

**SYNTHESIS AND CHARACTERIZATION OF
BENZOYL KAPPA-CARRAGEENAN DOPED
SODIUM PERCHLORATE AS HIGHLY
CONDUCTIVE GEL POLYMER ELECTROLYTE**

NORSYABILA BINTI SHRGAWI

**MASTER OF SCIENCE
(CHEMISTRY)**

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MALAYSIA**

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Thesis submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional
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(Chemistry)

2023

ABSTRACT

Benzoyl kappa carrageenan (Bz- κ car) which is the derivative of κ -carrageenan (κ car) was successfully synthesized by chemical modification through Friedel-Craft acylation reaction. Bz- κ car is designed for use as a gel polymer electrolyte in a variety of electrochemical devices. κ -carrageenan is known for its high hydrophilicity due to the number of hydroxyl (OH) groups in its monomer units. In this case, κ car has strong interactions with water molecules, as the hydroxyl groups are capable of forming hydrogen bonds with polar water molecules. The presence of moisture in most of the electrochemical devices is not favorable. The interaction of moisture with air/moisture sensitive metal/parts in the devices might have caused an explosion and risked the surroundings. Therefore hydrophobic benzoyl chloride salt was used in the modification of κ car to produce Bz- κ car with reduced hydrophilicity. The ionic conductivity of Bz- κ car was enhanced by the addition of sodium perchlorate, (NaClO₄) salt as a charge carrier in the Bz- κ car gel electrolyte systems. Several characterizations were performed in order to investigate the physicochemical and electrochemical properties of Bz- κ car derivatives and assess their suitability as potential gel polymer electrolytes. The successful substitution of benzoyl molecule into κ car polymeric chain was confirmed by the Fourier transform infrared spectroscopy (FTIR) analysis based on the formation of new carbonyl (C=O) and C=C bonds in Bz- κ car. The OH band intensity also reduced. Nuclear magnetic resonance (¹H-NMR) analysis further proved the benzylation by the appearance of new multiple resonance peaks at $\delta = 6.6\text{--}9.50$ ppm, which belonged to the characteristic signals of protons in the aromatic benzoate group. X-ray diffraction (XRD) analysis showed the reduced degree of crystallinity of

the synthesized carrageenan, while elemental analyzer analysis revealed increased percentages of carbon in Bz- κ car upon the substitution. The highest degree of substitution obtained was 0.27. Thermogravimetric analysis (TGA) showed lower degradation temperature in the synthesized carrageenan, while water contact angle analysis demonstrated that Bz- κ car was less hydrophilic as compared to the pristine κ car. Solubility tests showed that Bz- κ car was best dissolved in ethylene glycol. The benzylation also improved the ionic conductivity (σ) of Bz- κ car to $3.10 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperature. The modification of Bz- κ car was further proven to increase the ionic conductivity with the addition of salt. Gel biopolymer electrolytes based on Bz- κ car as polymer host and NaClO₄ as ionic dopant was successfully produced. The concentration of NaClO₄ was varied from 0.5 to 3.0 wt.% in order to investigate its effects on the chemical interactions and the σ of the electrolytes. Significant changes in the FTIR spectra were detected indicating the chemical interactions between Bz- κ car and NaClO₄. The electrochemical impedance analysis (EIS) revealed that the σ of the gel electrolytes increased with a higher concentration of NaClO₄, suggesting that NaClO₄ was an effective charge carrier in the system. The highest σ of the gel electrolyte with the addition of 30% NaClO₄ attained at ambient temperature (298 K) was $1.29 \times 10^{-3} \text{ S cm}^{-1}$. The same gel electrolyte was tested for the temperature dependence of conductivity and confirmed is Arrhenian in the studied temperature range and achieved elevated σ of $7.90 \times 10^{-3} \text{ S cm}^{-1}$ at 100 °C. Small values in the activation energy (E_a) were observed in all the electrolytes prepared. Hence, these results suggest that suggest that the Bz- κ car/NaClO₄ gel electrolyte shows potential to be applied in electrochemical devices.

