ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

STORAGE OF ELECTRICAL ENERGY IN ION DOPED GELS

M.Sc. THESIS

Ahmet Talha ÜZÜMCÜ

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2013

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

STORAGE OF ELECTRICAL ENERGY IN ION DOPED GELS

M.Sc. THESIS

Ahmet Talha ÜZÜMCÜ
(515101045)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Yaşar YILMAZ

JANUARY 2013

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

İYON KATKILI JELLERDE ELEKTRİK ENERJİSİNİN DEPOLANMASI

YÜKSEK LİSANS TEZİ

Ahmet Talha ÜZÜMCÜ
(515101045)

Polimer Bilimi ve Teknolojisi Anabilim Dalı

Polimer Bilimi ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Yaşar YILMAZ

OCAK 2013

Ahmet Talha ÜZÜMCÜ, a M.Sc. student of ITU Graduate School of Science Engineering and Technology 515101045 successfully defended the thesis entitled **"STORAGE OF ELECTRICAL ENERGY IN ION DOPED GELS"**, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Yaşar YILMAZ** Istanbul Technical University	.....
Jury Members :	**Prof. Dr. Yaşar YILMAZ** Istanbul Technical University	.....
	Prof. Dr. Hüseyin YILDIRIM Yalova University	.....
	Assoc. Prof. Dr. Orhan GÜNEY Istanbul Technical University	.....

Date of Submission : **17 December 2012**
Date of Defense : **25 January 2013**

To my brothers,

FOREWORD

I would like to express my sincere gratitude to Prof. Dr. Yaşar Yılmaz for giving me the opportunity to join his research group to conduct this study which in turn gave me the chance to became a scientist. I am also thankful for his guidence through my master studies.

I also would like to express my special thanks to Dr. Ali Gelir for his guidence through my project and the advises he has given me on my study. It was a great honour to work with him on my thesis. I have to admit that without his guidence this thesis would never be complete.

With his self sacrificing support, I would like to express my graditutes to my collegue Res. Asist. Alptekin Yıldız and also I would like to thank Res. Asist. Sevcan Tabanlı and Res. Asist. Nesrin Çelebioğlu for their sense of humour and support.

I would like to thank Dr. Esra Alveroğlu Durucu for her guiding studies which turned out to this study.

Last but not least I would like to thank to my all family members for helping me during all my life and this study.

January 2013

Ahmet Talha ÜZÜMCÜ
(Physicist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

AAm : Acrylamide (monomer)
Al : Aluminum
Al_2O_3 : Aluminum Oxide
APS : Ammonium persulfade
BIS : N-N'-methylene bisacyrlamide (crosslinker)
DC : Direct Current
PAAm : Polyacrylamide
PMMA : Poly(methyl methacrylate)
PHEMA : Polyhydroxyethylmethacrylate
Pt : Platinum
Pyr : Pyranine

LIST OF TABLES

Page

LIST OF FIGURES

Page

STORAGE OF ELECTRICAL ENERGY IN ION DOPED GELS

SUMMARY

One of the most important problems that humanity has to deal with, is energy. After the invention of transistors, researches and developments about microelectronic industry has grown exponentially. With the development of organic materials which can be used as an alternative circuit elements, scientists focused their studies mostly on organic electronics. More specificially, conductive polymers and hydrogels are top materials that has still been working on.

Besides its conductivity, these materials also can show compatible property with human body. Nowadays it is common that biological implants such as artificial muscle, is mostly produced by using hydrogels.

Polymers or industrially plastics, were known as good insulating materials until a few decades ago. Following the invention of condutcive polymers, it has been possible to produce synthetic materials that have tunable conductivity as it is in semiconductor metals. This tunability of conductivity make possible to produce some microelectronic circuit elements in an easy and flexible way.

Upon following all these developments in organic electronics and more generally conductive polymers, this study is based on a different aspect of electrical property within the polymeric hydrogels. In the introduction part it is briefly explained that in this study it is worked on the novel property of hydrogels which has capability of creating flowing current within the gel itself without applying any voltage. This property made this study unique, because there is no any parallel or similar study. The self current producing property was noticed accidentally, but after a while we realized that it is worth to think about and develop brandnew ideas.

This unfamiliar property was very peculiar to us and straitened for better understanding with continuous experiments. Bearing in mind that there is no enough infromation in the current literature, these experiments are conducted fussily. In the first three chapters, it is given some theoretical backround informations regarding with definition, properties and applications of hydrogels. It is also informed to the reader about the concept of elecrtical and ionic conductivity by giving simple examples from the current literature.

Finally in the experimental part of this study, at first some information is given about the synthesizing procedure of the gels and talked about their general properties. Later it is given information about the system that has been used througout whole this study, which was a handmade apparatus. After all these stuff it is discussed the results of numerous experiments which also includes the current measurements during the gelation process. The study is finished with a conclusion part in which there some dicsussions about possible applications and developments about these specific hydrogels.

With all the deficits and limited time, these thesis is still a canditate to become a milestone on this promising research area.

İYON KATKILI JELLERDE ELEKTRİK ENERJİSİNİN DEPOLANMASI

ÖZET

Polimerik hidrojeller yoğun bir şekilde kullanılmakta olan malzemeler halini almıştır. Özellikle iletken polimerlerin keşfi ve akabinde bazı küçük devre elemanlarında kullanılmaya başlanılması bu çok disiplinli çalışma alanına ilginin günden güne artmasına neden olmuştur. İletken yapıda polimerler üretilmeye başlanmadan önce polimerler genel olarak yalıtkan yapıya sahip malzemeler olarak biliniyordu.

Hidrojeller ise genel olarak bugün kullanıldığı alanın dışında kullanılıyordu. Polimerik hidrojellerin su tutabilme özelliği ve insan vücuduna biyolojik olarak uyumlu bir yapıda sentezlenebilmesi ile önü açılan çalışmalar, günümüzde daha çok medikal uygulama alanlarında kullanılır hale gelmiştir.

Bu çalışmada ise bütün bu bilinen özelliklerinin dışında polimerik hidrojellerin, daha önce literatürde bir örneği bulunmayan fakat çok ciddi mana önem arzedebilme potansiyeli olan bir özelliği üzerinde durulmuştur. Bilindiği gibi saf veya çeşitli molekül katkılı hidrojeller belli düzeylerde iletkenlik gösterebilmektedirler. % 90-95 oranında suyu içerisinde barındıran hidrojeller aynı zamanda hidrofilik bir iç morfolojiye sahip olup, farklı varyasyonlardaki bu morfolojik yapı da farklı karakterde iletken özellik göstermektedir. Bu tezin genel konusunu oluşturan ise üzerine bir akım uygulandığında akımı geçiren yani iletken olan bu jellerin aynı zamanda herhangi bir voltaja ya da daha farklı bir dış etkiye maruz kalmadan bulunduğu ortamda bir doğru akım üretebilmesidir.

Gözlemlenen bu akım her ne kadar mikroamper seviyelerinde olsa bile, kendiliğinden böyle bir özellik gösterebilmesi çalışmayı değerli kılmaktadır. Bu dikkat çekici özellik farkedildikten sonra çalışmalar bu akıma sebep olabilecek mekanizmalar üzerinde yoğunlaştırılımış olup deneysel çalışmalar ile ilgili olan bölümün giriş kısmında bunlardan kısaca bahsedilmiştir.

Deneysel kısma gelmeden önce akım, elektronik ve iyonik iletkenlik ile ilgili genel hususlardan bahsedilip konuyla ilgili bir ön çalışma yapılmış bunu takiben deneysel kısımda detaylı bir şekilde jellerin hazırlanması ölçüme uygun hale getirilmesi ve değişik iç yapıya sahip olan jellerin sentezlenmesi ile alakalı bilgiler verilmiştir. Normal stokiyometriye bağlı kalınarak jelller sentezlendikten sonra çapraz bağlayıcı konsantrasyonu normale göre iki kat fazla ve az olan jeller de sentezlenek değişik sıklıktaki ağ yapısının görülmekte olan akım üzerindeki etkileri incelenmiştir. Bu kısma gelmeden önce hidrojelin % 90-95 lik bir kısmının sudan meydana geldiği bilindiği için saf suyunda böyle bir akıma sebep olup olamayacağı sorusu gündeme gelmiş bunun üzerine ilk önce oda sıcaklığında ve daha sonra jelleşme reaksiyonunun gerçekleştiği sıcaklık olan $60^{\circ}C$ de saf su ile akım ölçümleri yapılmış (metal elektrodlar arasına özel bir sistem ile enjekte edilerek) ve bu ölçümler sonucunda saf suda meydana gelen akımın jeldekine kıyasla çok küçük bir değere sahip olduğu ve bu

çalışma için önemsenmeyecek bir şiddette olduğu görülmüştür. Bu sonuca vardıktan sonra asıl sebeb olan mekanizmanın jelin iç yapısından kaynaklandığı tesbit edilmiş olup jelleşme anında yapılan deneylere geçilmiştir.

Jellerin farklı oranlarda ve saf ya da yüklü olarak sentezlendiği gibi jelleşme esnasında yapılacak olan ölçümler için de ayrı ayrı jelleşme öncesi çözeltiler hazırlanmıştır. Elde edilen her bir jele karşılık gelen bir ilave jelleşme reaksiyonu ölçümü gerçekleştirilmiştir.

Yapılan ölçümlerde görülmüştür ki reaksiyonun ilk başladığı esnada ciddi bir pik gözlenmektedir. Reaksiyonun başlangıcını takip eden ilk 10-15 dakika içerisinde $100 - 150\,\mu A$ seviyelerine gelen akım değeri daha sonra şiddetli bir düşüş göstermiş ve sıfıra doğru düşmeye devam etmiştir. Bu etki değişik konsantrasyonlara sahip olan jeller için de benzer nitelik gösterip ilk birkaç dakika içerisinde şiddetli bir pik verip daha sonra sıfıra doğru azaldığı gözlemlenmiştir.

Bu yeni çalışma sentezlenmiş olan jelin neden akım geçirebileceğini anlamaya yardımcı olabilmesinin yanında, jelleşme anının tesbiti içinde kullanılabilecektir. Jelleşme ile ilgili deneyler tamamlandıktan sonra, asıl konu başlığını ilgilendiren ve tartışmaların temelinde olan ölçümlere geçilmiştir.

Daha önce bahsedilen değişik oran ve katkılandırılan jeller, ölçüme hazır hale getirildikten sonra sistem üzerinde gerekli kontroller yapılmış ve ölçümlere başlanmıştır. Her bir jel için ölçüm şişme oranı 1 ve 2 olmak üzere toplamda 2 defa tekrarlanmıştır. Şişme oranının 1 olması jelin kuru halindeki ağırlığının 2 katına çıkması, aynı şekilde şişme oranının 2 olması da kuru haldeki kütlesinin üçkatına yükselmesiyle açıklanmış ve ilgili formül verilerek doğrulanmıştır. Farklı şişme derecelerinde olan jeller ile ölçüm yapılmış ve deney sonuçlarında değerlendirilen kriterlerden biri olmuştur. Şişme oranındaki değişikliğin yanısıra jellerin iç yapısındaki çapraz bağlayıcı molekülün miktarında göre de bir sınıflandırma yapılmış normal stokiyometrik oranda hazırlanan bu jellere ilaveten normalin yarısı ve iki katı kadar olan jeller de sentezlenmiştir. Saf ve belirlenen miktarda piranin molekülü katkılandırılmış olan bu jellerin hepsi yukarıda bahsedilen sınıflandırmaya tabi tutulmuş ve netice itibariyle toplamda 6 adet saf ve 6 adet piranin katkılı 12 jel ile ölçümler gerçekleştirilmiştir. Çalışmanın ana kısmını oluşturan bu 12 adet jel her farklı elektrot konfigürasyonu için ayrı ayrı hazırlanmış, ve şişmeden önceki ve sonraki ağırlıkları, boyutları ve yaklaşık şişme oranları tablo halinde sunulmuştur.

İçinde büyük oranda su bulunduran bu şişmiş jeller oda sıcaklığında buharlaşmaya maruz kalmakta ve şişirilip boyutları saptandıktan sonra hızlı bir şekilde ölçüme başlanmaktadır. Tasarlamış olduğumuz deney düzeneği her ne kadar havanın jele nüfuzunu engelleme maksadıyla yapılmış olsa bile, belli miktarda su kaybının önüne geçilememiştir. Fakat bu durum aynı ortamda bulunan bütün jeller için geçerli olduğundan dolayı ölçümlerin bütünü dikkate alındığında, alınmış olan sonuçlara doğrudan bir etkisinin olmayacağı anlaşılmıştır. 3 farklı metal elektrot konfigürasyonunun denendiği sistemde ilk olarak iki eş büyüklükteki dairesel platin tabakalar ile ölçümler alınmış, alınan bu ölçümler sonucunda elde edilen sonuçlardaki genel davranışlara bakıldığında Platin kontaktlar arasındaki jeller üzerinden herhangi bir akımın geçmediği gözlenmiştir. Bu davranışın muhtemel nedenleri üzerinde tartışılıp ortaya makul bir öneri atılmıştır. Çalışmanın devamında hazırlanan diğer 12 adet jel bu sefer dairesel platin tabaka ve platinden yapılmış olan enjektör iğnesi kalınlığındaki platin tel arasına yerleştirilerek aynı ölçümler tekrarlanmıştır. İlk

kısımdaki ölçümlerden farklı olarak, bu sefer farklı şiddetlerde akımlar gözlenmiş ve bu akımların şiddeti, akma süresi ve akım-zaman grafiği üzerindeki genel davranışı her bir jel için farklılık göstermiştir. Değişen elektrot yapısına bağlı olarak gözlemlenen bu akım hareketinin muhtemel sebepleri üzerinde yine tartışılıp bir sonuca bağlanmaya çalışılmış ve jelin moleküler düzeydeki iç yapısından hareketle bazı tahminlerde bulunulmuştur. Üçüncü ve son kısımda ise aynı cins ama farklı şekillderdeki elektrotlar yerine bu defa da aynı geometrik yapıya sahip olan farklı iki metal elektrot kullanılmıştır. Ölçüm alınacak olan jeller platin ve aliminyum plakalar arasına yerleştirilip daha önce olduğu gibi aynı şartlarda deneyler tekrarlanmıştır.

Burada ilginç olan akım şiddetinin diğer ölçümlere göre çok daha fazla olması ve aynı zamanda bu akımın şiddetinin ve süresinin jelin şişme oranından ciddi bir şekilde etkilenmesidir. Jeldeki şişme oranı artırıldıkça ulaşılan maksimum akım değeri ve sonlanana kadar geçen sürenin muazzam bir şekilde etkilendiği görülmüştür.

Bütün bu deneylerden elde edilen sonuçlar zaman karşı doğru akım grafiğinde yorumlanmış, yorum yapılırken her bir ölçüm şişme derecesine ve çapraz bağlayıcı oranına göre olmak üzere iki ayrı kıstas üzerinden tartışılmıştır.

Çalışmanın en sonunda ise bütün bir çalışma derlenerek istenen amaca ulaşılıp ulaşılamadığı konusunda fikirler beyan edilmiştir. Ayrıca bu enteresan olaydan yola çıkılarak, sistemin muhtemel uygulama alanları üzerinde tartışılmış, sürdürülebilirliği ve geliştirilebilirliği üzerinden fikirler ortaya atılmıştır.

Bütün bu deneylerin sonuçların ve yorumların yanısıra, üzerinde çalışılmış olan konunun tamamıyla yeni bir bakış açısıyla ele alındığı akıldan çıkarılmamalı, üzerinde daha derin ve detaylı çalışmaların yapılması halinde günümüzdeki en önemli problemlerden biri olan enerji konusunda pozitif bir katkıda bulunabileceği göz ardı edilmemelidir.

1. INTRODUCTION

Providing materials for the benefit of humanity is an indispensable necessity for thousands of years. Before discovering synthetic materials like polymers; people were insufficient to supply raw materials due to high cost, difficulties in processibility, lack of resources.. etc.

In addition to its industrial utilization, polymers and polymeric materials are also used in many areas such as electronics, solar energy systems, surgical implants and other technological applications [3, 4].

To achieve such a technological development, scientists and researchers are continuously working on novel studies regarding Polymer Science, which includes Polymer Chemistry, Polymer Engineering, Polymer Physics and etc.

Gels are defined as a substantially dilute cross-linked polymeric system, and are categorised principally as weak or strong depending on their flow behaviour in steady-state. The term hydrogel describes three-dimensional network structures obtained from a class of synthetic and/or natural polymers which can absorb and retain significant amount of water.

Hydrogels may be described as crosslinked hydrophilic polymers that are swollen by, but do not dissolve in, water [5]. They are polymeric networks, which absorb and retain large amounts of water. In the polymeric network, hydrophilic groups or domains are present which are hydrated in an aqueous environment thereby creating the hydrogel structure. As the term 'network' implies, crosslinks have to be present to avoid dissolution of the hydrophilic polymer chains/segments into the aqueous phase.

Increase of water content in hydrogels has been found to increase, in general, molecular mobility, similar to an increase in temperature In particular, the water content-dependent electrical conductivity has been found to reflect ionic mobilities in the water-swollen gel.

By using this capacity to mobilize ions in swollen state, hydrogels has became a focus of intensive research as an organic semiconductor material.

