMA, and (iv) TMSPM10/NVP90 copolymers containing different concentrations (0-4%) of EGDMA. The occurrence of translucency or opacity in some of the xerogels suggests the existence of more than one species, i.e. at least two polymers, which are immiscible. The transparency of xerogels and hydrogels could be enhanced by varying the concentration of EGDMA. The absence of EGDMA allows an easy diffusion of water molecules to the gel phase. The influence of the comonomer composition on equilibrium water content (EWC), weight loss, volumetric fraction of water ( $\phi_1$ ) and linear expansion (ER) to hydration on the resultant hydrogels were investigated. All degree of swelling (with and without EGDMA) increased as the amounts of NVP in feed composition increased, this can be attributed to the hydrophilicity of NVP.

More detailed investigations on effect of EGDMA on the properties of TMSPM30/NVP70 and TMSPM10/NVP90 were conducted. The swelling capacity and swelling parameters significantly decreased with increasing crosslinker content, due to the restrained mobility of the macromolecular chains. The mechanical properties of TMSPM30/NVP70 with (0-2%) EGDMA and TMSPM10/NVP90 with (0-4%) EGDMA xerogels were investigated using stress-strain test. Thermal analysis revealed that with an increase in EGDMA content, the glass transition temperature ( $T_g$ ) increased, and weight loss decreased due to the restriction of the segmental mobility of the polymer chains. Oxygen permeability of hydrogels increases as TMSPM and water content increase. In conclusion, the reactivity ratios for four new copolymers; TMSPM-co-NVP, TMEVS-co-NVP, TMSPM-co-AM and TMEVS-co-AM have been determined. These copolymers possess new properties with potential use in different medical applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

**PENYEDIAAN, PENCIRIAN DAN NISBAH KEREAKTIFAN KOPOLIMER  
3-(TRIMETOKSISILIL)PROPILMETAKRILAT DAN  
TRIS(METOKSIETOKSI)VINILSILANA DENGAN N-VINILPIROLIDON  
DAN AKRILAMIDA**

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Penggabungan dua monomer berlainan dengan ciri fizikal dan/atau kimia yang berbeza, dalam molekul polimer yang sama dalam perkadaran yang berbeza membawa kepada pembentukan bahan baru dengan kepentingan sains dan komersial yang besar. Keperluan asas untuk bahan polimer dalam beberapa aplikasi perubatan adalah hidrofilik, lembut dan oksigen telap. Tujuan projek ini adalah untuk menyediakan dan mencirikan empat siri kopolimer pada penukaran yang rendah, menentukan hubungan kereaktifan kopolimer, untuk menyediakan dan mengkaji sifat hidrogel yang boleh digunakan bagi tujuan perubatan.

Monomer vinilsilana (3-(trimetoksisilil)propil metakrilat (TMSPM) dan tris(metoksietoksi)vinil silana (TMEVS)), N-vinil pirolidon (NVP) dan akrilamida (AM) telah digunakan dalam penyediaan kopolimer. TMSPM-co-NVP, TMEVS-co-NVP, TMSPM-co-AM dan TMEVS-co-AM dengan komposisi yang berbeza disediakan melalui pempolimeran radikal bebas pada penukaran yang rendah menggunakan benzoil peroksida (BPO) sebagai pemula. Kopolimer telah dicirikan menggunakan spektroskopi infra-merah Fourier (FTIR) dan spektroskopi resonans magnet nuklear proton ( $^1\text{H-NMR}$ ) dan komposisi mereka ditentukan melalui analisis unsur. Nisbah kereaktifan monomer telah dihitung dengan kaedah linear yang dicadangkan oleh Fineman-Ross dan Kelen-Tudos, kaedah persilangan yang dicadangkan oleh Mayo-Lewis dan kaedah tak linear dicadangkan melalui prosedur penyuaian lengkung. Nisbah kereaktifan ( $r_1$ ,  $r_2$ ) yang diperolehi bagi TMSPM-co-NVP, TMEVS-co-NVP, TMSPM-co-AM dan TMEVS-co-AM adalah masing-masing (3.722, 0.097), (0.504, 0.328), (1.872, 0.801) dan (0.240, 1.242). Struktur mikro kopolimer dan taburan urutan monomer dalam kopolimer dihitung dengan kaedah statistik berdasarkan nisbah kereaktifan purata dan mendapati bahawa keputusan adalah selari dengan nilai ( $r_1$ ,  $r_2$ ). Tiada kajian telah dilaporkan tentang pengkopolimeran dan hubungan kereaktifan monomer hidrofobik (TMSPM, TMEVS) dengan monomer hidrofilik (NVP, AM).