ABSTRAK

Benzoil κ -karagenan (Bz- κ car), yang merupakan terbitan κ -karagenan (κ car), telah berjaya disintesis melalui pengubahsuaian kimia melalui tindak balas asilasi Friedel-Crafts. Bz- κ car direka untuk digunakan sebagai elektrolit polimer gel dalam pelbagai peranti elektrokimia. κ -karagenan dikenali kerana sifat hidrofiliknya yang tinggi disebabkan bilangan kumpulan hidroksil (OH) dalam unit monomernya. Dalam kes ini, κ car berinteraksi kuat dengan molekul air, kerana hidroksil mampu membentuk ikatan hidrogen dengan molekul air yang polar. Kehadiran kelembapan dalam kebanyakan peranti elektrokimia tidak digalakkan. Interaksi kelembapan dengan logam atau bahagian yang sensitif terhadap udara/kelembapan dalam peranti mungkin menyebabkan letupan dan membahayakan persekitaran. Oleh itu, garam benzoil klorida hidrofobik digunakan dalam pengubahsuaian κ car untuk menghasilkan Bz- κ car yang kurang hidrofilik. Konduktiviti ion Bz- κ car ditingkatkan dengan penambahan natrium perklorat (NaClO₄) sebagai penghantar cas dalam sistem elektrolit gel Bz- κ car. Beberapa pencirian dilakukan untuk menyiasat sifat fizikokimia dan elektrokimia terbitan Bz- κ car dan menilai kesesuaiannya dan berpotensi sebagai elektrolit polimer gel. Penggantian molekul benzoil ke dalam rangkaian polimer κ car disahkan melalui analisis spektroskopi inframerah transformasi Fourier (FTIR) berdasarkan pembentukan ikatan karbonil (C=O) dan ikatan C=C baru dalam Bz- κ car. Keamatan jalur OH juga berkurang. Analisis resonan magnet nuklear (¹H-NMR) mengesahkan benzoilasi dengan kemunculan puncak resonan berganda baru pada $\delta = 6.6-9.50$ ppm, yang berkaitan dengan isyarat proton dalam kumpulan benzoat aromatik. Analisis pembelauan sinar-X (XRD) menunjukkan pengurangan darjah

kehabluran karagenan yang disintesis, manakala bagi penganalisis unsur menunjukkan peratusan peningkatan karbon dalam Bz- κ car semasa penggantian. Darjah penggantian tertinggi yang diperoleh ialah 0.27. Analisis termogravimetri (TGA) menunjukkan suhu degradasi yang lebih rendah dalam karagenan tersintesis, manakala analisis sudut sentuhan air menunjukkan bahawa Bz- κ car kurang hidrofilik berbanding dengan κ car tulen. Ujian keterlarutan menunjukkan bahawa Bz- κ car paling baik dilarutkan dalam etilena glikol. Benzoilasi juga meningkatkan konduktiviti ion (σ) Bz- κ car kepada $3.10 \times 10^{-4} \text{ S cm}^{-1}$ pada suhu bilik. Modifikasi Bz- κ car juga terbukti meningkatkan konduktiviti ion dengan penambahan garam. Elektrolit biopolimer gel berasaskan Bz- κ car sebagai perumah polimer dan NaClO_4 sebagai dopan ionik berjaya dihasilkan. Kepekatan NaClO_4 diubah dari 0.5 hingga 3.0 wt.% untuk menyiasat kesan interaksi kimia dan σ elektrolit. Perubahan ketara dalam spektra FTIR dikesan menunjukkan interaksi kimia antara Bz- κ car dan NaClO_4 . Analisis impedan elektrokimia (EIS) mendedahkan bahawa σ elektrolit gel meningkat dengan kepekatan NaClO_4 yang lebih tinggi, menunjukkan bahawa NaClO_4 adalah penghantar cas yang berkesan dalam sistem ini. σ tertinggi elektrolit gel dengan penambahan 30% NaClO_4 pada suhu bilik (298 K) adalah $1.29 \times 10^{-3} \text{ S cm}^{-1}$. Elektrolit gel yang sama diuji untuk kebergantungan suhu konduktiviti dan disahkan bersifat Arrhenian dalam julat suhu yang dikaji, mencapai σ yang meningkat kepada $7.90 \times 10^{-3} \text{ S cm}^{-1}$ pada 100°C . Nilai kecil dalam tenaga aktivasi (E_a) diperhatikan dalam semua elektrolit yang disediakan. Oleh itu, daripada keputusan ini menunjukkan bahawa elektrolit gel Bz- κ car/ NaClO_4 menunjukkan potensi untuk digunakan dalam peranti elektrokimia.