Organic electronics have become an active research area in recent years because they are an alternative to the traditional semiconductor technology and challenges in design on a smaller scale from microscale to nanoscale. Moreover, organic materials have vast potential for integration in low-cost microelectronic devices. Organic based semiconductors, for example polymeric gels, may have superior properties due to their flexibility against to regulate some physical properties of the materials even after the production, e.g., by changing the volume of the gel. Circuits and displays based on organic electronics may also be flexible, low-weight, and environment friendly. Due to great diversity and functionality of the polymers, they may also be produced for specific requirements, like biocompatible semiconductors.

To produce an organic semiconductor material, insulating polymers have been made conductive so far by using various methods such as ion implantation press contacting and photochemical doping. The impressive properties of these materials that have been taken advantage are the ability to manipulate electronic properties by changing their molecular structure.

With these capability to manipulate molecular structure, it is possible to synthesize p and n-type polymeric gels like metallic semiconductor materials [6]. Principle of the electrical conductivity in polymeric gels can be changed by doping static (inactive) ions having counter ions as charge carriers and these gels can be used to form pn junctions that work similar to inorganic semiconductors. These semiconductor polymeric gels can be doped with both negative (n-type) and positive (p-type) counter ions as charge carriers.

Besides all these issues and developments about organic semiconductor materials, this thesis is focused on very peculiar property that has never been mentioned before in the literature which is observing a DC current through swollen hydrogel, when it is placed between two metal electrodes such as Platinum, Aluminium or Gold.

As it is mentioned above dried Hydrogel is an insulating material itself and has no capability to conduct electricity. Meanwhile if it absorbs enough water, hydrogel become conductive and can easily conduct electricity due to gained mobility of

polymer molecules in its crosslinked structure [7]. Instead of applying any voltage, this time Hydrogel is placed between metal electrodes and connected to an ampermeter to observe current if there exist such a thing.

Suprisingly we observed a DC current on the order of microamperes. Even if the value of current is too small, the result is still confusing. To figure out what is going on in the internal structure of hydrogels and assert a plausible theory, this whole study is dedicated to give a reasonable and satisfying explanation to this unexpected behaviour.

In the first part of thesis some basic concepts about polymers and hydrogels are briefly explained. Types of polymerization reactions and gelation as a reaction is simply mentioned. For the next chapter, mechanism of current flowing for both metals and conductive polymers are described. It is important to build a theoretical background for producing electrical current in materials to put forward an idea about the possibility of current producing hydrogels if such a thing really exists. In the experimental part of this study a simple explanation is made about how our hydrogels are synthesized and also given information about our handmade system for making measurements successfully. Before starting experiments on swollen hydrogels, it is tried to understand the sol-gel transition mechanism by means of capacity to produce electrical current. The technique was identical as in hydrogels, that pregel solution is filled to a plastic tube which has platinum electrodes on both sides.

Finally synthesized hydrogels are swollen to some degrees to make the measurement. Neutral and ion doped gels are prepared for measurements and with different stoichiometric ratios. After finalizing all these measurements it is tried to understand that why these gels produce a current and discussed if it is possible to produce organic materials which can produce its own electrical energy.

2. BASIC CONCEPTS ABOUT POLYMERS AND HYDROGELS

2.1 Polymers

To understand the experimental part of this study, it is essential to know some basic phenomena about polymers. It is also important to know about reacting monomers, polymers, gels and polymerization reactions that take place under specific conditions to obtain desired polymer.

2.1.1 Definition of polymers

Chemically, polymers are long-chain molecules of very high molecular weight, often measured in the hundreds of thousands. For this reason, the term macromolecules is frequently used when referring to polymeric materials. The behavior of polymers represents a continuation of the behavior of smaller molecules which are called as monomers at the limit of very high molecular weight. The entire structure of a polymer is generated during polymerization, the process by which elementary units (chemical monomers) are covalently bonded together. The number of monomers in a polymer molecule is called chemical monomers are the repeating unit that corresponds to the small molecules that were linked together to make the polymer chain. At a first glance, we may consider the normal alkane hydrocarbon series, which shown in Figure 2.1 [8].

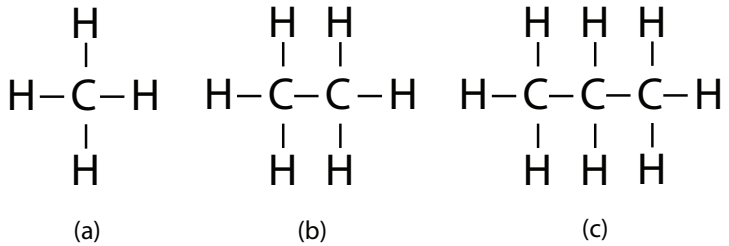


Figure 2.1: A schematic representation of simple alkanes, (a) Methane, (b) Ethane, (c) Propane.

These molecules have the general structure as it is depicted in Figure 2.2.

Figure 2.2: General structure of hydrocarbons.

where the number of $-CH_2-$ groups, n, is allowed to increase up to several thousand. Macromolecules that contain monomers of only one type are called homopolymers.

$$-A-A-A-A-A-A-A-A- \quad \text{homopolymer}$$

Homopolymers are made from the same monomer, but may differ by their microstructure, degree of polymerization or architecture. These factors determines many properties of polymeric systems. If a molecule consists of only a small number of monomers (generally, less than 20) it is called an *oligomer*. Linear polymers contain between 20 and 10 billion (for the longest known chromosome) monomers. Polymer architecture is one of the most important parameters that affect polymers physical properties like crystallization,miscibility and glass transition temperature. systems is polymer architecture. Types of polymer architectures include linear, ring, star-branched, H-branched, comb, ladder, dendrimer, or randomly branched are also combining several different types of monomers into a single chain leads to new macromolecules, called *heteropolymers*, with unique properties [9]. The properties of heteropolymers depend both on composition (the fraction of each type of monomers present) and on the sequence in which these different monomers are combined into the chain. Macromolecules containing two different monomers are called *copolymers*. Copolymers can be alternating, random, block or graft depending on the sequence in which their monomers are bonded together. In nature most of the polymers are copolymers, like proteins which may be consisting of several types of amino acids [1].

2.1.2 Types of polymerization reactions

The study of polymer science begins with understanding the methods in which these materials are synthesized. Polymer synthesis is a complex procedure and can take place in a variety of ways. Among all these complicated methods, there two main reactions nearly all polymerization reactions take place in [10]: *Addition polymerization and Condensation polymerization*. In condensation polymerization, monomers, oligomers and polymer chains combine by the elimination of small molecules to form longer chains in a process known as *Step-Growth*. Each monomers that contributes the

growing chain during step growth reaction contains a minimum of two functional groups.

In addition polymerization, monomers that contain double bonds are added squentally to the growing end of a chain, that is why this polymerization is also called as chain growth polymerization [1].

Because Polyacrylamide hydrogels are synthesized in chain polymerization, it is useful to give some extra information about reaction mechanism which includes the initiation, propogation and termination steps respectively.

The steps mentioned above are constitutes the so called *free radical polymerization*, which is very common and as the name suggests that reaction is initiated with a free radical in the media. The synthesis of poly(ethyl acrylate) will be used as an example of free radical polymerization. Benzoyl peroxide is a common initiator. On heating, benzoyl peroxide decomposes to give two free radicals as shown in Figure 2.3 [8].

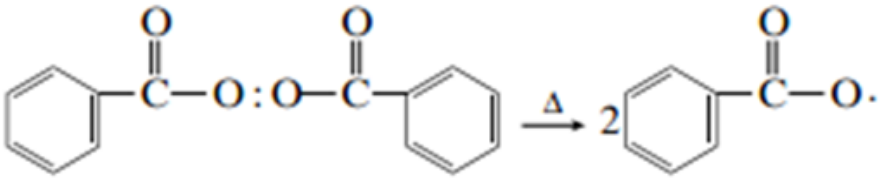


Figure 2.3: Decomposing of benzoyl peroxide upon heating.

In this reaction the electrons in the oxygen-oxygen bond are unpaired and become the active site. With R representing a generalized organic chemical group, the free radical can be written as (R·). It should be pointed out that hydrogen peroxide undergoes the same reaction on a wound, giving a burning sensation as the free radicals *"kill the germs"*. The initiation step usually includes the addition of the first monomer molecule which is shown in Figure 2.4. In this reaction the free radical attacks the monomer and adds to it. The double bond is broken open, and the free radical reappears at the far end. After initiation reactions many monomer molecules are added rapidly, perhaps in a fraction of a second.

On the addition of each monomer, the free radical moves to the end of the chain. Finally in the termination reaction, two free radicals react with each other. Termination is either by combination, where R now represents a long-chain portion, or by

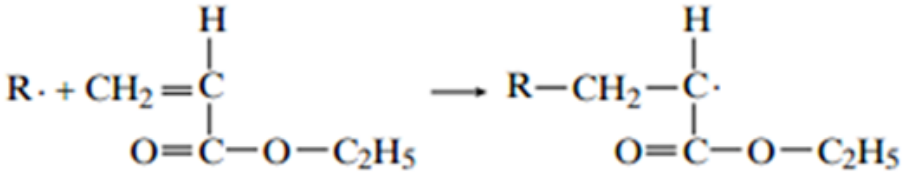


Figure 2.4: Initiation step of the reaction resulting a dimer molecule

disproportion, where a hydrogen is transferred from one chain to the other. This latter result produces in two final chains.

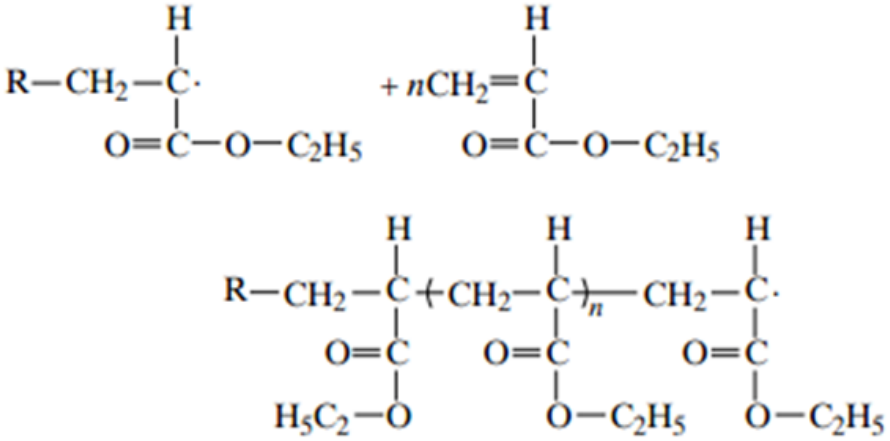


Figure 2.5: Initiation step of the reaction resulting a dimer molecule [1].

While the normal mode of addition is a head-to-tail reaction, this termination step is normally head-to-head. As a homopolymer, poly(ethyl acrylate) is widely used as an elastomer or adhesive, being a polymer with a low Tg, $-22\,°C$. As a copolymer with other acrylics it is used as a latex paint [8].

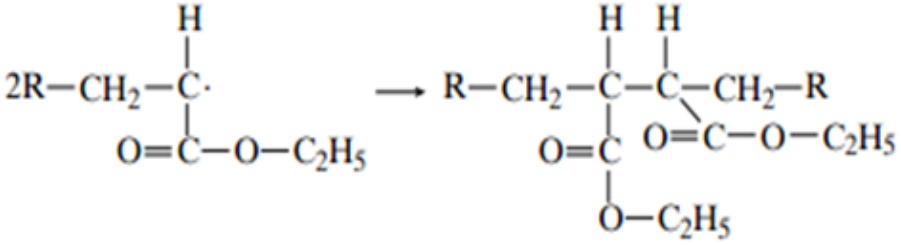


Figure 2.6: Termination step which result with two final chains of polymers [1].

2.2 Gelation

A polymer gel consists of an elastic cross-linked polymer network with a fluid filling the interstitial space of the network. The network of polymer molecules holds the

liquid in place and so gives the gel what rigidity it has. Gels are wet and soft and look like solid material, but are capable of undergoing large deformations. This is in contrast with most industrial materials, such as metals, ceramics, and plastics, which are dry and hard. In this section it is aimed to give some brief description of basic concepts about gelation, percolation and types of gels that is mostly studied for recent years.

2.2.1 Definition of gelation

During gelation reaction, polymers may be cross-linked to several distinguishable levels. At the lowest level, branched polymers are formed. At this stage the polymers remain soluble, sometimes known as the *sol stage*. As cross-links are added, clusters form, and cluster size increases. Eventually the structure becomes infinite in size and becoming three dimensional network; that is, the *composition gels*. Continued cross-linking produces compositions where, eventually, all the polymer chains are linked to other chains at multiple points, producing, in principle, one giant covalently bonded molecule. This is commonly called a *polymer network*. At the gel point the viscosity of the system becomes infinite, and the equilibrium modulus climbs from zero to finite values. In simple terms the polymer goes from being a liquid to being a solid [8].

Alternatively, gelation may be conceived as the point where a three-dimensional network is formed. From a physical point of view, the viscosity of the reacting mass goes to infinity at the gelation point.

The general features of structural evolution during gelation are described by *percolation (or connectivity) theory*, where one simply connects bonds (or fills sites) on a lattice of arbitrary dimension and coordination number.

The first quantitative theories of gelation the mean-field theories were formulated in the 1940s by Flory and Stockmayer. Critical percolation theory was successfully applied to gelation in the 1970s [2]. A number of growth models (diffusion limited aggregation, cluster-cluster aggregation, kinetic gelation) have been developed in the 1980s to describe the kinetic aspects of aggregation and gelation [11].

Figure illustrates a two-dimensional system at the gel point. It must be noted that gels at and just beyond the gel point usually coexist with sol clusters. These can also be seen in Figure. It is common to speak of the conversion factor, p, which is the fraction of bonds that have been formed between the mers of the system. For the two-dimensional schematic illustrated in Figure, $p = 1/2$ yields the gel point.

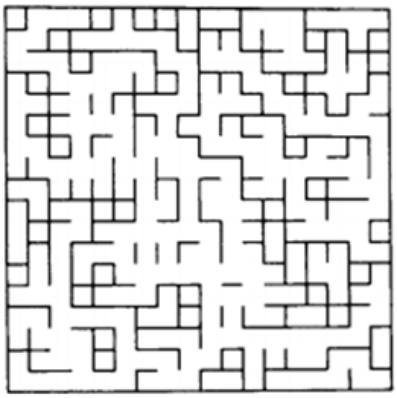


Figure 2.7: Schematic represantation of gel point where $p = 1/2$.

According to Flory and Stockmayer [8], the critical extent of reaction, P_c at the gel point is given by the Eq. 2.1.

$$P_c = \frac{1}{f - 1^{1/2}} \tag{2.1}$$

where f represents the functionality of the branch units that is, of the monomer with functionality greater than 2. This simple equation has been modified many times for particular stoichiometries and mixtures of monomers.

From the beginnig of this chapter it is aimed to make ourselves clear about some phenomena about polymers, their sytnhesis and gelation processes. It is now time to focus our attention to types of gels and of course mostly hydrogels.

2.2.2 Types of gels

There are several ways to classify gel according to desired manner. They can be classified as physical and chemical gels, elastic and inelastic gels or hydrogels, organogels and aerogels (xerogels). In this thesis, classification has been made according to solvent which they synthesized in and they are simply; hydrogels, organogels and aerogels (xerogels).

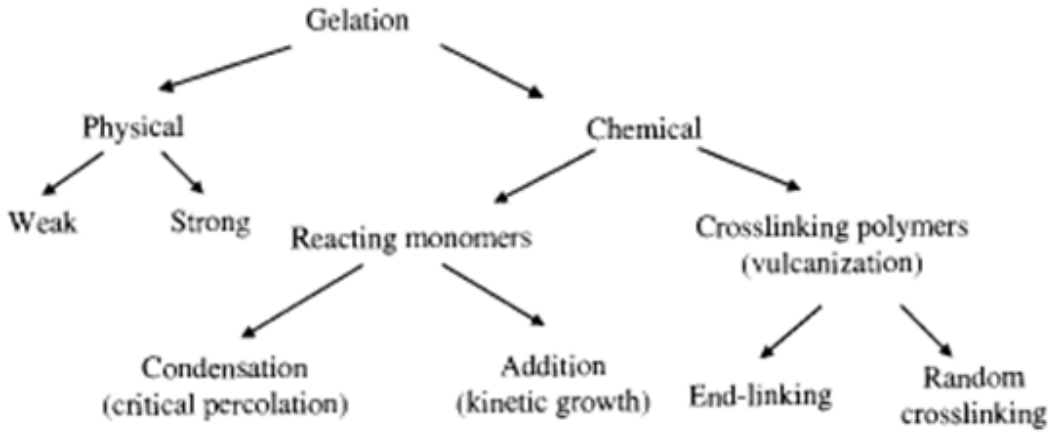


Figure 2.8: Types of gelation processes [2].

Because it is dealt with polyacrylamide gels, hydrogels will be explained deeply in a seperated caption.

Organogel, a viscoelastic system, can be regarded as a semi-solid preparation which has an immobilized external apolar phase. The apolar phase gets immobilized within spaces of the three-dimensional networked structure formed due to the physical interactions amongst the self-assembled structures of compounds regarded as gelators. In general, organogels are thermodynamically stable in nature.As it is stated above, the main difference between and organogel and hydrogel is the polarity of the solvent. For organogels, solvent is apolar and for hydrogels it is polar.

