

Electrochemical Impedance Studies on Block Copolymer Nanocomposites

Submitted in partial fulfillment of the requirements

for the award of

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IN PHYSICS

By

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MAY-2022

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BONA FIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **KEERTHANA R (Reg. No.40590011)** who carried out the project entitled "**Electrochemical Impedance Studies on Block Copolymer Nanocomposites**" under our supervision from November 2021 to March 2022

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Abstract

Due to the three-dimensional network and its associated porosity and high surface area, gels can quickly and effectively adsorb/trap ionic molecules. In this project a polyvinylpyridine based gel will be constructed by chemical cross-linking. Small-angle X-ray scattering, Light scattering and rheological studies will be carried to investigate the structure and mechanical properties of the gel. Heavy metal removal capacity of the gel will be investigated.

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LIST OF ABBREVIATIONS

CRP	Controlled/living radical polymerization
RAFT	Reversible addition-fragmentation chain transfer
P4VP	Poly(4-vinylpyridine)
CTA	Chain Transfer Agent
AIBN	Azobisisbutyronitrile
DMF	Dimethylformamide
DBD	Dibromododecane
APC	Advanced polymer chromatography
FTIR	Fourier transform infrared Spectroscopy

NMR	Nuclear Magnetic Resonance Spectroscopy
CR	Congo red
BB	Brilliant blue R-250
MO	Methyl orange
BG	Bromocresol green

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CHAPTER 1

INTRODUCTION

POLYMER

A polymer is a large molecule (macromolecule) composed of repeating structural units or chains typically connected by covalent chemical bonds. While polymer in popular usage suggests plastic, the term actually refers to a large class of natural and synthetic materials with a variety of properties and purposes.

Well-known examples of polymers include plastics and proteins. A simple example is polypropylene, whose repeating unit structure is shown at the right. However, polymers are not just limited to having predominantly carbon backbones, elements such as silicon form familiar materials such as silicones, examples being silly putty and waterproof plumbing sealant. The backbone of DNA is in fact based on a phosphodiester bond.

Natural polymer materials such as shellac and amber have been in use for centuries. Biopolymers such as proteins and nucleic acids play crucial roles in biological processes. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

Characteristics of polymers

- ❖ Low Density.
- ❖ Low coefficient of friction.
- ❖ Good corrosion resistance.
- ❖ Good mould ability.
- ❖ Low mechanical properties.

Properties of polymers

The physical properties of a polymer, such as its strength and flexibility depend on

- **Chain length** - in general, the longer the chains the stronger the polymer.
- **Side groups** - polar side groups give stronger attraction between polymer chains, making the polymer stronger.
- **Cross-linking** - if polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt.

COPOLYMER

A copolymer is a polymer formed when two (or more) different types of monomer are linked in the same polymer chain, as opposed to a homopolymer where only one monomer is used.

Types of Copolymer

- ❖ Homopolymer
- ❖ Alternating copolymer
- ❖ Random copolymer
- ❖ Block copolymer
- ❖ Graft copolymer

BLOCK COPOLYMER

A block copolymer is a polymer that consists of multiple different types of polymer chains that are covalently attached to each other. The polymerized subunits that make up a block copolymer are chemically different, and they form adjacent blocks. For instance, a monomer A might bond at both of its ends to polymer B, forming a triblock BAB structure.

An important property of block copolymers is the propensity for the blocks to self-assemble into nanostructures, the size of which is determined by the length of the constituent monomers. This results in regions that are highly enriched for a single type of monomer, with the covalent bonds between blocks crowding at the interphases

between the domains. Such copolymer structures will disappear and be replaced with a disordered structure upon an increase in temperature of a sufficient magnitude. If there were no covalent bond between the blocks of a copolymer there would be a macrophase (rather than microphase) separation, such as one sees when oil and vinegar separate into droplets in a salad dressing.

Block copolymers have a tendency to mix the properties of their constituent blocks, resulting in the change of one polymer by the second component, and this feature differentiates them from traditional random copolymers that do not exhibit the characteristics of every in their components. Most studies on BCPs have focused on coil-coil diblock copolymers, where each block is a fully flexible polymer chain. Structures generated by these BCPs are well understood. For virtually all coil-coil BCPs, the various equilibrium morphologies can be completely described by a phase diagram such as that depicted. In a typical BCP, the dimension of the domains range from 10 nm to 100 nm and can be controlled by changing the overall molecular weight of the macromolecule.