Empat siri kopolimer TMSPM-co-NVP disediakan melalui kaedah pempolimeran pukal untuk  $\sim 100\%$  penukaran menggunakan BPO sebagai pemula: (i) kopolimer TMSPM/NVP meliputi pelbagai komposisi (10-90% NVP), (ii) kopolimer TMSPM/NVP meliputi pelbagai komposisi yang luas (10-90% NVP), tetapi dengan kandungan tetap etilena glikol dimetakrilat (EGDMA) (1% w/w) sebagai ejen penyilang, (iii) kopolimer TMSPM30/NVP70 dengan kandungan kepekatan EGDMA yang berbeza (0-2%) dan (iv) kopolimer TMSPM10/NVP90 dengan kandungan kepekatan EGDMA yang berbeza (0-4%). Kejadian lut cahaya atau kelegapan dalam beberapa xerogels menunjukkan kewujudan lebih daripada satu spesies, iaitu sekurang-kurangnya dua polimer, yang tak boleh campur. Ketelusan xerogel dan hidrogel boleh dipertingkatkan dengan mengubah kepekatan EGDMA. Ketiadaan EGDMA membolehkan satu penyebaran yang mudah dari molekul air ke fasa gel. Pengaruh komposisi komonomer pada kandungan air keseimbangan (EWC), penurunan berat, pecahan isipadu air ( $\phi_1$ ) dan pengembangan linear (ER) untuk penghidratan pada hidrogel yang terhasil telah disiasat. Semua parameter pengembangan (dengan dan tanpa EGDMA) telah meningkat apabila jumlah NVP dalam komposisi bahan tindak balas meningkat, ini boleh dikaitkan dengan sifat hidrofilik NVP.

Kajian yang lebih terperinci mengenai kesan EGDMA ke atas sifat TMSPM30/NVP70 dan TMSPM10/NVP90 telah dijalankan. Kapasiti pengembangan dan parameter pengembangan menurun dengan ketara dengan peningkatan kandungan ejen penyilang, kerana mobiliti rantai makromolekul yang terhalang. Sifat mekanik xerogel TMSPM30/NVP70 dengan (0 - 2%) EGDMA dan TMSPM10/NVP90 dengan (0 - 4%) EGDMA disiasat menggunakan ujian tegasan-terikan. Analisis terma mendedahkan bahawa dengan peningkatan dalam kandungan EGDMA, suhu peralihan kaca ( $T_g$ ) meningkat, dan kehilangan berat menurun disebabkan sekatan mobiliti segmen daripada rantaian polimer. Kebolehtelapan oksigen hidrogel bertambah apabila TMSPM dan kandungan air meningkat. Kesimpulannya, nisbah kereaktifan untuk empat kopolimer baru; TMSPM-co-VP, TMEVS-co-VP, TMSPM-co-AM dan TMEVS-co-AM telah ditentukan. Kopolimer tersebut mempunyai ciri baharu yang berpotensi digunakan dalam aplikasi perubatan yang berbeza.