They behave like a solid at lower shear rates and hence shows an elastic property. The organogels when viewed under polarized light appears as a dark matrix. This can be accounted to the isotropic nature of the organogels which does not allow the polarized light to pass through the matrix. As the organogels are heated up above a critical temperature, the organogels loses its solid matrix- like structure and starts flowing. But as the heated organogels systems are subsequently cooled down, the physical interaction amongst the organogelators prevail and the organogels revert back to the more stable configuration.This has been attributed to Thermoreversible propety of organogel.

Initially, organogels were developed using various non-biocompatible organogels wh ich rendered the organogels non-biocompatible. Of late, research on organogels using various biocompatible constituents has opened up new dimensions for the use of the same in various biomedical applications [12]. Xerogels designate dried gels with a

very high relative pore volume. These are versatile materials that are synthesized in a first step by low-temperature traditional sol-gel chemistry. A xerogel may be defined as a polymeric network devoid of water. The water holding capacity of a xerogel depends on the number of the hydrophilic groups and crosslinking density. Higher the number of the hydrophilic groups, higher is the water holding capacity while with an increase in the crosslinking density there is a decrease in the equilibrium swelling due to the decrease in the hydrophilic groups [13]. As the crosslinking density increases, there is a subsequent increase in the hydrophobicity and a corresponding decrease in the stretchability of the polymer network. As xerogels combine the properties of being highly divided solids with their metastable character, they can develop very attractive physical and chemical properties not achievable by other means of low temperature soft chemical synthesis. In other words, they form a new class of solids showing sophisticated potentialities for a range of applications. The particularly interesting properties of aerogels arise from the extraordinary flexibility of the sol-gel processing, coupled with original drying techniques [14]. The wet chemistry is not basically different for making xerogels and aerogels. Compared to traditional xerogels, the originality of aerogels comes from the technique used to evacuate the liquid. Conventionally, the term "aerogels" has been used to designate gels dried under supercritical conditions. More recently, materials dried by other techniques such as freeze-drying, produce materials initially known as cryogels, now also termed aerogels.

2.2.3 Hydrogels

The hydrogel can be defined as a crosslinked polymeric network which has the capacity to hold water within its porous structure [5]. The water holding capacity of the hydrogels arise mainly due to the presence of hydrophilic groups, as amino, carboxyl and hydroxyl groups, in the polymer chains. According to Hoffmann, the amount of water present in a hydrogel may vary from 10% to thousands of times of the weight of the xerogel [15].

Hydrogels can be classified into two groups depending on the nature of the crosslinking reaction. If the crosslinking reaction involves formation of covalent bonds, then the hydrogels are termed as permanent hydrogels. If the hydrogels are formed due to

the physical interactions, as molecular entanglement, ionic interaction and hydrogen bonding, among the polymeric chains then the hydrogels are termed as physical hydrogels . The examples of physical hydrogels include polyvinyl alcohol-glycine hydrogels, gelatin gels and agar gels. Hydrogels can also be categorized as conventional and stimuli responsive hydrogels. Conventional hydrogels are the crosslinked polymer chains which absorb water when put in an aqueous media and there is no change in the equilibrium swelling with the change in the pH, temperature or electric field of the surrounding environment while the stimuli responsive hydrogels are the polymeric networks which change their equilibrium swelling with the change of the surrounding environment [16].

As stated above, the hydrogel starts to imbibe water when it is put in an aqueous media. Hence, determination of the amount of water imbibed within the hydrogel is an important criterion for characterizing the hydrogel and is often represented in terms of % percentage swelling S%. The % of percentage swelling of the hydrogel is directly proportional to the amount of water imbibed within the hydrogel [17].

Amount of water imbibed within the hydrogel influences the diffusional properties of a solute through the hydrogel. In general, the higher the % percentage swelling, the higher is the amount of water imbibed and the higher is the diffusion rate of the solute, though other factors, as micro-architecture of the polymer chain, may also play an important role. Experimentally, % percentage swelling can be determined by weight difference method and is expressed by the following equation:

$$S\% = \frac{W_s - W_d}{W_d} x\,100 \tag{2.2}$$

where, W_s is weight of swollen gel and W_d is weight of dry gel. The % percentage swelling or so called degree of swelling plays a key role in this study, because the experiments for current measurements has been done according to different degree of swollen gels, so it is vital to understand the swelling concept in terms of intra-molecular forces and interactions [18].

3. MECHANISM OF CURRENT FLOW

For a material, the conductivity is to allow moving charged particles flowing in one direction. In electronic conduction, moving charges are simply electrons. The movement of the charges due to any external applied electric field cause the electric current. Metals are known as the most conductive materials in nature while ametals or synthetic materials are insulating. Between these two types of materials, there exist semiconductors, which are insulating but capable of gaining conductive characteristic due to increase of the temperature or doping with atoms.The basic unit of resistance is ohm (Ω) , conductance is the reciprocal of resistance and its unit is Siemens (℧). Conductivity is the measure of conductance between the opposite faces of a 1 cm cube of material. This measurement has the unit of Siemens/cm. The electrical conductivity of metallic solids generally decreases with increasing temperature although more electrons are excited. This is because of the thermal motion of the atoms that lead to collisions between electrons and atoms. Subject to these collisions, the electrons become less efficient in transporting charge [19].

3.1 Current flow in metals (Electronic conductivity)

We can visualize our perception about current flow with a simple example; marbles in a tube. As each electron moves uniformly through a conductor, it pushes on the one ahead of it, such that all the electrons move together as a group. The starting and stopping of electron flow through the length of a conductive path is virtually instantaneous from one end of a conductor to the other, even though the motion of each electron may be very slow. An approximate analogy is that of a tube filled end-to-end with marbles:

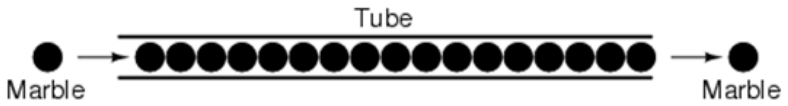


Figure 3.1: An example of how electrical current flow in a direction..

The tube is full of marbles, just as a conductor is full of free electrons ready to be moved by an outside influence. If a single marble is suddenly inserted into this full tube on the left-hand side, another marble will immediately try to exit the tube on the right. Even though each marble only traveled a short distance, the transfer of motion through the tube is virtually instantaneous from the left end to the right end, no matter how long the tube is.

If we explain it more scientifically; the electric current depends on the mobility of the electrons in valence band. The valence band is the band made up of the occupied molecular orbitals and is lower in energy than the so-called *conduction band*. It is generally completely full in semiconductors. When the semiconductors are heated, electrons from this band jump out of the band across the band gap and go into the conduction band, making the material conductive [19].

The occupancy of valence band determines the thermal and electrical property of any metal.To complete the theory scientists suggested an upper band called as conduction band which is completely empty at $T = 0$ Kelvin. In semiconductor materials the Energy gap (Eg) between these two band are relatively bigger than metals, so they need energy to breakdown the covalent bond and to jump into the conduction band.

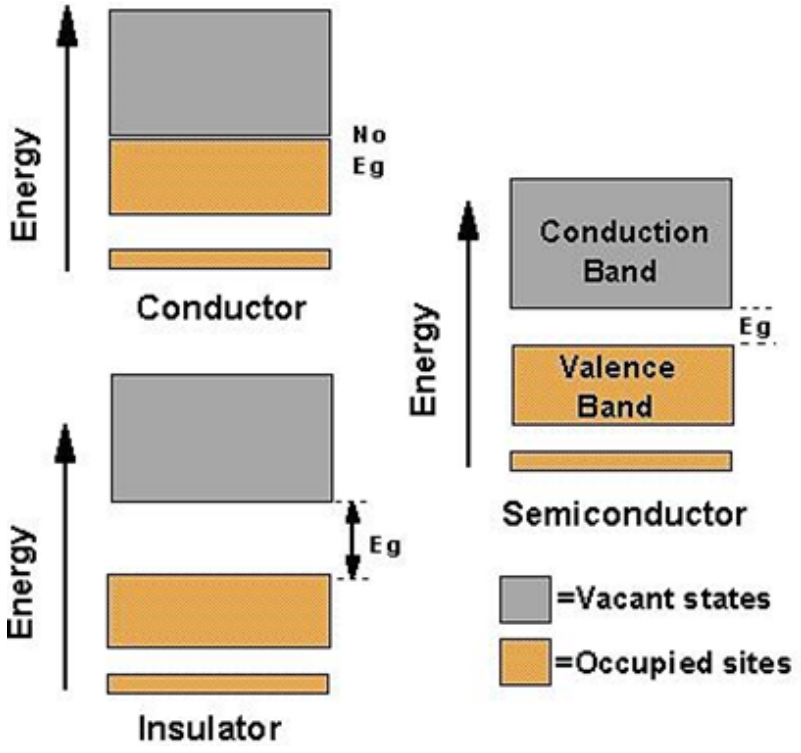


Figure 3.2: Energy band gaps for different types of materials.

The semiconductor is neutrally charged. This means that, as the negatively charged electron breaks away from its covalent bonding position, a positively charged "empty state" is created in the original covalent bonding position in the valence band. As the temperature further increases, more covalent bonds are broken, more electrons jump to the conduction hand, and more positive "empty states" are created in the valence band. The numbers of charge carriers in semiconducting solids, such as silicon, can also be increased by the addition of small amounts of foreign atoms into the otherwise pure material. If these so-called dopants carry fewer electrons than the host, an additional narrow band is formed in the energy gap, which accepts electrons. The electrons from the valence band can move easily into this acceptor band and the semiconductor is called *p*-doped or a *p*-type semiconductor. The introduction of such a dopant does not inject a charge into the system. It does, however, lead to the formation of additional states between the valence band and the conduction band, which were not present before. Alternatively, a dopant with more electrons than the host leads to a donor band in the energy gap and an *n*-type semiconductor [20].

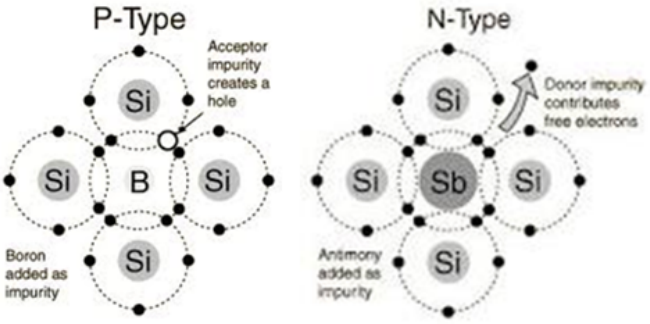


Figure 3.3: Schematic representation of p-type and n-type semiconductors in atomic scale.

Materials that has energy bands either completely empty or completely full is an *insulator*. The resistivity of an insulator is very large or, conversely, the conductivity of an insulator is very small. There are essentially no charged particles that can contribute to a current. Up to here it is tried to give some information about current flow mechanism in metals and other non-metallic solid materials conduct with electronically. All the informations above constitutes the main structure about our knowledge about current flow and conductivity. By using these facts we are now feel more confident to assert ideas about electrical properties about organic materials, especially polymers and hydrogels.In the following section it is aimed to

finalize thoretical backround with the most important part. It is now time to talk about ionic conductivity, which is more relevant to our study because conductive polymers and hydrogels may exhibit conductive property via ionic conduction due to their specialized internal structure.

It is now time to talk about ionic conductivity, which is more relevant to our study because conductive polymers and hydrogels may exhibit conductive property via ionic conduction due to their specialized internal structure [20].

3.2 Current flow in polymers and gels (Ionic conductivity)

Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase (the electrode) and a conductive solution, or electrolyte. A process of this kind can always be represented as a chemical reaction and is known generally as an electrode process. Electrode processes (also called electrode reactions) take place within the double layer and produce a slight unbalance in the electric charges of the electrode and the solution. Much of the importance of electrochemistry lies in the ways that these potential differences can be related to the thermodynamics and kinetics of electrode reactions. In particular, manipulation of the interfacial potential difference affords an important way of exerting external control on an electrode reaction [21].

In analogy to electrical conductivity in metals, ionic materials produce a current under an external applied electric field due to diffusion or movement of anions and cations. In order for an ion to move through a crystal it must hop from an occupied site to a vacant site. Thus ionic conductivity can only occur if defects are present. The two simplest types of point defects are *Schottky* and *Frenkel* defects [22]. One of the most important aspects of point defects is that they make it possible for atoms or ions to move through the structure. If a crystal structure were perfect, it would be difficult to envisage how the movement of atoms, either diffusion through the lattice or ionic conductivity (ion transport under the influence of an external electric field) could take place [23].

Ionic conductivity, σ, is defined in the same way as electronic conductivity $\sigma = nZe\mu$, where n is the number of charge carriers per unit volume, Ze is their charge (expressed

as a multiple of the charge on an electron, $e = 1.602189x10^{-19}$ C), and μ is their mobility, which is a measure of the drift velocity in a constant electric field. Table below lists the sort of conductivity values one might expect to find for different materials. As we might expect, ionic crystals, although they can conduct, are poor conductors compared with metals. This is a direct reflection of the difficulty the charge carrier (in this case an ion, although sometimes an electron) has in moving through the crystal lattice.

Table 3.1: Typical Values of Electrical Conductivity.

Material	Conductivity(S/m)
Ionic crystals	$< 10^{-16}$to10^{-2}
Solid elecrolytes	10^{-1}to10^{3}
Strong(liquid electrolytes)	10^{-1}to10^{3}
Metals	$< 10^{3}$to10^{7}
Semiconductors	10^{-3}to10^{4}
Insulators	$< 10^{-10}$

Before the spectecular work of Shirakawa and his collegues in 1977, polymers were known as good insulating materials. After publishing their study on halogen derivatives of polyacetylene, scientists w suddenly diverted their studies mostly on conductive polymers [24]. The conductivity mechanism is easy to understand, as current flows on alternating double and single bonds in polymer. In saturated polymers, such as polyethylene, all valence electrons are used in covalent σ-bonds. Hence, the gap between the valence band and the conduction band is very large and the material shows typical insulating properties [25]. In conjugated polymers a π system is formed along the polymer backbone.

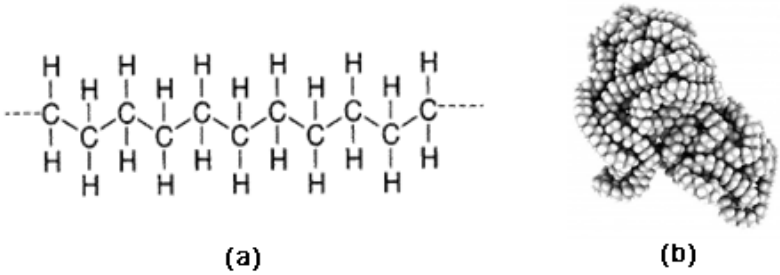


Figure 3.4: Simple model of polyethylene oligomer and particle polymer. (a)molecular structure of polyethylene. (b) A particle of insulating polyethylene polymer.

The carbon atoms typically involved in the formation of the polymer backbone form three σ-bonds with neighboring atoms and the remaining π orbitals typically described

as pz orbitals engage in the π system. In some conjugated polymers, such as polyaniline, nitrogen atoms are also involved in the conjugation path. Polyacetylene is the simplest conjugated polymer. Each carbon is σ-bonded to two neighboring carbon atoms and one hydrogen atom.

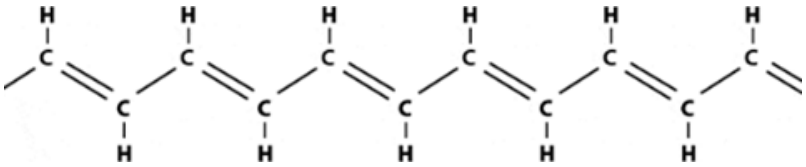


Figure 3.5: Molecular Structure of Polyacetylene.

If the carbon-carbon bonds were equally long, the remaining π electrons would be found in one half filled continuous band. In the case of polyacetylene, a lattice distortion leads to a repeat unit with two carbon atoms closer together and the next two carbon atoms further apart. Hence, the repeat unit can be described as -CH=CH- instead of -CH-. The electronic result is an energy gap between a completely filled π band and an empty π^* band. The energy savings due to the new band gap outweighs the energy cost of rearranging the carbon atoms [26].

This bond alternating structure is typical for all conjugated polymers. Since there are no partially filled bands, conjugated polymers are typically semiconductors. Similar to inorganic semiconductors, such as silicon, conjugated polymers show very low conductivities in their pristine state. However, since they are organic molecules, there is a variety of ways to introduce charges into this material and to radically change their electronic properties. The first way of charge introduction is so-called chemical doping. If, for example, Polyacetylene is treated with iodine, the latter oxidizes the polymer chain [27]. The polymer becomes positively charged and iodide is formed as counterion. The term doping is in some way misleading since it was originally used in solid state physics for the introduction of a foreign neutral atom into a host lattice, changing the electronic structure in that lattice. In the context of conductive polymers, doping refers to a chemical reaction oxidation or reduction. However, in both cases new electronic states are created and a previously semiconducting material becomes conductive. Both electron donating (*n*-type) and electron accepting (*p*-type) dopants, that is, reducing agents and oxidants, have been used to introduce charges into conjugated polymers and render them conductive. The charges can also be introduced

electrochemically. The necessary counterion is drawn from the surrounding solution [27].