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APPROVAL

The Examination Committee has met on **19 September 2023** to conduct the final examination of **Norsyabila binti Shrgawi** on his degree thesis entitled **Synthesis and Characterization of Benzoyl Kappa-Carrageenan Doped Sodium Perchlorate as Highly Conductive Gel Polymer Electrolyte**.

The committee recommends that the student be awarded the of Master of Science (Chemistry).

Members of the Examination Committee were as follows.

Prof. Madya Ts. Dr. Norli binti Abdullah

Center for Defence Foundation Studies
Universiti Pertahanan Nasional Malaysia
(Chairman)

Dr. Siti Hasnawati binti Jamal

Center for Defence Foundation Studies
Universiti Pertahanan Nasional Malaysia
(Internal Examiner)

Prof. Madya Dr. Famiza binti Abd Latif

Fakulti Sains Gunaan
Universiti Teknologi Mara (UiTM) Shah Alam
(External Examiner)

APPROVAL

This thesis was submitted to the Senate of Universiti Pertahanan Nasional Malaysia and has been accepted as fulfilment of the requirements for the degree of **Master of Science (Chemistry)**. The members of the Supervisory Committee were as follows.

Dr. Intan Juliana binti Shamsudin

Center for Defence Foundation Studies
Universiti Pertahanan Nasional Malaysia
(Main Supervisor)

Prof. Madya Dr. Siti Aminah binti Mohd. Noor

Center for Defence Foundation Studies
Universiti Pertahanan Nasional Malaysia
(Co-Supervisor)

Dr. Norherdawati binti Kasim

Center for Defence Foundation Studies
Universiti Pertahanan Nasional Malaysia
(Co-Supervisor)

Dr. Hussien bin Hanibah

Centre of Foundation
Universiti Teknologi MARA (UiTM)
(Co-Supervisor)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

DECLARATION OF THESIS

Student's full name : Norsyabila binti Shrgawi
Date of birth : 19 February 1992
Title : Synthesis and Characterization of Benzoyl Kappa-Carrageenan Doped Sodium Perchlorate as Highly Conductive Gel Polymer Electrolyte
Academic session : 2019/2020

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LIST OF ABBREVIATIONS

A_c	-	Crystallinity area
AC	-	Alternating current
A_t	-	Total area
BC	-	Benzoyl chloride
BN	-	Benzoyl kappa-carrageenan doped sodium perchlorate
Bz- κ car	-	Benzoyl kappa-carrageenan
C	-	Carbon
CMC	-	Carboxymethyl carrageenan
CMChit	-	Carboxymethyl chitosan
DMSO	-	dimethyl sulfoxide
DS	-	Degree of substitution
DSC	-	Differential scanning calorimetry
DSSC	-	Dye-Sensitized solar cell
DTG	-	Derivative thermogravimetric
EA	-	Elemental analysis
EIS	-	Electrical impedance spectroscopy
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared spectroscopy
^1H	-	proton
IP	-	<i>Impomea pes-caprae</i>
KC	-	Kappa-carrageenan
κ car	-	Kappa-carrageenan
L	-	Electrolyte thickness
NMR	-	Nuclear magnetic resonance
M	-	Molar concentration
OMPC	-	O-methylene phosphonic kappa-carrageenan
PVA	-	Polyvinyl alcohol
R	-	Resistance
RMSE	-	Root mean square error

S	-	Sulphur
S	-	Electrolyte cross-sectional area
SPE	-	Solid polymer electrolyte
STA	-	Simultaneous Thermal Analyzer
THF	-	Tetrahydrofuran
TGA	-	Thermogravimetric analysis
UV	-	Ultraviolet
VTF	-	Vogel–Tammann–Fulcher
WCA	-	Water contact angle
Xcl	-	Crystallinity index
XRD	-	X ray diffraction