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I certify that a Thesis Examination Committee has met on 7 March 2017 to conduct the final examination of Ameen Hadi Mohammed on his thesis entitled "Preparation, Characterization and Reactivity Ratios of Copolymers 3-(Trimethoxysilyl) Propylmethacrylate and Tris (Methoxyethoxy)Vinylsilane with N-Vinylpyrrolidone and Acrylamide" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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## LIST OF ABBREVIATIONS

A	The hydrogel effective area
AM	Acrylamide
BPO	Benzoyl peroxide
b	Thickness of the disc
$C_p$	Specific polymer content in a hydrogel
$C_w$	Specific water content in a hydrogel
C	Concentration
DSC	Differential scanning calorimetry
d	The diameter of fully hydrated disc
$d_0$	The diameter of dried disc
$d[M_1]$	Concentration of monomer $M_1$ in a copolymer
$d[M_2]$	Concentration of monomer $M_2$ in a copolymer
E	Young's modulus
EGDMA	Ethylene glycol dimethacrylate
ER	Extension ratio
ESC	Equilibrium saline content
ETC	Equilibrium toluene content
EWC	Equilibrium water content
FTIR	Fourier transform infrared spectroscopy
F	Ratio of mole fraction of $M_1$ to $M_2$ in copolymer
$F_1$	The mole fraction of monomer-1 in the copolymer
$F_2$	The mole fraction of monomer-2 in the copolymer
f	Ratio of mole fraction of $M_1$ to $M_2$ in feed
$f_1$	The mole fraction of monomer-1 in the feed

$f_2$	The mole fraction of monomer-2 in the feed
G	Shear modulus
HEMA	Hydroxy ethylmethacrylate
$^1\text{H-NMR}$	Proton nuclear magnetic resonance
I	Initiator
$K_{(11, 12, 21, 22)}$	Rate constant in propagation state in copolymerization
L	Hydrogel thickness
M	Monomer
$[M_1]$	Concentration of monomer $M_1$ in feed
$[M_2]$	Concentration of monomer $M_2$ in feed
$M_c$	Average molecular weight between consecutive crosslinks
NVP	N-Vinyl Pyrrolidone
N%	Percent Nitrogen in a sample (polymer)
P	Permeability
$\Delta P$	Pressure through the sample
PVA	Poly vinyl alcohol
$P_{11}$	Probability of finding monomer1 to be followed by monomer1
$P_{12}$	Probability of finding monomer1 to be followed by monomer2
$P_{21}$	Probability of finding monomer2 to be followed by monomer1
$P_{22}$	Probability of finding monomer2 to be followed by monomer2
Q	Gas flow
q	Swelling ratio
R	Molar gas constant

$r_1$	Reactivity ratio of monomer-1
$r_2$	Reactivity ratio of monomer-2
$S_{1-1}$	Mole fraction of monomer1 – monomer1 in the copolymer
$S_{1-2}$	Mole fraction of monomer1 – monomer2 in the copolymer
$S_{2-2}$	Mole fraction of monomer2 – monomer2 in the copolymer
$T$	Temperature
TGA	Thermogravimetric analysis
TMEVS	Tris (methoxyethoxy) vinyl silane
TMSPM	3-(trimethoxysilyl) propyl methacrylate
$T_g$	Glass transition temperature
$t$	Time
$V_1$	The molar volume of water
$W_0$	Weight of the disc before swelling
$W_d$	Weight of the disc after drying
$W_s$	Weight of the swollen disc after 30 days
$W_t$	Weight of the swollen disc at time $t$
$v_e$	Effective cross-linking densities of hydrogel
$v_t$	Theoretical cross-linking densities of hydrogel
$\rho$	The density of xerogel
$\Phi_1$	The volume fraction of solvent within the hydrogel or organogel at swelling equilibrium
$\Phi_2$	The volume fraction of polymer within the hydrogel at swelling equilibrium
$\mu_1$	Number-average sequence length of monomer-1 in copolymer
$\mu_2$	Number-average sequence length of monomer-2 in copolymer

$\tau$	The force acting per unit cross-section area
$\lambda$	The deformation ratio, deformed length (I) / initial length (I <sub>0</sub> ) of hydrogel
$\chi$	The polymer-solvent interaction parameter at swelling equilibrium