If we talk about conductivity and electrical properties of gels we must start with the definition of polyelectrolytes and gel electrolytes. A polyelectrolyte gel is a charged polymer network with macro ions fixed on the polymer chains and micro counter-ions are localized in the network frame. Polyelectrolyte gels exhibit the ability to absorb a significant amount (up to 2000 times the polymer weight) of water within its network structure, but do not dissolve in water [28]. When a polyelectrolyte gel is interposed between a pair of plate electrodes and a DC current is applied, it undergoes electrically-induced chemomechanical contraction and concominant water exudation in the air. Polyelectrolyte gels exhibit various unique electrical responses different from those of linear polyelectrolyte solutions [29]. The replacement of the solvent by liquid electrolyte having high value of conductivity results in polymer gel electrolytes. They are generally salt-solvent-polymer hybrid systems in which first a salt solution is prepared and then it is immobilized with the help of a suitable polymer matrix. Since the first report of high conductivity in lithium ion conducting polymer gel electrolytes (Feuillade and Perche 1975), these materials are receiving much attention due to some of their unique properties like high value of conductivity at room temperature ($10^{-2} - 10^{-4}\, S/cm$), ease of preparation, wide range of composition and hence wider control of properties, good adhesive properties [21, 30].

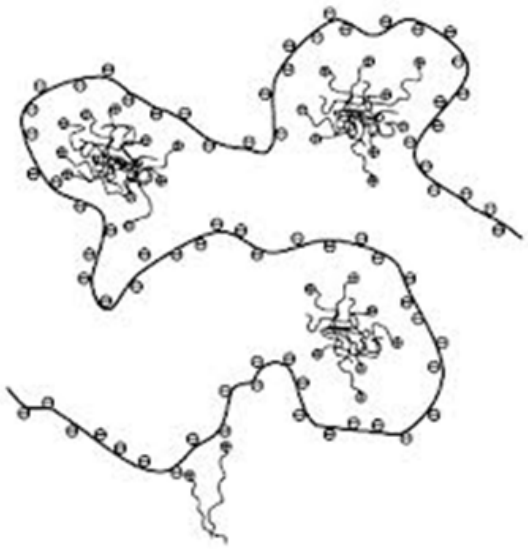


Figure 3.6: Molecular Structure of Polyacetylene.

Flexible, long-chained polyelectrolyte polymers are crosslinked by covalent bonds into a three-dimensional network. The network imbibes a solution and swells, resulting in a polyelectrolyte gel. The ionizable groups on the polymers dissociate, so that polymers carry fixed charges. The counterions and the co-ions, as well as solvent molecules, are mobile and can cross the interface between the gel and the external solution [31]. Polymer electrolytes and nowadays, particularly gel polymer electrolytes can be used in several different cases. In accumulators and supercapacitors they can replace liquid electrolytes, as they are more stable in the meaning of chemical and electric stability and also in electrochromic displays and devices as it is very handful to prevent devices from drying out or leaking electrolyte [21].

With the information of electrical conductivity in polymers and gels, it is finalized our theoretical background part. Next section will be about my experimental studies, outcomes and analysis about certain elecrtical properties of polyacrylamide hydrogels.

4. EXPERIMENTAL

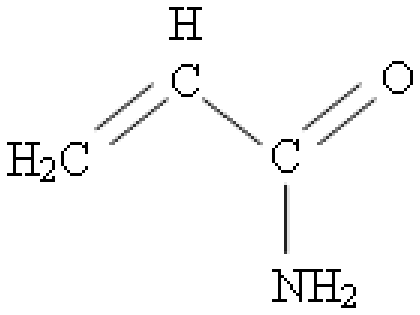
Throughout this whole study, it is aimed to enlighten ourselves about newborn property of neutral and ion doped polyacrylamide hydrogels. To do so, 2 Mol/L neutral and charged hydrogels are stynhesized with different crosslinker ratios in our laboratory, and tried to measure its electrical properties with our handmade system. Besides this investigation of DC current, we also measured the DC current during gelation of our solution to put forward more concrete ideas. Here it is important to note that no voltage was applied for current measurements.

In this part of the thesis, everything is tried to explained in a detailed manner including, sytnthesizing and preparing gels, designing of the measuring system and etc.

4.1 Synthesis of gels for current measurements

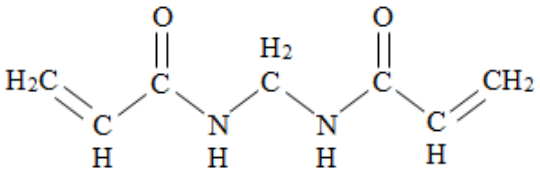
For measurements, sytnhesized gels are separated into two groups which are neutral and charged gels. The molecular structures and general informations about the molecules that is used in the synthesis are explained and illustrated below [32].

Monomer: Akrilamid (AAm)
Molecular Weight: 71.08 g/mol
Appearance: White – Crystal Powder
Molecular Formula: C_3H_5NO
Density: 1.13 g/cm^3
IUPAC Name: prop-2-enamide
Solubility in Water: 2.04 kg/L (25 °C)



Acrylamide is used as monomer throghout all studies, resultant gel was Polyacrylamide (PAAm) hydrogel.

Cross Linker: Bisakrilamid (BIS)



Molecular Weight: 154.17 g/mol

Appearance: White – Crystal Powder

Molecular Formula: $C_7H_{10}N_2O_2$

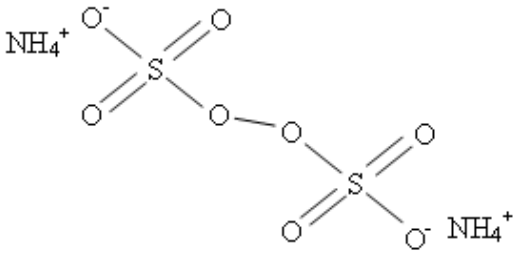
Density: 1.235 g/cm^3

IUPAC Name: N-[(Prop-2-enoylamino)methyl]prop-2-enamide

Solubility in Water: 0.01-0.1 g/100mL (18 °C)

BIS (N,N'-methylene bisacryrlamide) has the characteristic of establishing multiple chemical bonding, meaning multiple fucntionality which is four, it constitutes a network structure by bonding monomers with each other. As it is stated above this monomer is used as cross-linker during this study.

Initiator: Amonyum persülfat (APS)



Molecular Weight: 228.18 g/mol

Appearance: White – Crystal Powder

Molecular Formula: $(NH_4)_2S_2O_8$

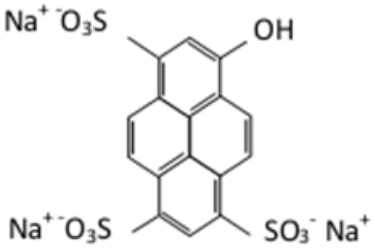
Density: 1.98g/cm^3

IUPAC Name: diammonium sulfonatooxy sulfate

Solubility in Water: 80 g/100mL (25 °C)

APS, ammonium persulfade is been used as initiator in this study. By thermal energy The oxygen bond breaks, and occuring radical initiates the reaction.

Doped Molecule: Pyranine



MMolecular Weight: 524, 38g/mol g/mol

Appearance: Yellow – Crystal Powder

Molecular Formula: $C_{16}H_7NA_3O_{10}S_3$

Density: 1.98g/cm^3

IUPAC Name: 8-hydroxy-1,3,6-pryenetrisulfonate

Solubility in Water: : 2.04 kg/L (25 °C)

Pryanine is used as doping molecule for charged hydrogels. Because of its structure it enables to ions to move and contribute the ionic conductivity [6].

When preparing pregel solutions, the required amount of monomer (AAm) and cross-linker (BIS) weighed on balance and solved in distilled water according to the stoichiometry. After obtaining solution, the tube is deoxyganated with Nitrogen gas for 20 minutes and sealed immediately before inserting into the heat bath in 60° C. Solutions are kept at least 24 hour in a heat bath to complete the gelation successfully. Obtained gels via free radical polymerization reaction are sliced 1.5 mm thickness each and kept in room temperature for one week. In order to eliminate the roughness of gels, they become smoother by using sandpaper to make them ready for electrical measurements. While synthesizing natural and ion doped Polyacrylamide gels, it is obeyed to the stoichiometric raitos for molecules which is defined in similar studies as (0.62 Mol/L AAm + 70 mg BIS/50 ml water + 50 mg APS/50 ml) [33].

In addition to this ratio, we also synthesized the gels by double and half amount of BIS that introduced in normal stoichiometric ratio. Stoichiometric ratio is defined for determining the minimum required amount of molecules to obtain gel. By changing the ratio of cross-linker, it is aimed to loose and tighten the network and investigate its influence on electrical properties.

The required amount of substances for 1ml Polyacrylamide gel is calculated and tabulated in Table 4.1.

Table 4.1: Stoichiometric ratios for synthesis of neutral PAAm gel.

AAm		BIS		APS	
mol/l	mg/ml	mol/l	mg/ml	mol/l	mg/ml
1	71.08	0.0146	2.258	0.0071	1.613
2	142.16	0.0293	4.516	0.0141	3.226
3	213.24	0.0439	6.774	0.0212	4.839
4	284.32	0.0586	9.032	0.0283	6.452
5	355.40	0.0730	11.290	0.0355	8.065

Schematic representation of Polyacrylamide network structure is given 4.1 [32].

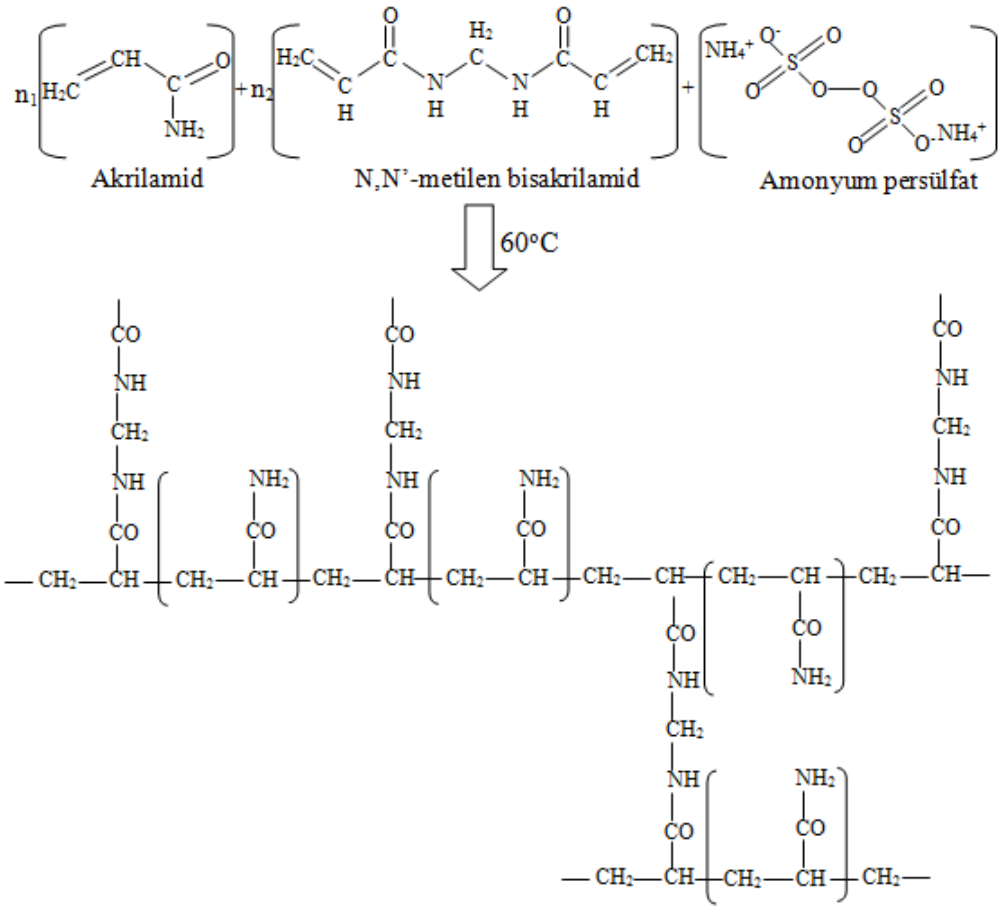


Figure 4.1: Schematic representation of Polyacrylamide network structure.

4.2 Experimental setup and designing of the system

Gels which has been synthesized in a heath bath under certain circumstances (sealed from the top, in 60°*C*) are sliced about 1.5 to 2.5 mm thickness and kept in an oven for nearly one week until they dried. After getting dried, two ends of sliced gels are smoothed by using sandpaper.

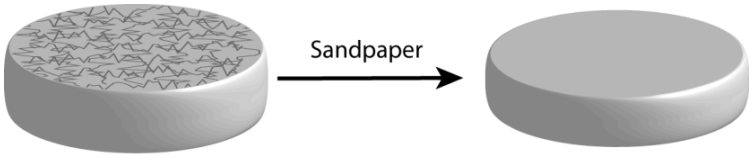


Figure 4.2: Sliced hydrogels before and after smoothened with sandpaper.

While making it smoother with sandpaper, sliced pieces of gels became thinner due to the friction between surfaces of the gel and sandpaper. It is continued to rubbing gel on sandpaper until it smoothness well enough and the thickness became about 1 mm.

After completing this task, our gels are ready to make measurement with our designed handmade system.

By designing system it is aimed to keep environmental effects stable so that our discussions and comments about the results would be more appropriate. Because our measurements taken with swollen hydrogels, it was very important to be sure about there is no contact with air, in order to prevent the water to be vaporized. It was also crucial to make the experiment in a dark site, because direct sunlight or light bulb could initiate any reaction as we familiar with photoinitiation reactions. In addition to all these constraints, Platinum and Aluminum electrodes should have been stayed still during the measurement.

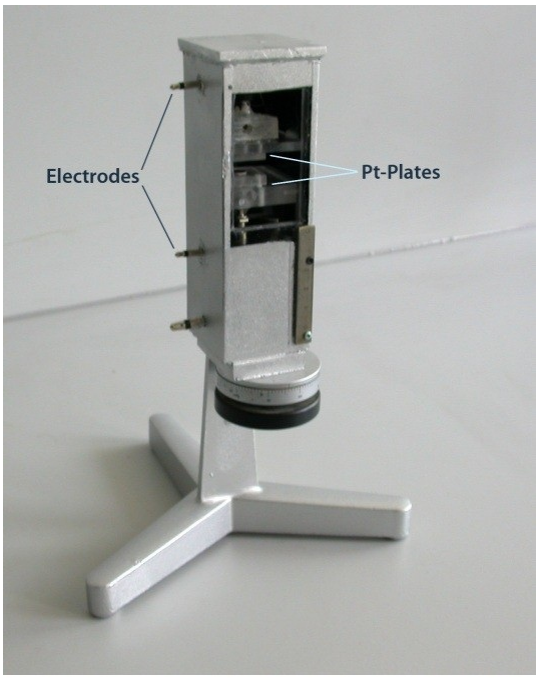


Figure 4.3: Designed system for current measurements of swollen gels.

As you can see from the figure, our system is opaque and electrodes are fixed so that there would not be any shift during the experiment.The system is kept closed by using an acrylic shutter in order to prevent the contact with air as it is stated above.

Besides making experiment with this system, numerous measurements during gelation has also been taken. To succeed that experiments we used plastic tubes and elastic tampons with platinum electrodes attaches on one side, and make the measurements under $60\,^{\circ}C$ in the heat bath. Our intention was to be sure that there was no leakage of solution from the tube or any water from heat bath.

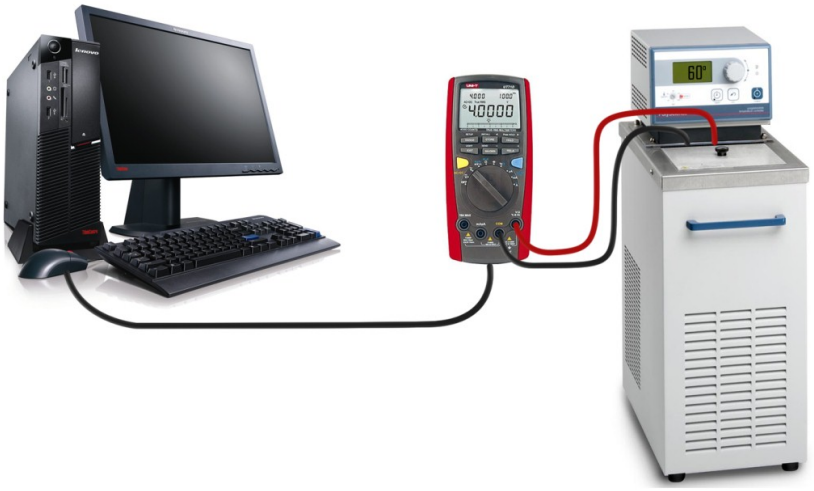


Figure 4.4: Experimental set-up for current measurements during gelation.

4.3 Current Measurements

In this part, the results of the current measurements of PAAm hydrogels during the gelation and after the gelation will be discussed. In both conditions no potential difference was applied between the terminals of the cell which contains the sample.