LIST OF SYMBOLS

$^{\circ}$	-	Degree
$^{\circ}\text{C}$	-	Degree Celcius
%	-	Percentage
%T	-	Percentage of transmission
π	-	Pie
Θ	-	Theta
Ω	-	Ohm
δ	-	Delta (chemical shift)
σ	-	Conductivity
σ_0	-	Pre-exponential factor
K	-	Kappa
λ	-	Lambda
ι	-	Iota
cm	-	Centimeter
cm^{-1}	-	Reciprocal wavelength
E_a	-	Activation energy
g	-	Gram
Hz	-	Frequency (Hertz)
K	-	Temperature in Kelvin
k	-	Boltzman constant
MHz	-	MegaHertz
ml	-	Mililiter
mg	-	Miligram
mm	-	Milimeter
R	-	Resistance
R_b	-	Bulk resistance
S	-	Siemen
s	-	Second (time)
T	-	Temperature

T_g	-	Glass transition temperature
eV	-	Electron volt
V	-	Voltage
Wt.%	-	Weight percentage
Z'	-	Real impedance axis

LIST OF NOMENCLATURES

[Bmim][Ac]	-	1-butyl-3-methylimidazolium acetate
(CH ₂ CO) ₂ O	-	Succinic anhydride
C ₆ H ₅ CO	-	Benzoyl
C ₇ H ₅ ClO	-	Benzoyl chloride
C ₆ H ₆	-	Benzene
CH ₂ PO ₃ H ₂	-	Phosphonomethyl phenylalanine
C ₅ H ₅ N	-	Pyridine
C ₂ H ₆ O	-	Ethanol
C ₂ H ₆ O ₂	-	Ethylene glycol
C ₂ H ₃ N	-	Acetonitrile
Cl ⁻	-	Chloride ion
ClO ₄ ⁻	-	Perchlorate ion
H ⁺	-	Proton ion
KCl	-	Potassium chloride
LiCl	-	Lithium chloride
MgCl ₂	-	Magnesium chloride
Mg(ClO ₄) ₂	-	Magnesium perchlorate
MnSO ₄	-	Magnesium sulphate
Na ⁺	-	Sodium ion
NaClO ₄	-	Sodium perchlorate
NaFSI	-	bis(fluorosulfonyl) imide
NaTFSI	-	sodium bis(trifluoromethylsulfonyl) imide
NH ₄ Cl	-	Ammonium chloride
NH ₄ COOH	-	Ammonium formate
NH ₄ Br	-	Ammonium bromide
NH ₄ I	-	Ammonium iodide
NH ₄ SCN	-	Ammonium thiocyanate
OH	-	Hydroxyl
ZnSO ₄	-	Zinc sulphate

CHAPTER 1

INTRODUCTION

1.1 Research background

Energy production, storage, and distribution are essential requirements in modern society and industry, with the electrolyte playing a pivotal role as the most crucial component in these devices. Many researchers have been driven to develop polymer electrolytes in the last three decades since they have applications in electrochemical devices such as supercapacitors, sensors, solid-state batteries, and portable electrochemical devices (Silva et al., 2019).

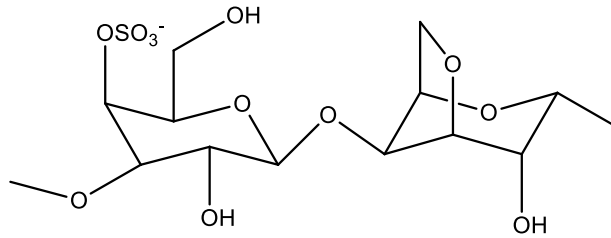
The study on polymer electrolytes has been focused on biopolymer electrolytes by researchers globally. Biopolymer, also known as a natural polymer, is a polymeric substance occurring in living organisms such as plants and microorganisms. Extensive research has been conducted to investigate the potential of natural polymers due to their abundance and “green” properties which have become the most concerning issues nowadays. According to the structure and monomeric units of the biopolymer form, there are three significant biopolymer classifications: Polynucleotides (RNA and

DNA), polypeptides- short polymers of amino acids, and polysaccharides (Sukumaran & Gopi, 2021).