Principle of Block Copolymer

Multiple reactions of synthesis of block copolymers are based on two main principles: the interaction of the macromolecular initiator with the monomer and the interaction of two or more polymers or macro radicals with each other. Synthesis of block copolymers significantly expands the possibilities for modifying the properties of polymers, as the macromolecule allows to combine regions of polymers varying in structure and properties: natural and synthetic, carbo- and heterochain, flexible and rigid, hydrophobic and hydrophilic, regular and irregular, etc. However, the correlation between the composition and structure of macromolecules and properties of block copolymers is not easy to define due to difficulties in isolating and identifying individual blocks, which explains the small number of block copolymers with a strictly defined structure among those applied in practice.

Block Copolymers Prepared

Block copolymers are normally prepared by controlled polymerization of one monomer, followed by chain extension with a different monomer to form AB or ABC block copolymers. When ATRP is employed to form each block in a block copolymer the composition and molecular weight and, to some extent, the PDI of each block can be independently controlled. Multifunctional initiators can also be used in the process to prepare ABA or AB-star multi-armed block copolymers.

Types of Block Copolymers

- AB diblocks
- ABA and ABC triblocks
- ABCD tetrablocks
- (AB)_n multiblocks etc.

Properties of Block Copolymer

The properties of block copolymers are similar to the properties of polymer mixtures, but the presence of chemical bonds between the blocks ensures their stability and prevents their separation with the release of individual components.

Application of Block Copolymer

- The most important and popular application of block copolymer is their use as thermoplastic elastomers (TPEs). These materials are so versatile that they can be used for wine bottle stoppers, jelly candles, outer coverings for optical fiber cables, or in artificial organ technology.
- Block copolymers of ethylene oxide with propylene oxide (hydrophobic block), like PEO-b-PPO-b-PEO triblocks, or with b-benzyl-L-aspartate (Basp), like PEO-b-PBAsp, are good candidates for drug targeting using water-insoluble anticancer drugs.
- By using the micelle-forming ability of block copolymers, the removal/recovery of toxic organic compounds (as, i.e., halogenated and polyaromatic

hydrocarbons) from contaminated water (coastal, surface, and ground) can be achieved.

- Used to make automobile tires called SBS RUBBER which is a block copolymer.

POLYMERIZATION TECHNIQUES

Controlled/living radical polymerization (CRP) is the most widely used technique to synthesize copolymers than conventional methods. The main drawback of the conventional radical polymerization techniques is the inability to control the molecular weight and its distributions. It is also challenging to tailor the macroscopic chain. On the other hand, living ionic polymerization techniques make it possible to prepare copolymers with well-defined copolymers such as controlled molecular weights, narrow molecular weight distribution, and defined copolymer compositions. However, the drawbacks of CRP are the limitation of monomers, sensitivity to moisture, carbon dioxide, etc. CRP includes nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization.

WASTEWATER TREATMENT

Wastewater treatment is a process used to remove contaminants from wastewater and convert it into an effluent that can be returned to the water cycle. Once returned to the water cycle, the effluent creates an acceptable impact on the environment or is reused for various purposes (called water reclamation). The treatment process takes place in a wastewater treatment plant.

Types of Treatment Plants

Wastewater treatment plants may be distinguished by the type of wastewater to be treated. There are numerous processes that can be used to treat wastewater depending on the type and extent of contamination. The treatment steps include physical, chemical and biological treatment processes.

- ✓ Sewage treatment plants.
- ✓ Industrial wastewater treatment plants.
- ✓ Agricultural wastewater treatment plants.
- ✓ Leachate treatment plants.

Wastewater Dyes

Textile industries are responsible for one of the major environmental pollution problems in the world, because they release undesirable dye effluents. Textile wastewater contains dyes mixed with various contaminants at a variety of ranges. The presence of dyes stuffs in wastewater can cause severe problems to aquatic life and human beings. Therefore, the removal of dyes from wastewater is important in order to minimize their hazardous effects on the environment.