4.3.1 Current measurements during gelation

Here 15 ml stock solution of 2 Mol/L neutral and 2 Mol/L ion doped, which includes 5x10^{-4} Mol/L pyranine as doping agent, pregel solutions were prepared. The chemical composition of the pregel solutions are given in Table 4.1. After bubbling the stock solutions with nitrogen gas for 10 minutes, the stock solutions were put in refrigerator. For the measurement, enough amount of stock solution was transferred to the cell of the measurement system which was kept at 25$^{\circ}C$ and 60$^{\circ}C$ in a heat bath and the current values with respect to time were recorded automatically via a computer based high sensitive multimeter. Before discussing the results of the current measurements during the gelation, the results of the current measurements of the distilled water must be discussed first as background information. Here it was aimed to see whether the characteristics of the current have been affected by water or simply to find out that if the distilled water make any contribution to the current flowing through the pregel solutions.

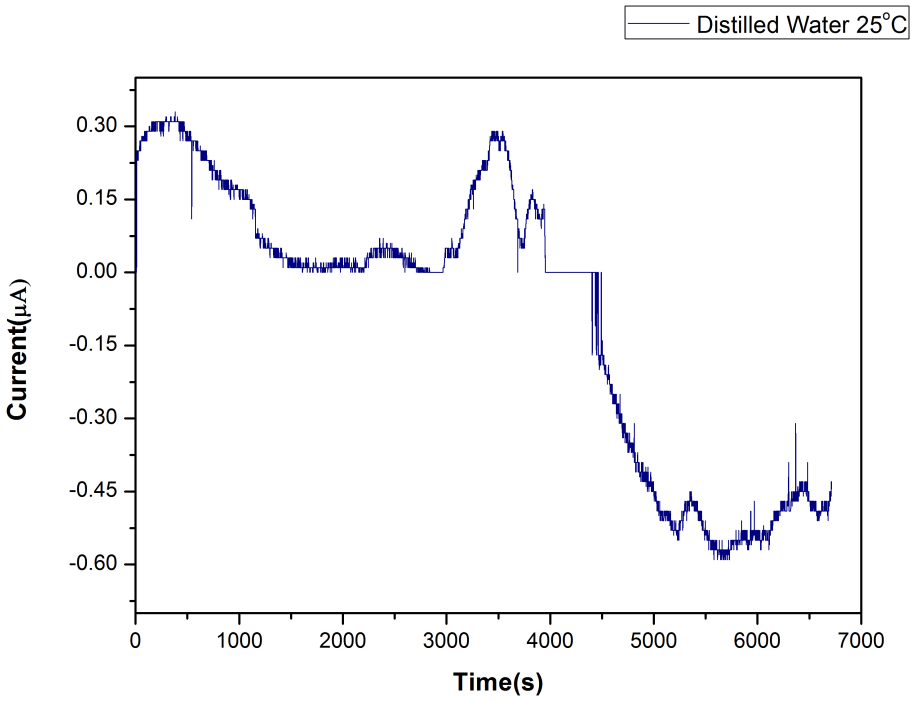


Figure 4.5: Current measurement for disttiled water in 25°C.

The purpose here was to see if any current exist in the system without any pregel solution. If it would be observed such a current in the system, there were a high possibility that the current during the gelation is affected directly by distilled water. Distilled water has a pH value around 5.5, which could contribute the current with its H^+ ions in acidic manner.After making measurements a few times it is observed that the current produced by distilled water is relatively ignorable if we compare it with the current of pregel solution. In distilled water the current increases up to 0.30 microampere (μA), which is very low in contrast to the pregel solutions. From the Figure 4.5: Current measurement for distilled water in 25 $^\circ C$ we can also see that the current is changing its direction after one hour approximately. This behaviour reinforce our conclusions about distilled water because if something triggered the current in the system it should have been in the same direction forever. After analyzing this result, the experiment is repeated with same distilled water this time at. 60 $^\circ C$. This temperature is chosen because we did all the gelation experiments in 60 $^\circ C$. Increasing temperature may trigger something in the system so that we observe a DC current.

The result of second measurement were meaningful because if we set the temperature to 60 $^\circ C$, we see an increase in the DC current.This result would be very useful if it was measured with all the remaining parameters stayed same.But the amount of water

and physical situation of electrode contacts may differ the result. Considering this fact it is avoided to give a conclusive comment about the increasing DC current but we can still say that the increase may come from the increasing temperature which possibly gave moving ions some kinetic energy. In addition to these comments we thought that the fluctuation of this current from one direction to another, may cause from the multimeter. In order to measure the current flow in the system, the multimeter could be apply some alternating voltage which may give rise to a current in both directions.

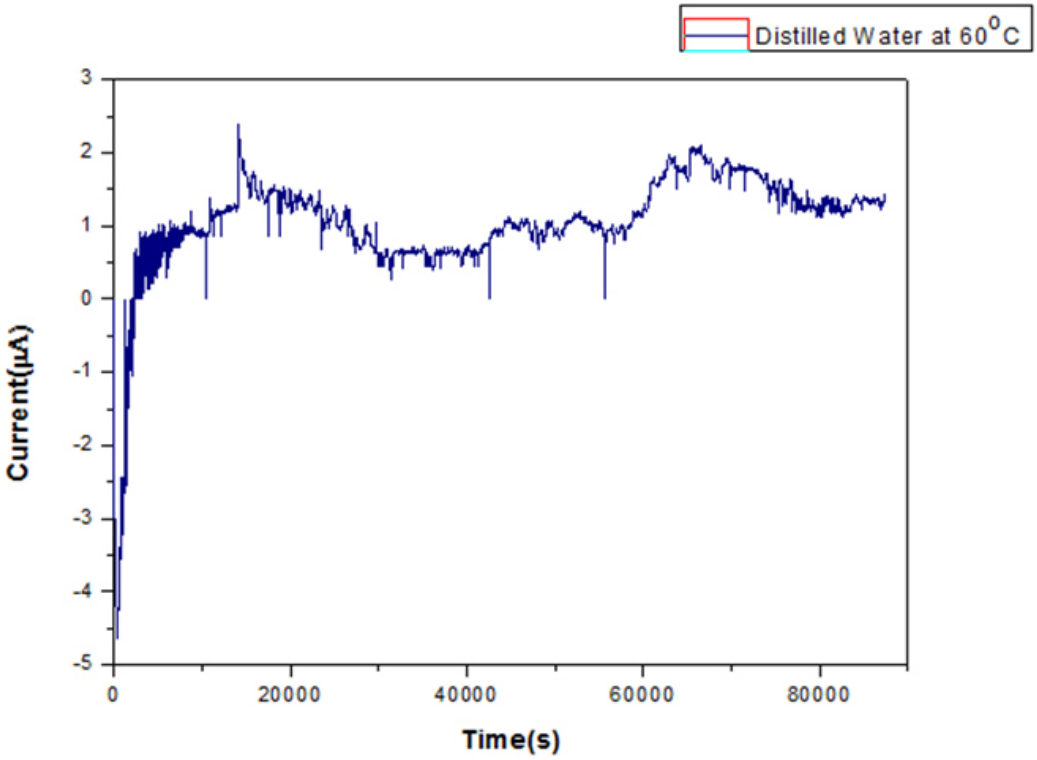


Figure 4.6: Current measurement for disttiled water in 60°C.

4.3.1.1 Measurement of neutral gels during gelation

Here the current measurements were performed during the gelation experiments. First we started with normal stoichiometric neutral pregel solution.

According to ratios which are tabulated in Table 4.1, we prepared 15 ml solution and kept it in a cell. For each measurement approximately 3-4 ml solution is consumed because the volume of the cells were around 3-4 ml. After filling the cell with the solution, the remaining part is kept in refrigerator roughly in $-10\,^{\circ}C$.

Each measurement has been taken for 24 hours or less and this procedure is repeated four times with every single sample. The stock solution was kept in refrigerator because the initiator molecule Ammoniun persulfade (APS) could initiate the gelation

at room temperature before we use them [34]. As we can see from the Figure 4.7 the DC current increase up to a maximum level, making a peak and starts falling down immediately.

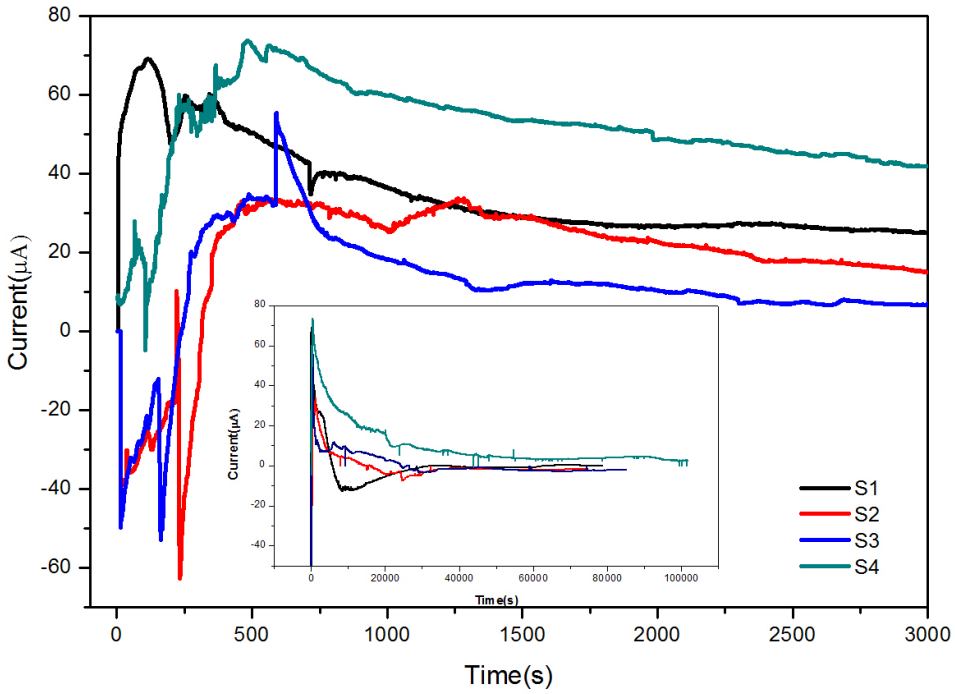


Figure 4.7: Current measurements during the gelation of 2 Mol/L pregel solution with normal stoichiometry. The inset figure shows the whole range of time during the gelation. S1, S2, S3 and S4 show the repeated experiments for the same concentrations.

If we compare four of these samples in a row, all of them are making a peak then suddenly current decreases and goes to 0 μA in a general perspective.

The peak point may represent the critical point pc which has the meaning of the starting point of formation of network or simply gelation. It is also noticed that except first sample, for all measurements, direction of the current changes. This could be very meaningful because the current flow in one direction should indicate ion movement from one end to the other.

Even if we put stock solution under very low temperatures, they still may had a chance to react and polymerization could start.After observing these results the same experiment repeated with neutral pregel solutions with amount of cross-linker (BIS) is doubled.

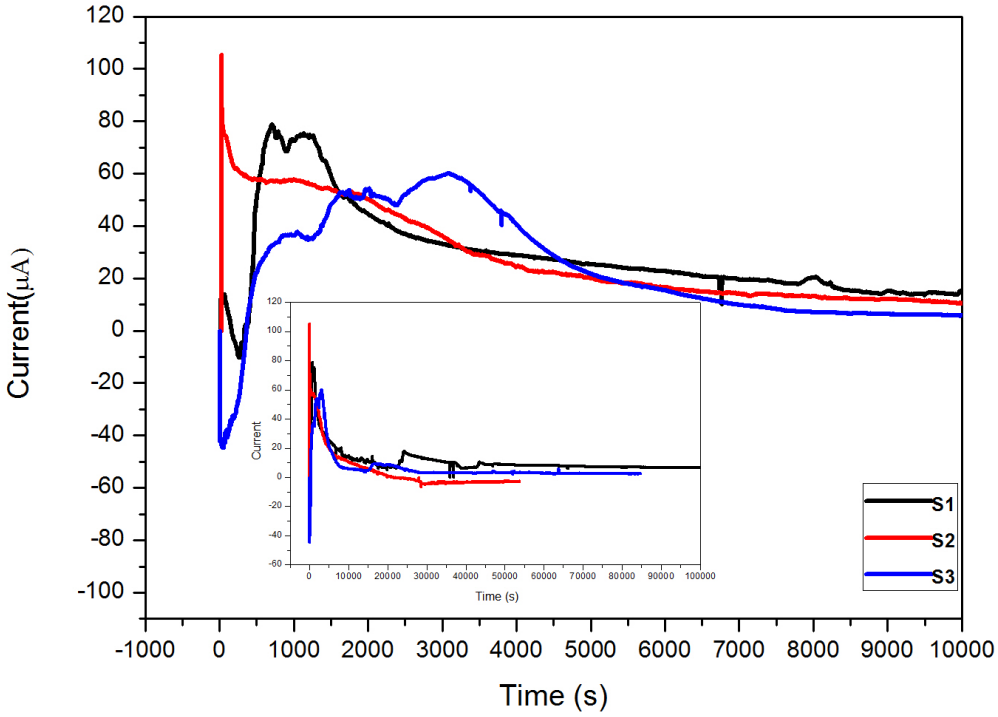


Figure 4.8: Current measurements during the gelation of 2 Mol/l pregel solution with doubled cross-linker. The inset figure shows the whole range of time during the gelation. S1, S2, S3 and S4 show the repeated experiments for the same concentrations.

Parallel to the results of the first part, again it is observed some oscillations immediately after measurements were started. If we compare the results of Figure 4.7 and Figure 4.8 from the smaller graphs, we can say that changing ratio of cross-linker molecule does not effect the general behaviour of the system. Because the network is formed in 1500-4000 seconds, the remaining parts are similar to each other. It is also verified by checking the cell in heat bath that the gelation occurred after 20 to 45 minutes.

4.3.1.2 Measurement of ion doped gels during gelation

Same technique is used for Pyranine doped gels. To prepare the gels doped with the charged molecules, pyranine was added to the pregel solutions in different concentrations. That is, the other chemicals: monomer, initiator, crosslinker and water were mixed with pyranine when the solution was prepared for polymerization.[ref]. Obeying the stoichiometric ratios for neutral PAAm gel, we needed (0.62 mol/l AAm + 70 mg BIS/50 ml water + 50 mg APS/50 ml) amount of molecules as it was mentioned

before. In addition to this, if we doped with pyranine for $5x10^4$ mol/l for 1ml pregel solution, we would need 0.26 mg pryanine molecule. We prepared 15 ml solution for measurements so required amount of pyranine molecule was 3.9 mg.

In Figure 4.9 below, it is depicted the gelation of 2 Mol/L PAAm gel with $5x10^{-4}$ mol/L pyranine doped, with normal crosslinker ratio.

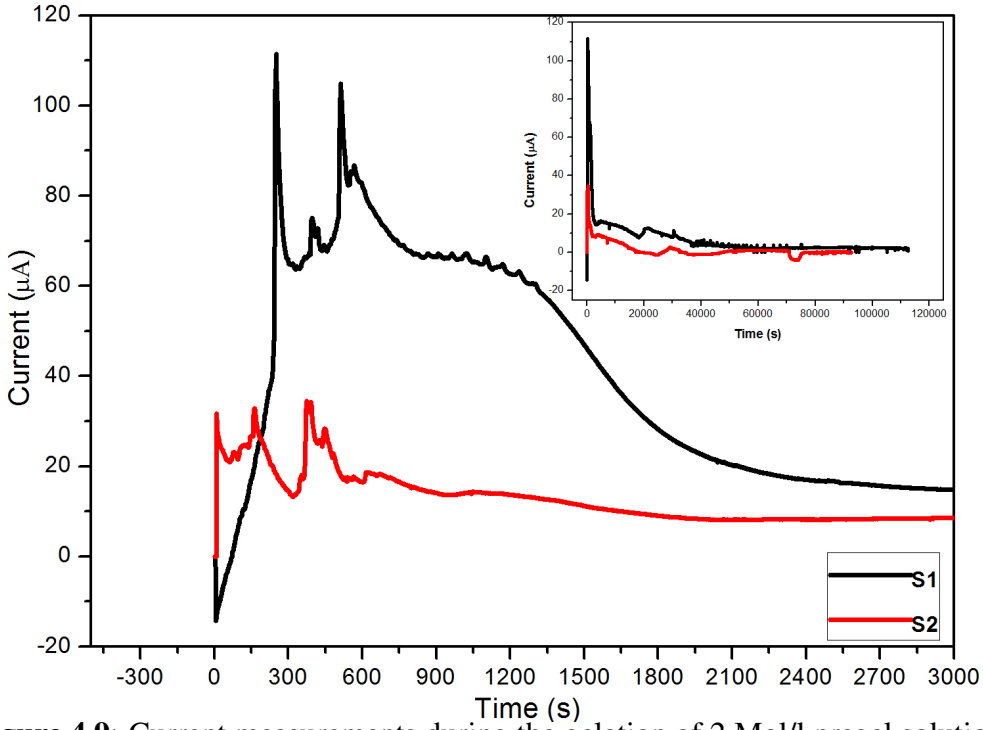


Figure 4.9: Current measurements during the gelation of 2 Mol/l pregel solution with $5x10^{-4}$ mol/L pryanine doped.

Like we did in previous measurements for neutral pregel solutions, we kept remaining solution in refrigerator under $-10°C$. After the first sample is put in heatbath, multimeter started to measure the results immediately.