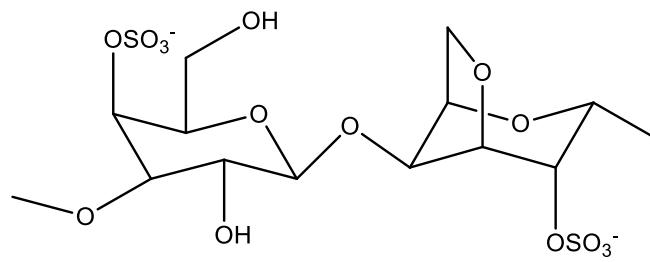
Among biopolymers, polysaccharides and proteins are the best candidates for electrolytes in modern devices due to their abundance in the environment. Other than that, the backbone of biopolymers contains functional groups that can be modified to vary their properties (Musa et al., 2022). As for this study, the main focus is polysaccharides. Polysaccharides are polymeric carbohydrate molecules made up of long chains of monosaccharide units linked together by glycosidic linkages. When hydrolysed, the constituent monosaccharides or oligosaccharides are released, including storage polysaccharides (starch and glycogen) and structural polysaccharides (cellulose and chitin) (Maji, 2019; Xu, 2017). Starch, cellulose, chitin, pectin, chitosan, and carrageenan are examples of polysaccharides.

The host polymer in this study is carrageenan. Carrageenan is a linear sulfated polysaccharide extracted from various edible red algae species, consisting of alternating units of D-galactose and 3,6-anhydro-galactose (3,6-AG) linked by -1,4 and -1,3-glycosidic linkage (Tran, 2019; Zia et al., 2017). It is classified into various types such as kappa (κ), iota (ι), and lambda (λ) based on their position and the number of the sulfate groups on the repeating galactopyranose units. The chemical structure of the types of carrageenan are shown in Figure 1.1.

(a)



(b)



(c)

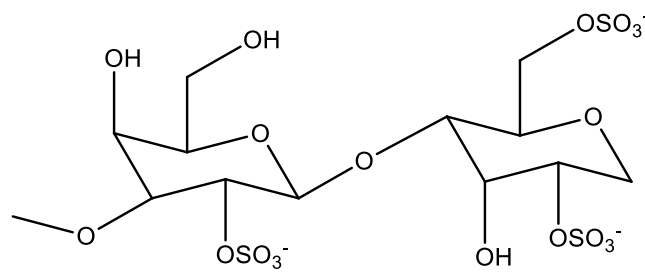


Figure 1.1 The chemical structures of (a) kappa (κ), (b) iota (ι), and (c) lambda (λ) carrageenan

Carrageenan is frequently used in the food industry due to its superior gelling, thickening, viscosity, and delivery of bioactive chemicals for stability (Dong et al., 2021; Hotchkiss et al., 2016). Apart from that, carrageenan has been proven to be an important excipient in tablet preparation for the pharmaceutical industry because of its good compatibility, high robustness, and persistent viscoelasticity (Guan et al., 2017). Other than that, carrageenan is also used to moisturise the skin, act as an anti-inflammatory, and increase skin resiliency which are all beneficial in the skincare and cosmetics industries (Hakimin et al., 2022).

K-carrageenan (κ car) was selected as the polymer host for the preparation of the electrolyte system in this study rather than other types of carrageenan. The selection of κ -carrageenan in this study rather than other types of carrageenan such as iota-carrageenan and lambda-carrageenan is because its chemical structure has the most hydroxyl group in the monomer unit. The hydroxyl group (OH) is expected to be more favourable in reacting with the benzoyl chloride (BC) molecule in the synthesis reaction to produce benzoyl κ -carrageenan (Bz- κ car). Since OH is an electron rich functional group, BC can bond to the κ -carrageenan backbone with the help of pyridine as the nucleophile. While both κ -carrageenan and lambda-carrageenan have the same number of hydroxyl groups, they differ in their gel-forming abilities. Kappa-carrageenan forms firmer and more stable gels when compared to lambda-carrageenan (Lahaye, 2001). This characteristic is particularly significant as the study aims to produce a highly conductive gel polymer electrolyte. Moreover, κ -carrageenan can exhibit higher ionic conductivity due to its gel network, making it a more efficient conductor of ions, which is essential for the functioning of electrolytes in various applications (Rani, M.S.A.A, 2018).