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# CHAPTER 1

## INTRODUCTION

### 1.1 General Introduction

The properties of polymers can be most effectively modified with the help of the technique of copolymerization (Patel *et al.* 2009). This technique is designed to manipulate the intra- and inter-molecular forces that are exerted amongst similar and dissimilar polymer segments, engendering broad variation in properties like temperature of glass transition, melting point, solubility, permeability, dyeability, adhesion, elasticity and chemical reactivity. The basic explorations of structure property correlations and the variety of commercial and biological applications all attest to the fact that copolymerization is highly useful (Schacher *et al.* 2012; Schoonbrood *et al.* 1995). A copolymer composition equation relies greatly on reactivity ratios, which not only indicate the relative reactivity of pairs of monomers, but also outline the elements making up the copolymers. To understand how its utility has developed, it is first necessary to understand the copolymer composition itself. As emphasised above, the reactivity ratios are essential for copolymer composition and the manner in which it is distributed. The empirical data regarding copolymer composition and monomer feed mixtures must be mathematically processed before the monomer reactivity ratios can be determined. The reactivity of various comonomers can be calculated via a range of techniques. Furthermore, different analytical methods have been proposed to find out how much of a comonomer has been included in the copolymer (Parambil *et al.* 2012; Ashenagar *et al.* 2013; Patel *et al.* 2008).

New scientifically and commercially relevant materials can be obtained when two distinct monomers with various physical and or chemical attributes are incorporated in the same polymer molecule at different ratios. The monomer reactivity ratios of copolymerization enable the determination of the relative reactivity of a monomer toward a specific polymer radical.

Siloxane derivative compounds have been used in copolymers for biomedical applications. Copolymers of these compounds with MMA present interesting permeation properties and have been proposed as potential polymers for contact lens and biomedical applications. More specifically, it has been suggested that a higher permeability of oxygen can be achieved, although these are glassy materials, due to the considerable contribution of the (-Si-O-) bonds to the solubility of oxygen in the film (Zhao *et al.* 2014).

Poly-N-vinylpyrrolidone (PNVP) is of prime importance among other macromolecular compounds. A combination of practically valuable characteristics of PNVP: solubility in water and in most organic solvents, absence of toxicity, biological compatibility, immune inactivity and also clearly pronounced capability for complex

formation with a wide variety of inorganic and organic compounds and biological systems, allows the use of this compound as a disintoxicant agent for drugs, engineering, medicine, pharmacy and agriculture. Therefore, copolymers of N-vinylpyrrolidone (NVP) have a still wider set of valuable characteristics. The copolymerization reactions allow modification of PNVP characteristics and therefore acquire growing practical importance (Sapir *et al.* 2016). NVP was chosen to prepare hydrogels for biomedical applications because NVP in contrast of AM has little immunogenicity and antigenicity.

Acrylamide can be prepared by the hydrolysis of acrylonitrile by nitrile hydratase. In industry, most acrylamide is used to synthesize polyacrylamides, which find many uses as water-soluble thickeners. These include use in wastewater treatment, gel electrophoresis, papermaking, processing, tertiary oil recovery, and the manufacture of permanent press fabrics. Some acrylamide is used in the manufacture of dyes and the manufacture of other monomers. The discovery of acrylamide in some cooked starchy foods prompted concerns about the carcinogenicity of those foods.

PAM is a synthetic water-soluble polymer made from monomers of AM. In cross-linked form it is highly water-absorbent, forming a soft gel used in such application as PAM gel electrophoresis and in manufacturing soft contact lenses. Neamtu and Nita (2006) prepared gels by polymerization of AM cross-linked with N,N-methylene-Bis-acrylamide using redox initiation (potassium persulfate / ascorbic acid) system. In the straight-chain form, it is used as a thickener, it has been used as a subdermal for aesthetic surgery. It has also been used as flocculants in waste water treatment application as drug reduction agent and drilling fluid in enhanced oil recovery as additives in papermaking and as a drug-delivery agent.