It is known that the pyranine was free in the sample before the polymerization, and bound chemically to the strands of the polymer via radical addition during the polymerization. So it was really important to monitor the electrical current results while pyranine molecules binding chemically to the strands of polymer. The pyranine binds to the polymer chains, over its OH group, chemically during the polymerization as it is discussed in detail in references, and they form stable charged sites doped with positive counter ions. Thus, the polyacrylamide gel is doped with pyranine having SO^{-3} ions as side groups and Na+ as counter ions, so-called p-type gel. In Figure 4.10

there is a schematic depiction of pyranine that is bounded to polymer strands during polymerization, or more specifically gelation reaction.

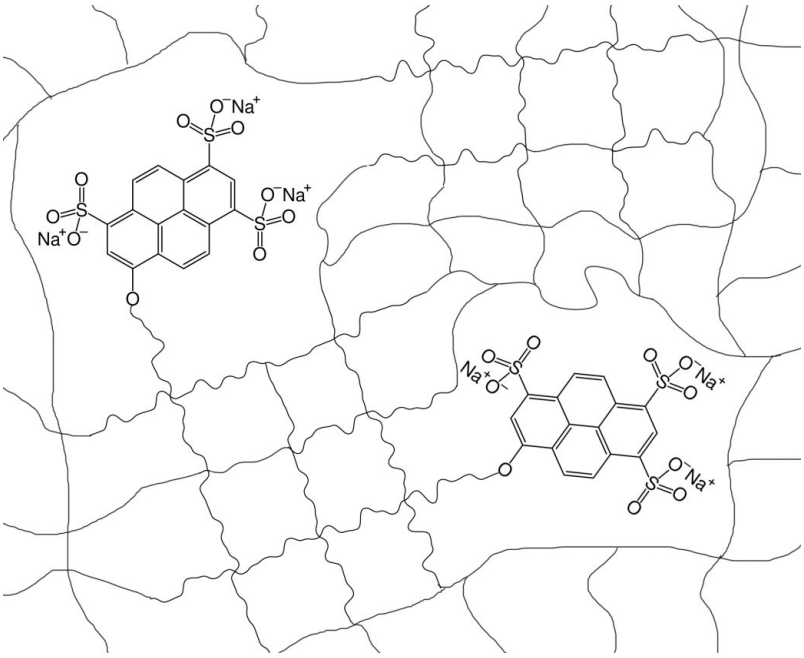


Figure 4.10: Schematic representation of (*p*-type) gel doped with pryranine.

In Figure 4.9, it is tried to depict both first 50 minutes of reaction and whole measurement which spanned around 120000 seconds, approximately 32 hours. Because gelation occurs at first hour of the reaction, we put first 3000 seconds as main graph, then whole measurement is added as inset to see the general trend of the current measurement.

S1 is the first sample that is used for measurements and S2 is the second.While the measurement is going on, S2 is kept in refrigerator with ammonium persulfade added, meaning that between two measurement there is approximately one day and a half. Before making any comment about these two measurements we again have to notice that the included initiator (APS) could start the polymerization very slowly even if the temperature is very low.

As it is observed from the Figure 4.9, Sample 1 is started around -20 μA and increased up to 120 μA while making a sharp peak. Reaching 0 μA and then increasing to 120 μA means, the current changes its direction by reversing the sign from negative to positive then continued to 120 μA and started to decrease and increase again in a short time interval.

If we look at second sample S2, the behaviour in first 3000 seconds is very similar except one difference. In S2, the current did not change its direction which was always positive and going to zero. After passing first 3000 seconds, the currents in both cases followed same path; they decayed very sharply and gone to 0 μ. Before explain these experimental results, it is beneficial to give some information about the concept of blob as preliminary workout. The internal structure of polyacrylamide gels consists of polymer dense regions with different densities, which are denoted as blobs [35]. The density difference between these blobs decreases when a gel is doped with charged molecules as has been shown experimentally and theoretically acrylamide (AAm)-based hydrogels exhibit inhomogeneous cross-linking distributions. Highly intra-molecular cross-linked blob clusters are formed in the pre-gel period due to the high extent of cyclization acting as junction points.

Here, one may consider that these different sized blobs could possibly played a key role concerning about the current flow for those two cases.When reaction is started at $60^{\circ}C$, different sized blobs and blob clusters are started to form.The different sized blob means different number of Na+ counter-ions in the system which was affecting the current flow. Forming fatherly bigger blobs will hold more counter ions and this trapping affect will alter the current flow in S1 and S2. Following the forming of blob clusters system will stabilize and current flow will cease due to decrease of the mobility of counter ions in the network.

Following this experiment, it is then measured for DC current with double cross-linked pre-gel solution which has been doped with same amount of pryranine molecule as in first part.

In the first hour of reaction, current for both for two samples were not stable, meaning that for S1 it was giving two peaks which are close to each other and for S2, the peak was appeared in 360th second or sixth minute. The maximum values for currents of S1 and S2 were nearly the same. This similiarity on the insentisities of the currents were attributed to BIS concentration, which was doubled according to the stoichiomtery. In contrast to first measurements with normal stoichiomtery, in these measurements it is observed that the current changed its direction in both samples.

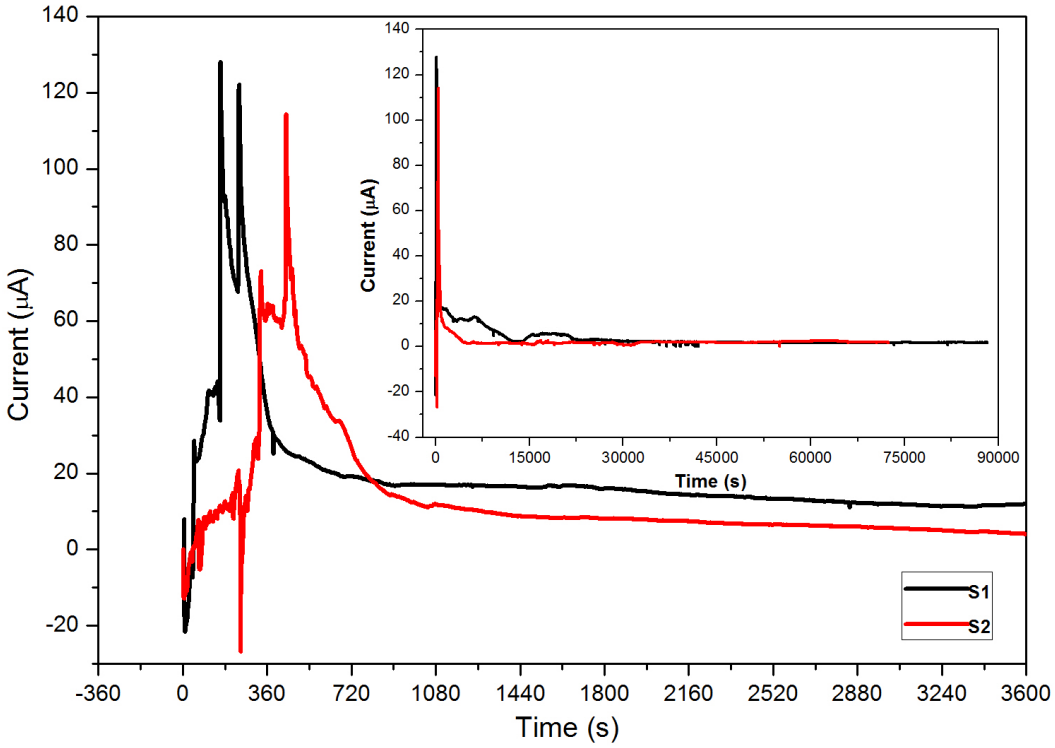


Figure 4.11: Current measurements during the gelation of 2 Mol/l double cross-linked pregel solution with 5x10-4 mol/L pryanine doped.

This behaviour can be explained in this way; even crosslinker (BIS) molecule mixed homogeneously in pregel solution, at the moment we make the experiment in heatbath, the random distribution of crosslinker momoners will react with acrylamide monomer and bind them. The density difference of crosslinkers in the sample may cause different current flow either from left to right or visa versa.

4.3.2 Current Measurements for hydrogels

In this section of the study, current measurements have taken for the gels, that were already cut and sliced for experiments.By using the experimental system in Figure 4.12, these measurements have been taken with Pt-Pt electrodes with two different geometries and with Pt-Al electrodes. By changing the geometry of electrodes, it is aimed to see the influence of different shaped electrodes on the system so to the current and, with changing the type of electrodes, is used to see the disparity between the same and the different metal electrodes.

Figure 4.12: Schematic representation of the experimental set up for measurements.

4.3.2.1 Measuring with platinum-platinum electrodes

We begin with Platinum-Platinum electrodes with same geometry, in disc shaped. In the Table below the dimensions, degree of swellings (or mass ratio) and the types of gels which were used for current measurement were presented.

Table 4.2: Dimensions and swelling degrees of prepared gels for Platinum-Platinum measurements.

	R_0(mm)	d_0(mm)	m_0(g)	R_1(mm)	d_1(mm)	m_1(g)	$\triangle m/m0$
H1	4.05	0.80	0.0148	4.65	1.30	0.0296	1.0000
H2	4.60	0.90	0.0144	7.40	1.30	0.0455	2.1597
N1	4.8	1.40	0.0225	5.50	1.42	0.0455	1.0222
N2	4.00	0.85	0.0149	5.50	1.00	0.039	1.6174
D1	4.30	0.97	0.0142	5.20	1.35	0.0278	0.9577
D2	4.10	0.60	0.0095	4.70	0.90	0.0286	2.0105
HP1	4.05	0.85	0.0125	4.90	1.00	0.025	1.0000
HP2	4.10	0.95	0.0151	6.45	1.65	0.0449	1.9735
NP1	4.37	1.00	0.0165	5.25	1.40	0.0338	1.0485
NP2	4.20	0.80	0.0136	5.10	1.50	0.0308	1.2647
DP1	4.20	0.90	0.0151	4.75	1.30	0.0302	1.0000
DP2	4.10	0.75	0.0127	6.50	0.98	0.0385	2.0315

As it can be seen from the Table 4.2 each type of gel is measured twice by changing the mass ratio ($\frac{\Delta m}{m_0}$). Reminding from Equation 2.2, the degree of swelling ratio can be approximated as the ratio of weight difference between swollen and dried gel to dried gel, considering that the density difference between the water and polymer is small enough. Each type of gel is measured twice with having the degree of swelling is 1 and 2. By doing this it is aimed to see some difference in the current rising from the free volume of polymer chains due to increasing volume. Gels are named in a simple

manner; the gels prepared with normal stoichiometric ratio are denoted as N1 and N2, while double crosslinked gels are denoted as D1 and D2 and gels which prepared with half amount of crosslinked ratio is denoted as H1 and H2 where the numbers indicate the degree of swelling for each gel.

Similarly pyranine doped gels are named with the same logic. This time it is added the letter "P" indicating that the gel is doped with pryanine.The doping concentration was the same for all those charged gels, which was $5x10^{-4}$ mol/L.

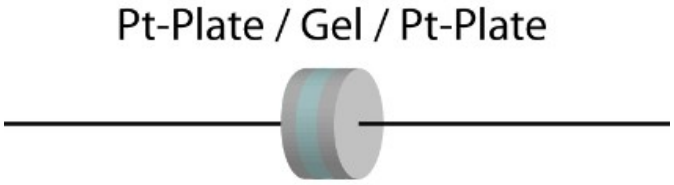


Figure 4.13: Schematic representation of Pt-gel-Pt configuration.

After making experiments with every single gel from Table4.13, no considerable DC current was observed. The only thing that was observed is some single pulses. These pulses were have some intensity around 0.2 and 0.8 μA. This result showed that in order to observe a current, there should have been some factors which could trigger the current flow similar to applied voltage or electric field.

Having the electrodes with same configuration in shape, somehow constitutes a kind of symmetry, that prevents ions to move along a direction. In order to distrupt this balance, the geometries and the types of the electrode were changed. In the following section the measurements with different geometrical shaped electrodes are discussed.

4.3.2.2 Measuring Platinum Electrodes with Different Geometries

To overcome this situation mentioned above, this time a different method is applied to see if any DC current within the gel. Instead of placing the gel between the two circular discs, this time we put it between a platinum disc and a platinum needle as shown in the Figure 4.14;

The expected result was that the current will flow to some direction due to this geometrical difference between these two metal electrodes. The different geometry causes an ionic current flow in a certain direction because of the different interactions of the ions near the interfaces of the gel with the electrons of the electrodes.

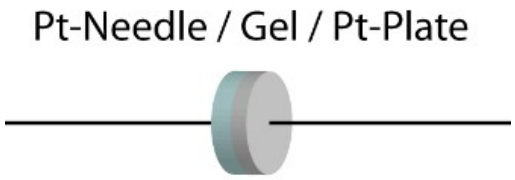


Figure 4.14: Schematic representation of Pt needle-gel-Pt configuration.

Table 4.3: Dimensions and swelling degrees of prepared gels for Platinum-Platinum needle measurements.

	R_0(mm)	d_0(mm)	m_0(g)	R_1(mm)	d_1(mm)	m_1(g)	$\Delta m/m0$
H1	4.1	0.8	0.0136	5.1	1.05	0.028	1.0588
H2	4.25	1.2	0.0194	5.7	1.75	0.058	1.9897
N1	4.35	1	0.0186	5.5	1.75	0.0392	1.1075
N2	4.2	1	0.018	6.75	2	0.0563	2.1278
D1	4.15	1	0.018	5.2	1.35	0.036	1.0000
D2	4.2	1	0.0144	6.7	1.2	0.0444	2.0833
HP1	3.9	1.15	0.0194	5.35	1.6	0.038	0.9588
HP2	4.1	1.17	0.0197	6	1.6	0.057	1.8934
NP1	4.1	0.95	0.0175	6	1.6	0.057	2.2571
NP2	4.1	1.08	0.0196	7	1.75	0.0598	2.0510
DP1	4.15	1	0.0174	5.25	1.35	0.0346	0.9885
DP2	4.1	1	0.0156	6.9	1.65	0.0423	1.7115

As it was given in Table 4.2, the classification of gels is the same. For each measurement it is tried to prepare gels which have a degree of swelling 1 and 2 respectively. As it can be seen from the last column of Table 4.3, the degree of swelling for each gel were nearly 1 and 2. The minor deviations from the desired degree of swellings come from the elapsed time to insert them in to our measuring system. We put the gel as quick as possible to the system when it reaches the desired degree of swelling, it was inevitable for some water molecules to vaporize. All these small deviations on the degree of swelling are ignorable effects on our current measurements, without effecting the general behaviour of the DC current vs. time scale.

Here the results of the experiments are discussed according to two criteria; first the results discussed according to the degree of swelling of the gels and after it is discussed according to their crosslinker (BIS) concentration.

As we see from the Figure 4.15, swollen gels exhibit different characteristics of current flow mechanism depending on their internal structure. Because it is focused on the effects of degree of swelling on the gels, we left this issue just for a moment and try to analyze only for swelling degrees. To do so, we need to see the other figure and

compare two of them. In Figure 4.16 it is shown the current trends which have a swelling degree around 2.

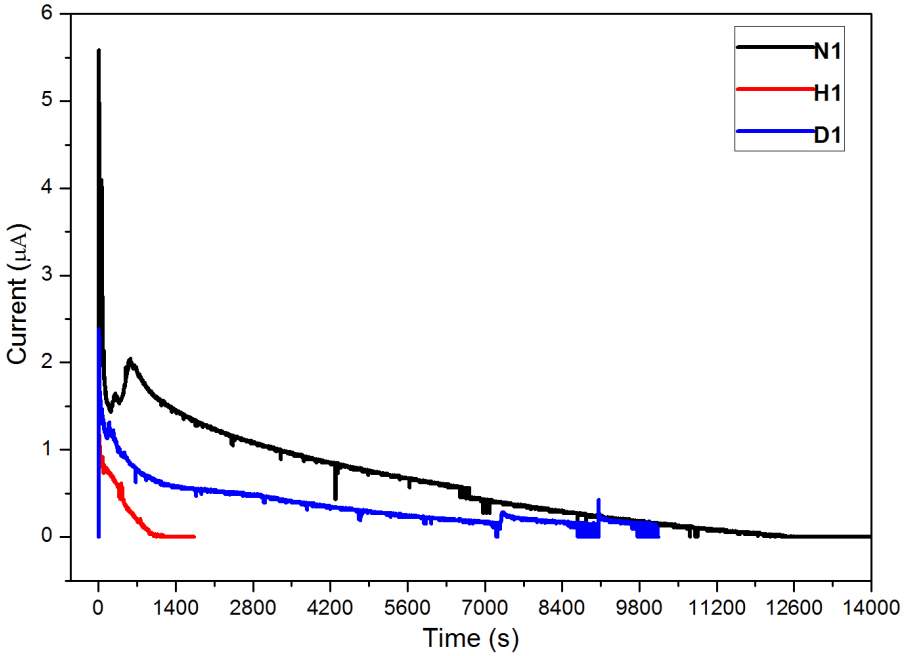


Figure 4.15: Current measurements for neutral gels of swelling degree around 1.