The Harmful Effects of Dyes

They have been shown to have carcinogens, as they are made with many chemicals. Textile dyes can also cause allergies such as contact dermatitis and respiratory diseases, allergic reaction in eyes, skin irritation, and irritation to mucous membrane and the upper respiratory tract.

Dye Removal Process

Physical dye removal methods are usually straightforward methods commonly accomplished by the mass transfer mechanism. Conventional physical dye removal methods are adsorption, coagulation or flocculation, ion exchange, irradiation, membrane filtration, nano filtration or ultra-filtration and reverse osmosis.

Chemical dye removal methods mainly include electrochemical method and advanced oxidation method.

GEL

A gel is a semi-solid that can have properties ranging from soft and weak to hard and tough. Gels are defined as a substantially dilute cross-linked system, which exhibits no flow when in the steady-state, although the liquid phase may still diffuse through this system. A gel has been defined phenomenologically as a soft, solid or solid-like material consisting of two or more components, one of which is a liquid, present in substantial quantity.

By weight, gels are mostly liquid, yet they behave like solids because of a three-dimensional cross-linked network within the liquid. It is the crosslinking within the fluid that gives a gel its structure (hardness) and contributes to the adhesive stick (tack). In this way, gels are a dispersion of molecules of a liquid within a solid medium. The word gel was coined by 19th-century Scottish chemist Thomas Graham by clipping from gelatine.

The process of forming a gel is called gelation.

Types of Gel

- ❖ Hydrogels.
- ❖ Organogels.
- ❖ Xerogels.
- ❖ Nanocomposite hydrogels.

Properties of Gel

Many gels display thixotropy – they become fluid when agitated, but resolidify when resting. In general, gels are apparently solid, jelly-like materials. It is a type of non-Newtonian fluid. By replacing the liquid with gas it is possible to prepare aerogels, materials with exceptional properties including very low density, high specific surface areas, and excellent thermal insulation properties.

POLYMERIC GELS

Gels are an important class of soft materials with numerous potential applications, such as drug delivery, sensing, biomedical, tissue engineering, pharmaceutical, water treatment, etc. A gel is a three-dimensional crosslinked polymeric network that is swollen in a solvent (dispersing medium). Gels exhibit densities similar to liquids and have the structural coherence of a solid (Rogovina et al. 2008). Polymeric gels exhibit swelling, non-Newtonian rheological behaviour, mechano-electric effect, aging, etc (Pal and Banerjee 2018). Stimuli-responsive gels can be constructed by adding responsive groups in the gel network formation. (Jagur-Grodzinski 2010).

Classifications of Polymeric Gels

Polymeric gels are classified into two based on the cross-link

- (i) **Physical gels:** Here, the gel network is formed by weak interactions, like, hydrogen bonds or Van der Waals interactions, or by the entanglement of the polymer chains. The structure of the physical gels is reversible, and they dissolve over time in their solvents,
- (ii) **Chemical gels:** These are gels formed by cross-linking polymer chains through strong covalent bonds. They are more stable and do not dissolve in solvents. Therefore,

chemically cross-linked gels are widely used for many applications (Costa-Júnior et al. 2009; Lou and Chirila 1999).

Based on the dispersing medium, gels can be termed hydrogels, organogels, aerogels, xerogels, etc. A hydrogel is one in which water is the dispersing medium. Hydrogels can absorb/hold a large amount of water. Organogels are those in which an organic liquid phase is a dispersing medium. Ionogels are materials consisting of ionic liquid immobilized by the polymer matrix. Aerogels are dry materials, where the dispersing medium is air.