## 1.2 Problem of Statement

Hydrophilicity, softness and oxygen permeability are the qualities that polymeric materials must fulfill to permit their use in certain medical application fields. The usefulness of a range of polymeric materials in applications related to medical fields (e.g. contact lenses) has already been demonstrated. However, despite their properties that make them suitable for different medical applications, polymeric materials also have features that constrict their use. For example, the Poly methylmethacrylate (PMMA) material employed in contact lenses lacks sufficient oxygen permeability and hydrophilicity, despite possessing the qualities of rigidity and durability (MacRae *et al.* 1994). On the other hand, the Poly hydroxyl ethylmethacrylate (PHEMA) material used in hydrogel contact lenses does possess hydrophilicity and softness, but it is not durable or dimensionally stable and lacks sufficient oxygen permeability (Opdahl *et al.* 2003). Similarly, another polymeric material popular in medical applications is silicone rubber, which displays softness, durability and high oxygen permeability, although it lacks hydrophilicity.

Hence, polymeric materials must meet all three requirements of being hydrophilic, soft and oxygen permeable in order to expand the medical applications and fields in

which they can be employed. The ideal contact lens material would incorporate the favourable properties of each of these materials, whilst not exhibiting their drawback, i.e. a copolymer of MMA, HEMA and silicon rubber may give the optimum properties for a contact lens (Findik, 2011). For other prosthetic devices, features such as increased hydrophobicity, softness after hydration and gas permeability are also very useful and desirable.

It is clear that the combination of a hydrophilic group with a siloxane group in the polymer may give a suitable biomedical material, and it may have the following properties:

- (a) Chemically stable compound.
- (b) Transparent.
- (c) A moderate elastic modulus.
- (d) Soft when hydrated with a good degree of swelling.
- (e) Oxygen permeable.

Based on what has been reported before, two types of monomers have been chosen to prepare xerogels for biomedical applications:

3-(Trimethoxysilyl)propyl methacrylate (TMSPM) was chosen as the hydrophobic component containing a siloxane group. PTMSPM has transparency, low wettability, a moderate elastic modulus and oxygen permeability. NVP was chosen as the hydrophilic component. The very high Glass transition temperature ( $T_g$ ) of its polymer makes it difficult to machine. Its high water content causes mechanical instability, but it is transparent and oxygen-permeable.

A copolymer of these two compounds, however, shows a range of incompatibility. This is interphase with a third component, viz. Ethylene glycol dimethacrylate (EGDMA) in addition to its basic function as a cross-linking agent.

### **1.3 Research Approach**

In these studies, hydrophobic monomers (TMSPM and TMEVS) and hydrophilic monomers (NVP and AM) were selected to prepare copolymers at low conversion. So far there has been no investigation on the preparation and study the reactivity ratios of these copolymers.

TMSPM and NVP monomers were chosen to prepare xerogels due to the low toxicity of NVP comparative with acrylamide monomer. The present study represents an attempt toward preparation hydrogels of TMSPM with NVP for biomedical applications. The primary interest is to study the effect of EGDMA as a crosslinking - agent on the properties of hydrogels.

The current study has been carried out in two directions. First, determination the reactivity relationship of copolymers at low conversion. Second, preparation and study the properties of hydrogel

#### 1.4 Objectives of Study

- 1- To prepare and characterize four series of copolymers at low conversion (TMEVS-co-NVP, TMEVS-co-AM, TMSPM-co-NVP and TMSPM-co-AM) by solution free radical copolymerization.
- 2- To estimate the monomer reactivity ratios by the application of linear and nonlinear mathematical methods, and the copolymer compositions by elemental analysis.
- 3- To determine the microstructure of copolymers and sequence distribution of monomers in the copolymers by statistical method based on the average reactivity ratios values.
- 4- To prepare four series of xerogels of TMSPM with NVP as a comonomer in the absence and presence of EGDMA as crosslinking agent, and to characterize and study the properties of xerogels and hydrogels: (optical clarity, swelling behavior, light transmittance, mechanical properties, thermal properties and oxygen permeability).



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