One of the most important result of the figures is that the current flow is taken more longer time with increasing swelling degree for all gels N1, H1 and D1. If we deal with them separately, for N1 the current was flowing until 12500th second which is approximately three hours and a half, while in N2 the current is ceased around nearly in 15000 seconds. This effect on the gel H1 and H2 is more dominant. If we compare the results from the Figure 4.15 and Figure 4.16, we can easily see that the duration of current flow is increased up to 5 times. Same thing is happening with the gels D1 and D2. From these observations it can be said that the degree of swelling directly affects positively to current flow for three different hydrogels.

This can be explained as follow: when the gel is swollen more and more, the counter ions which were trapped in blobs become free to move gradually. When this blobs start to swell by imbibing water, the counter ions diffuse into water at some rate. Because undoped neutral gels are more inhomogeneous than that of the doped ones with pyranine, the blob structures are more dense which cause current intensity get lower [35].

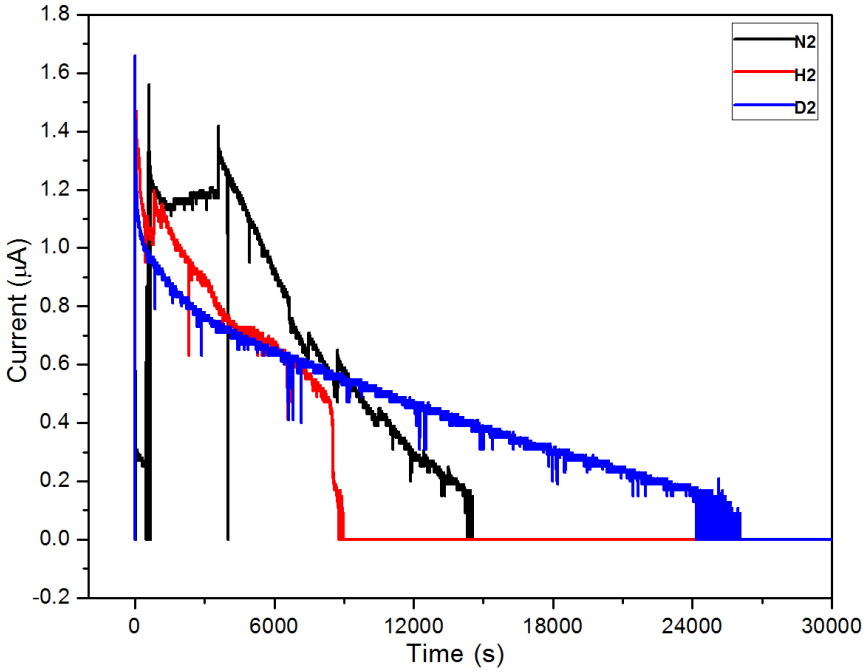


Figure 4.16: Current measurements for neutral gels of swelling degree around 2.

After completing this discussion it is time to put some ideas forward regarding the gels whose internal structure is different from each other. By saying internal structure it is implied their network formation. In the gels D1 and D2 the network is the most tighten one because it has double amount of crosslinker monomer to the gels N1and N2. By the same logic, the gels H1 and H2 has half amount of crosslinker inside meaning that their network is more loose according the all other gels.

Using the information in Figure 4.15 this time it will be discussed that whether the current flow is affected by this tightness or looseness of network. In N1, the current is rapidly decaying until 1.5 μA and suddenly increases up to 2 μA by making a peak, then continues to decrease until it reaches to 0 μA. Here there are two mechanisms. First, free ions in the water move through a certain direction resulting a current. While this ion movement become smaller when it approaches to 1.5 μA, the current is making a peak by increasing its intensity. The reason of this peak is that the coiled blobs are start to uncoil and become loose, which results an increase on the intensity of the current. This property did not appear in the other gels D1 and H1 because the BIS concentration was altered form the normal stoichiometry. This experiment is repeated

with pyranine doped gels as well as in neutral ones and the results are summarized in Figure 4.17

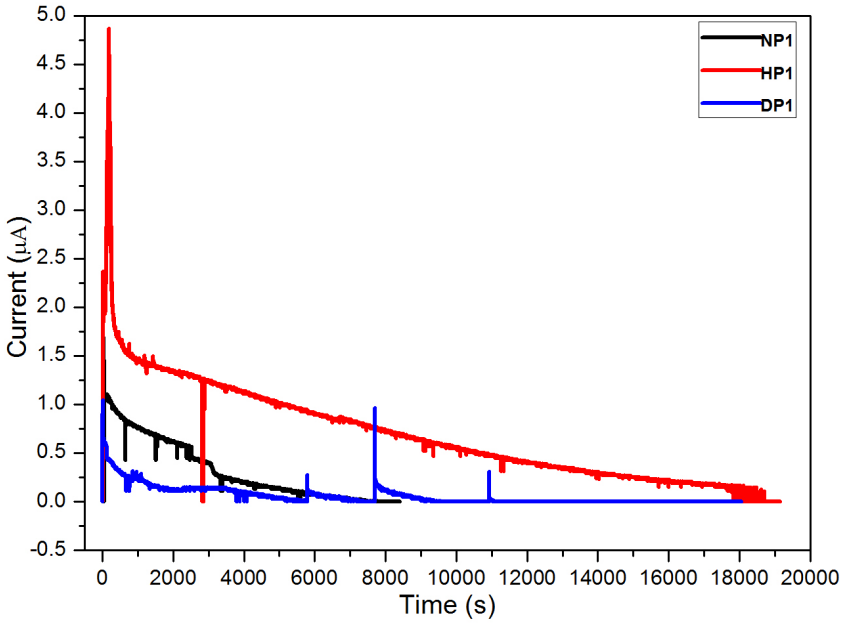


Figure 4.17: Current measurements for charged gels of swelling degree around 1.

As we did in the first part with the neutral gels, this time experiment is conducted with pyranine doped gels. To analysis the results in Figure 4.17; we need another figure which represents us the results of the gels whose degree of swelling is around 2.

The first remarkable conclusion form the Figure 4.17 and Figure 4.18 is the intensities of currents does not depend on the degree of swellings as they were in the neutral gels. When it comes to elapsing time for current flows, there is a peculiar behaviour for these gels which is the duration of the current did not changed significantly for H and D type of gels. As we see from the Figures above they are nearly same for both degree of swelling 1 and 2.

The only different result is observed from the gel NP1 and NP2 which are the gels synthesized according to normal stoichiometry. In N1 the duration of current was 7500 seconds, nearly 2 hours and a half but when we make it swell two times and measure the current, this time reaches up to 20000 seconds meaning 5 hours and a half. The reason of this behaviour could not be explained definitely but it is attributed to intrinsic property of the gels.

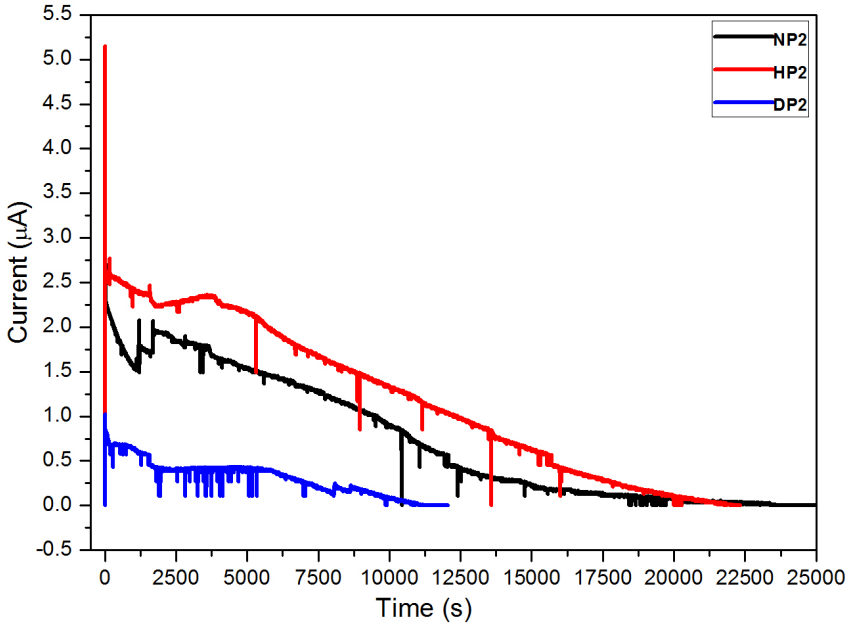


Figure 4.18: Current measurements for charged gels of swelling degree around 2.

Secondly if we give some comments about BIS concentration of the charged hydrogels, this time we see a different result than the neutral gels. In the H type of gels, which were synthesized with half of the crosslinker concentration according to stoichiometry, the current were making a sharp peak around 5.5 μA in the first 15 minutes of the experiment, then start to decrase as it happens for the other gels. All the gels are making a peak with some intensities of current but H type of gels have the most insensive and sharp peak among the others. In addition to these, it is also observed that the double crosslinked gels are making serious oscillations in the swollen state where it was equal to 2. When we tighten the network structure it will be difficult for pyranine counter ions to move freely in water. But after we swell the gel up to some level, it is obvious from the Figure 4.16 that these counter ions found a chance to move in water and contribute to current.

To finalize this section it can be concluded that pt-gel-needle configuration definitely produce some current in various intensities and this current were always positive meaning that the currents were flowing always in the same direction that was from disc to needle side, but there are some doubts and uncertainties about the reasons that affect the intensity and the duration of DC current for whole experiments.

In the last part of the study, this current measurement are conducted by using different metal electrodes, namely Platinum and Aluminum.

4.3.2.3 Measuring with platinum-aluminium electrodes

In this final part of the study, it has been used a different technique that would gave us a novel idea about the electrode effects on the current flow. As it is mentioned above sections, there was no observed DC current for platinum-platinum contacts because these same contacts were constitute a kind of symmetry that current could not flow within the solution. Because trapped ions inside the gel structure, cannot be triggered themselves in order to observe any current.

Here it is tried to show that the different metal electrodes distrupt this balance or symmetry and let the current flow throughout the swollen gel. These experiments were performed with the same system just replacing one of the platinum electrodes with aluminium. As you can see from the Figure 4.19 below system was quite simple.

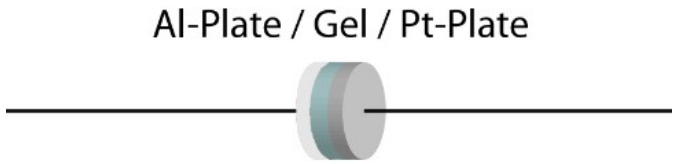


Figure 4.19: Schematic representation Al-gel-Pt configuration.

Paralleled to previous experiments the gels cut into 1 mm diameter thickness and smoothened with sandpaper. The physical properties of the gels as diameter, radius and the weight are tabulated in Table 4.4

Here it was aimed to swell the gels up to two and three times on weight meaning swelling them to the degree of 1 and 2, referring from Equation (2.2), but due to environmental factors such as vaporization the results are a little deviated from the desired values. It is started with neutral gels firstly.

When one of the electrodes replaced with Aluminum and repeated the same measurement, a notable difference now becomes obvious. The intensity of the DC current is much more greater than that of the experiments which has been made with needle. It is almost 6 or 7 times greater than the platinum plate-needle system showing that the different type of metal electrodes would interact ions in a different way. This difference is producing the current greater but duration of the current was shorter.

Here it can be said that Aluminum is an active metal which belongs to group 2A in periodic table. Increasing intensity of the current may be explained in such a way that Aluminum interacts with polymer surface in unique way. Because polymeric gel is consisting of water mostly when it make a contacts with Aluminum metal, it may cause Aluminium to oxide and this oxidation may give rise to the current even in a very short time [36].

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2(g)$$

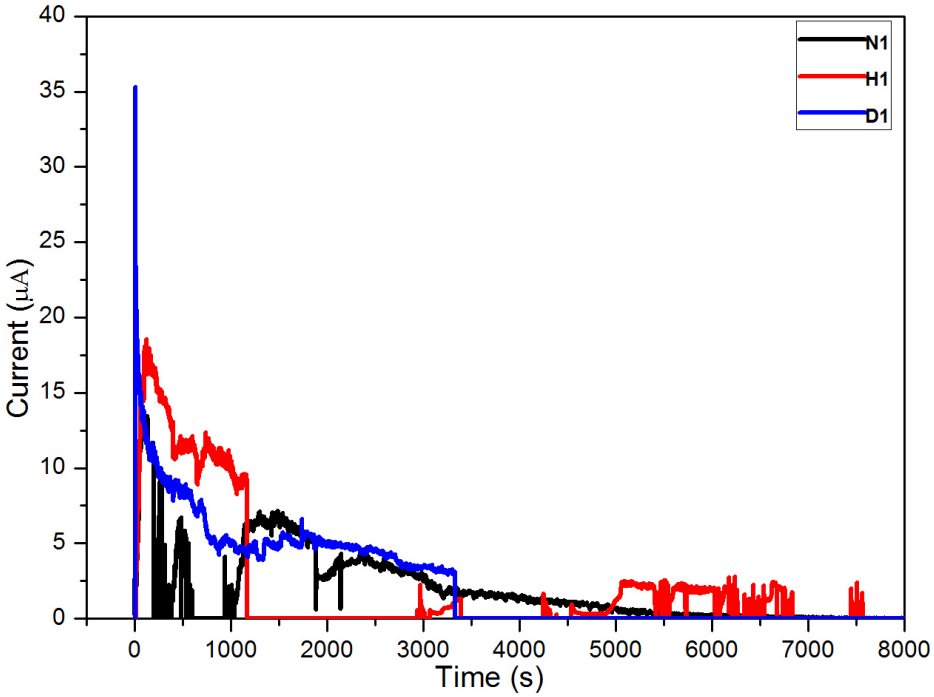


Figure 4.20: Current measurements for neutral gels of a swelling degree around 1.

According to this reaction, Aluminum metal could be oxidated and this could cause instant current flow in the system [37, 38]. For the polymeric gel of which inside water does not diffuse out surface could make it impossible to interact with aluminum electrode, but the water molecules in hydrogel diffuse out upon exposing to air. Under this diffusion, water molecules could oxidate the aluminum which results to a contribution the DC current in the system. Criticizing Figure 4.20 with Figure 4.21 may reveal the swelling effect on the current.

After collecting data from the computer and sketching on a current vs. time graph we have seen that if we double the swelling ratio, the intensity of the current will increase nearly twice. In Figure 4.18 the amplitude of D1 was 35 μA nearly. When it comes to Figure 4.19 meaning the doubled swelling ratio, the amplitude is reached to 70 μA. The results were very interesting as we look for the other gels N1, N2 and H1, H2. For

having a degree of swelling 1, the maximum intensity for N1 was 12 μA. When the gel swells until reaching the degree of swelling becomes 2, the intensity becomes almost 50 μA as it can bee seen for N2. The situation is valid for H1 and H2 also. For H1 the maximum amplitude was 17 μA while it reaches to 80 μA increasing approximately 5 times larger than its initial value. The increment is more dominant when the crosslinker concentration decreases.

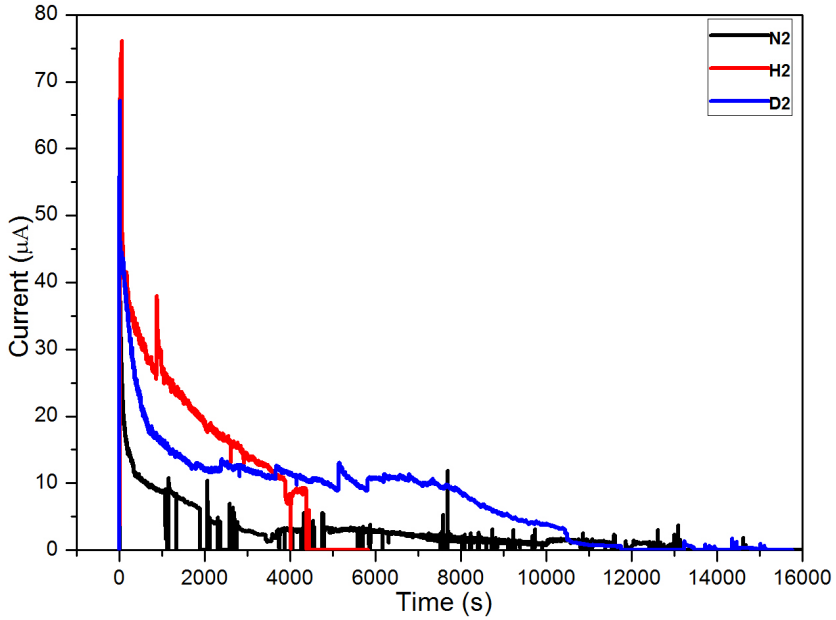


Figure 4.21: Current measurements for neutral gels of a swelling degree around 2.

One of the striking results obtained from the graphes is the duration of current flows.For every type of gels the current flow increased at least two times. This effect is more obvious on the gel which includes double amount of crosslinker concentration namely D2. Results obtained from the neutral gels made us wonder about the situation for doped hydrogels. In Figure 4.20 and Figure 4.21 pyranine doped gels are discussed from the same point of view.

The results were very similar with neutral gels for both intensities and durations. All the samples were making a peak and then decrease suddenly as happened in former examples. As it can be seen from the Figure 4.23, this time the amplitude or the intensity of the current did not change considerably from each other. There are some increases on the duration of the current for the gels but if we compare with the other examples this increase was not really big. It is can also bee seen from the Figure

4.22 that in HP2 there is a serious oscillation with decreasing to 0 μA several times. It seems that double crosslinked gels did not change its character by swelling more, while the others made some oscillations including 0 point.

Table 4.4: Dimensions and swelling degrees of prepared gels for Aluminium-Platinum measurements.

	R_0(mm)	d_0(mm)	m_0(g)	R_1(mm)	d_1(mm)	m_1(g)	$\triangle m/m0$
H1	4.1	0.85	0.0148	5.5	1.45	0.02969	1.006081
H2	4.15	0.8	0.0132	5.7	1.75	0.0386	1.924242
N1	4.5	1	0.0195	5.3	1.55	0.039	1
N2	4.05	0.9	0.0134	5.3	1.55	0.0393	1.932836
D1	4.35	0.9	0.0154	5.4	1.35	0.0313	1.032468
D2	4.15	1	0.0163	4.9	1.4	0.0345	1.116564
HP1	4	1.1	0.0162	5	1.45	0.0323	0.993827
HP2	4.2	12	0.0189	6.4	1.7	0.0534	1.825397
NP1	4.1	1.1	0.0162	5.25	1.5	0.0311	0.919753
NP2	3.9	0.95	0.0133	5.55	1.6	0.0413	2.105263
DP1	4.1	0.95	0.0154	4.9	1.35	0.0306	0.987013
DP2	4.3	1	0.0176	6.7	1.85	0.0521	1.960227

One notable event for this measurement is that the duration increase almost 8 times for H1 and this effect is appeared 3 times on D1 while it is 2 times for N1.

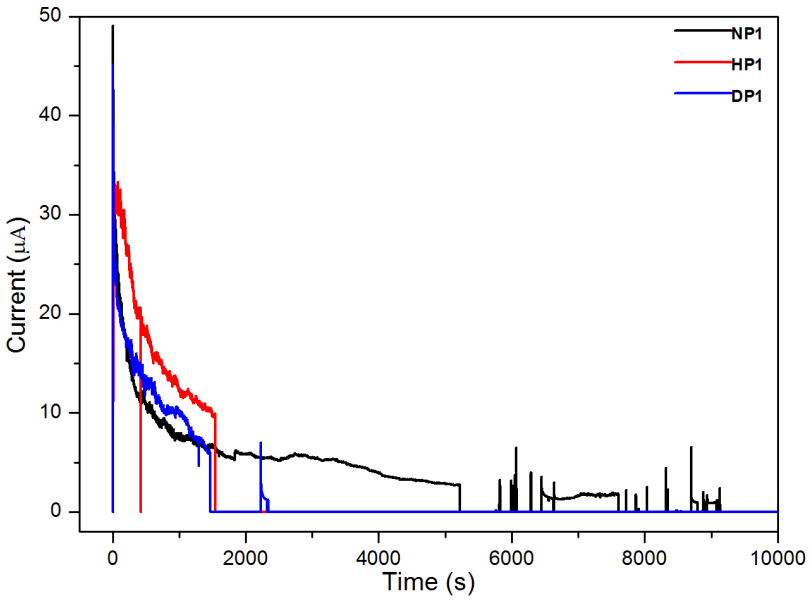


Figure 4.22: Current measurements for charged gels of a swelling degree around 1.

Up to here it is focused on the electrical characteristics of neutral and pryanine doped polyacrylamide hydrogels and also their behaviours when contacted with electrodes which have different geometrical shape and different materials.

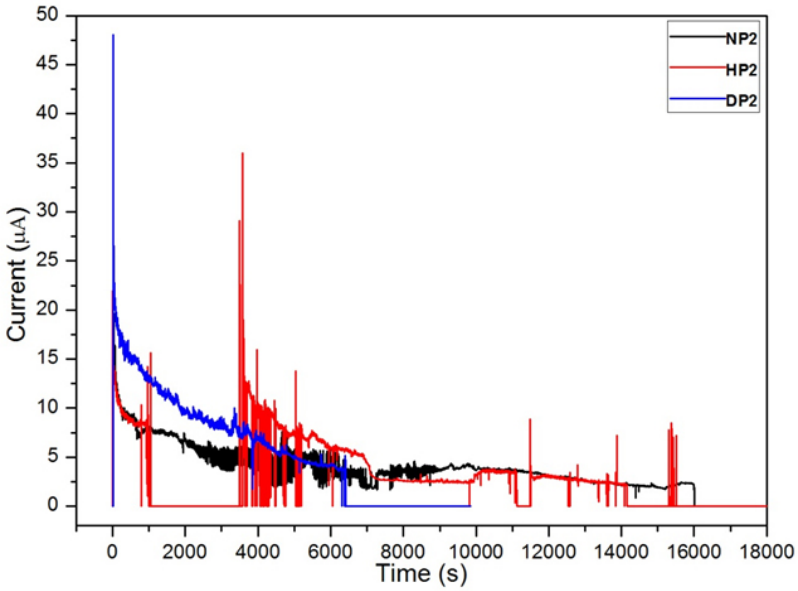


Figure 4.23: Current measurements for charged gels of a swelling degree around 2.

In the final chapter, all these results and discussions will be summarized and concluded with the ideas about what it could be done for further investigaton or to find out whether there could be a possible application for this current producing hydrogels.

5. CONCLUSIONS AND RECOMMENDATIONS

During throughout this whole study, it has been synthesized neutral and ion doped polyacrylamide hydrogels (PAAm) with different crosslinker ratios and it has been analyzed the electrical properties of these different structured hydrogels. While studying this exciting subject one of the most difficult tasks was to put forward some concrete logical theories about our studies.

It was really difficult to say something to be sure because this study was completely newborn and there was no example in the literature regarding the current producing property of metal-polymeric hydrogel contacts without applying voltage. Bearing in mind that this work is unique for all those studies about polymer physics, organic electronics and all relevant areas of studies, it is established a good theory about storage of electrical energy of hydrogels.

In the first part of the study, 2 Mol/l neutral and 2 Mol/l ion (pyranine) doped (with the amount of $5x10^{-4}$ Mol/l) hydrogels are synthesized carefully. By changing one of the parameter for gel formation (BIS) it is aimed to alter the tightness of the network formation. To do so, it might have been possible to see if any contribution comes from the loose or tighten networks.

After synthesizing these gels separately, they were treated well enough (the smoothening the surface of gels and waiting enough time to dry them up) to get ready for the measurements. These procedures took almost two weeks. Besides dielectric and conductivity studies about hydrogels, wtih these thesis it is intended to constitute a new research area dealing with observing DC current from hydrogels without applied any voltage.

Before measuring with hydrogels, it is thought that the occuring DC current during the gelation process may help us to understand the mechanism better. It may also a candidate to be a novel study which is determining the critical point (sol-gel threshold

point) by using electrical current method. This idea is just an assumption, which needs further discussion with numerous of examples.

During the experiments for gelation processes it has been observed that there is a serious amount of current produced, even its on the order of 10^{-6} amperes the results and conclusions are still promising. Current measurements during gelation processes showed us that the actual gelation process is completed in the first 30 minutes, because immediately after that time the current was started to decrease. This showed us by forming the 3 dimensional network in the plastic tube, the mobility of the ion restricted so that the electrical current became very low compared with the first 30 minutes. This result is confirmed by a conventional method that the plastic tube is taken away from the heat bath after 30 minutes and it is observed that the pre-gel solution transformed to a solid non-fluid gel. For each experiments the duration time of the measurement is limited with 24 hours.

In upcoming studies, it is thought that this electrical study will be improved by extra methods and analyzed in a more detailed version.

After making some measurements with gelation, it is focused the main part of this study which was, measuring the DC current for neutral and ion doped hydrogels. To do exact and specific experiments it was nearly important to make up a system that will measure the current, provide stability and protect the gel form the external effects such as direct sunlight, vaporizing, squeezing.. etc. With satisfying our necessities, a handmade system is constructed as seen in Figure 4.3 and tested before using it.

By using the lever which is located down side of the apparatus it is maintained that the sample gels are gently fixed within the system so that there is no possibly shifting from the initial position that could cause eliminate the effective current. In the second part of the experimental study, prepared gel have been used for current measurements by using this handmade system. Analyzing the results for neutral and doped gels could help us to understand the reason behind the ionic conductivity, because by doping the gel with pyranine, the internal structure of the gels became more homogeneous and including more counter ions which come from the pyranine molecule.

Second task was the configuration of the electrodes, which were also part of the system yet without these electrodes it was not possible to observe any current. By

configuration it is implied the different geometry of the electrodes and different types of electrodes. For each configuration there is a caption exist. After conducting these experiments one by one, the data are stored and started to analyze them correctly. It is clearly seen that if we use same type of electrodes like platinum-platinum, there is no considerable current observed. This behaviour is attributed to the symmetry of the gel itself and immobility of ions in the structure. The ions are kept in the system so tight that without any external triggering effect they are not tend to move, which results in a current of microampers.

To unbalance this symmetry in favour of a DC current, at first it is tried to change the geometry of the electodes by replacing one of the platinum plate's with a platinum needle. The surface area between needle and plate was enormously big and this difference could achieve to trigger a current. Assumptions were turned out to be true that a DC current is observed in the platinum-needle system. With different type of gels which are neutral and doped or having loose and tightened network, it is verified that the current within the gel both depends on the electrodes and the gels internal morphology. Even the observed current is so small, this results still look promising with possible developments.

In the final part of the study the swollen gels with two different degrees were measured with different metal electrodes which had nearly same geometry, as circular plates. Most striking results and data are collected in this part of the study, because the current were rising up to 80 μA and degree of swelling affected the amplitude of current vigorously. It could be possible to increase the current by 5 times greater than its initial value increasing the swelling two fold. The crosslinker concentration was also important for the current. The internal system of the gel affects the gel.

Finally considering the whole study and the results, it can be said that if we are able to overcome the short duration of the current, this study shows us it could be possible to produce new industrial products that can be used as an alternative to conventional batteries.

REFERENCES

[1] **J., P.A. and A., C.** (2006). *Polymer Chemistry: Properties and Applications*, Hanser Publishers, Munich.

[2] **Rubinstein, M. and R., C.** (2003). *Polymer Physics*, Oxford University Press, USA.

[3] **Young, R.J. and Lovell, P.A.** (2002). *Introduction to Polymers*, Nelson Thornes Ltd.,UK.

[4] **W., B.F.** (1984). *Textbook of Polymer Science*, John Wiley and Sons. Inc. USA.

[5] **Laftah, W., A.H. and Ibrahim, A.N.** (2011). Polymer Hydrogels: A Review,, *Polymer-Plastics Technology and Engineering*, ***50***, 051121– 4 pages.

[6] **E., A. and Y., Y.** (2010). Synthesis of *p*- and *n*- type Gels Doped With Ionic Charge Carriers, *Nanoscale Research Letters*, ***5***, 559–565.

[7] **Jabbari, E.T.J. and Sarvestani, A.S.** (2007). Swelling Characteristic of Acrylic Acid Polyelectrolyte Hydrogel in a DC Electric Field, *Smart Materials and Structures*, ***16***, 1614–1620.

[8] **H., S.L.** (1992). *Introduction to Physical Polymer Science*, John Wiley and Sons Inc. USA.

[9] **Bower, D.I.** (2002). *An Introduction to Polymer Physics*, Cambridge University.

[10] **B., B.** (1994). *Polimer Kimyası*, ODTU Basım İşliği, Ankara.

[11] **Pierre, A.** (1998). *Introduction to Sol-Gel Processing*, The Kluwer International Series in Sol-Gel Processing, Kluwer Academic Publishers.

[12] **Sahoo, S.**, **Kumar, N.**, **Bhattacharya, C.**, **Sagiri, S.S.**, **Jain, K.**, **Pal, K.**, **Ray, S.S. and Nayak, B.** (2011). Organogels: Properties and Applications in Drug Delivery, *Designed Monomers and Polymers*, ***14***(2), 95–108.

[13] **Erdoğan M., P.O.** (2005). Comparison of gel swelling under organic vapor and in organic solvent, *International Journal of Photoenergy*, ***07***, 37–43.

[14] **Pierre A. C., .P.G.** (2002). Chemistry of Aerogels and Their Applications, *Chem. Rev*, ***102***, 4243–4265.

[15] **Hoffman D., Komarneni S., R.R.** (1984). Preparation of a diphasic photosensitive xerogel, *Journal of Materials Science Letters*, ***3***, 439–442.

[16] **K. Pal, A.K.B..D.K.M.** (2009). Polymeric Hydrogels: Characterization and Biomedical Applications, *Designed Monomers and Polymers*, ***12***, 197–220.

[17] **S. K. H. Gulrez, S. Al-Assaf, G.P.** (2011). *Hydrogels: Methods of Preparation, Characterisation and Applications*, Progress in Molecular and Environmental Bioengineering - From Analysis and Modeling to Technology Applications.

[18] **Shamsudeen, R. K., N.S. and G., J.V.** (2005). Equilibrium swelling, Conductivity and Electroactive Characteristics of Polyacrylamide Hydrogels, *Indian Journal of Engineering and Material Sciences*, ***13***, 62–68.

[19] **E., H.R.** (2011). *Electronic Properties of Materials*, Springer Science and Business Media, USA.

[20] **M., G.** (2010). *The Physics of Semiconductors: An Introduction Including Nanophysics and Applications, Graduate Texts in Physics*, Splinger.

[21] **V., H.** (2003). *Polymer gel electrolytes*, Doctoral Thesis of Dept. of Electrical and Electronic Technology, FEEC, BUT.

[22] **Guo, J.** (2010). *Development of Ion Counductive Polymer Gel Electrodes and Their Electrochemical and Electromechanical Behaviour Studies*, Dissertation of The Graduated Faculty of The University of Akron.

[23] **Baolin Guo, A.F.W. and Albertsson, A.C.** (2011). Degradable and Electroactive Hydrogels with Tunable Electrical Conductivity and Swelling Behavior, *Chemistry Of Materials*, ***23***, 1254–1262.

[24] **Shirakawa, H., L.E.M.A.C.C.v.H.A.** (1977). Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH), *J. Chem. Soc., Chem. Commun*, (2), 578 – 580.

[25] **R., Z.** (2008). *The Physics of Amorphous Solids*, John Wiley and Sons New York.

[26] **Freund, M.S. and Deore, B.A.** (2007). *Self-Doped Conducting Polymers*, John Wiley and Sons, Canada.

[27] **Stockmayer, W.H.** (1943). Theory of Molecular Size Distribution and Gel Formation in Branched – Chain Polymers, *Journal of Chemical Physics*, ***11***, 45–55.

[28] **Hyuck Joon Kwon, Y.O. and Gong, J.P.** (2006). Polyelectrolyte Gels-Fundamentals and Applications, *Polymer Journal*, ***38***, 1211–1219.

[29] **Sekhon, S.** (2003). Conductivity behaviour of polymer gel electrolytes: Role of polymer, *Bulletin of Materials Science*, ***26***, 321–328.

[30] **Pissis, P. and Kyritsis, A.** (1997). Electrical conductivity studies in hydrogels, *Solid State Ionics*, ***97***, 105 – 113.

[31] **H., O.** (2005). *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, Inc.

[32] **Erdoğan, S.** (2012). *İyon Katkılı Hidrojel-Metal Kontaklarda Elektriksek Özelliklerin İncelenmesi*, İstanbul Teknik Üniversitesi, (Master Tezi).

[33] **Alveroğlu, E.** (2010). *Hafizalandırılmış polimerik jellerin spektroskopik ve elektriksel özelliklerinin incelenmesi*, İstanbul Teknik Üniversitesi, (Doktora Tezi).

[34] **Brinker, C. and Scherer, G.** (1990). *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, Newyork.

[35] **Alveroglu, E. and Yilmaz, Y.** (2011). Estimation of the Generation and the Weight Fraction of Dense Polymer Regions in Heterogeneous Hydrogels, *Macromolecular Chemistry and Physics*, ***212***(14), 1451–1459.

[36] **K., C.** (2007). *Uses of Metals and Metallic Materials*, New Age International Ltd.

[37] **Livage, J., H.M.S.C.** (1998). Sol-Gel Chemistry of Transition Metal Oxides, *Prog. Solid State Chem.*, ***18***, 259.

[38] **Yoldas, B.E.** (1975). Alumina gels that form porous transparent Al_2O_3, *Journal of Materials Science*, ***10***, 1856–1860.

CURRICULUM VITAE

Name Surname: Ahmet Talha ÜZÜMCÜ

Place and Date of Birth: Istanbul, 27.06.1987

Adress: Istanbul Technical University, Faculty of Science and Letters, Polymer Science and Technology Programme, Office: B4-Z22 Maslak, ISTANBUL

E-Mail: atuzumcu@itu.edu.tr

B.Sc.: Fatih University, Physics Department

List of Publications:

Mert, E. H., Yildirim H., **Uzumcu A. T.**, Kavas H. (2013): Synthesis and Characterization of Magnetic polyHIPEs with humic acid surface modified magnetic iron oxide nanoparticles, *Reactive and Functional Polymers*, ***73***, 175-181.

Tanriverdi E. E., **Uzumcu A. T.**, Kavas H. (2011): Conductivity study of Polyaniline-Cobalt Ferrite ($PANI-CoFe_2O_4$) Nanocomposites, Nano-Micro letters, ***3***, 99-107.