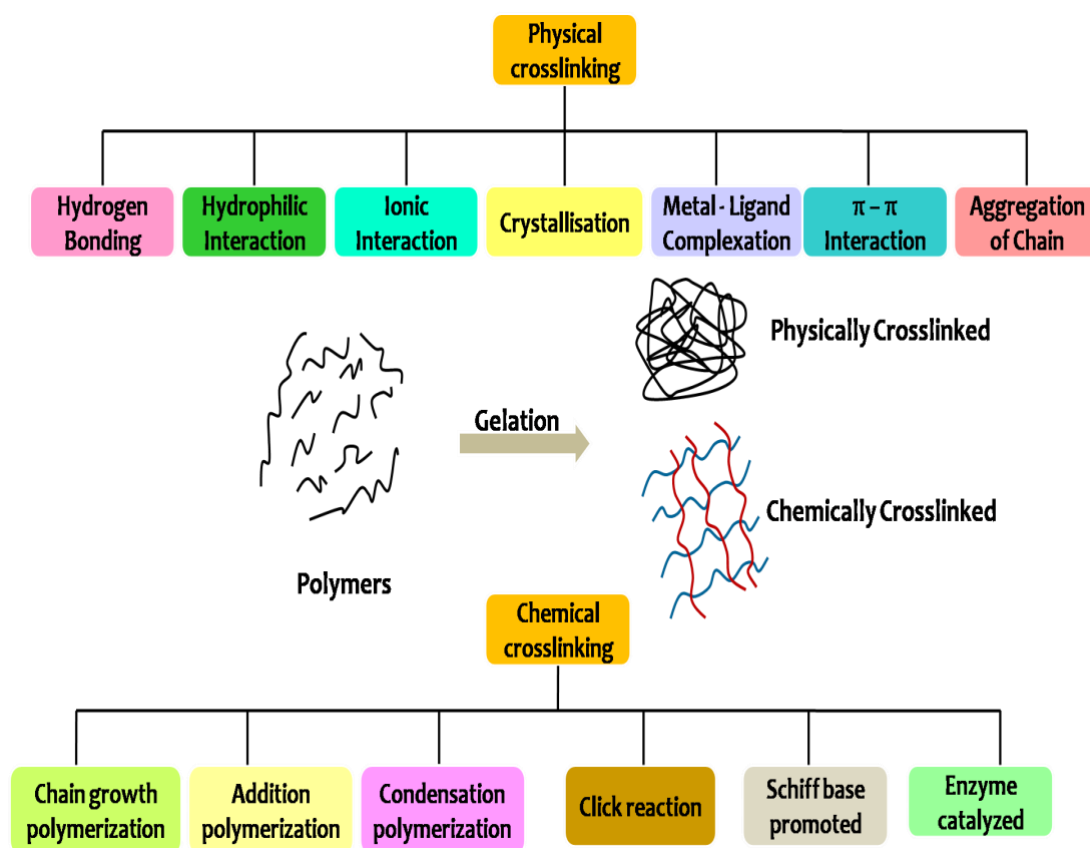


Fig1: Strategies of polymer gelation by means of physical and chemical cross-linking

Applications Of Gels

- Many substances can form gels when a suitable thickener or gelling agent is added to their formula. This approach is common in manufacture of wide range of products, from foods to paints and adhesives.
- In fiber optic communications, a soft gel resembling hair gel in viscosity is used to fill the plastic tubes containing the fibers.
- The main purpose of the gel is to prevent water intrusion if the buffer tube is breached, but the gel also buffers the fibers against mechanical damage when the tube is bent around corners during installation, or flexed. Additionally, the gel acts as a processing aid when the cable is being constructed, keeping the fibers central whilst the tube material is extruded around it.

ORGANOGE

An organogel is a class of gel composed of a liquid organic phase within a three-dimensional, cross-linked network. Organogel networks can form in two ways. The first is classic gel network formation via polymerization. This mechanism converts a precursor solution of monomers with various reactive sites into polymeric chains that grow into a single covalently-linked network. At a critical concentration (the gel point), the polymeric network becomes large enough so that on the macroscopic scale, the solution starts to exhibit gel-like physical properties: an extensive continuous solid network, no steady-state flow, and solid-like rheological properties. However, organogels that are “low molecular weight gelators” can also be designed to form gels via self-assembly. Secondary forces, such as van der Waals or hydrogen bonding, cause monomers to cluster into a non-covalently bonded network that retains organic solvent, and as the network grows, it exhibits gel-like physical properties. Both gelation mechanisms lead to gels characterized as organogels.

Gelation mechanism greatly influences the typical organogel properties. Since precursors with multiple functional groups polymerize into networks of covalent C-C bonds (on average 85 kcal/mol), networks formed by self-assembly, which relies on secondary forces (generally less than 10 kcal/mol), are less stable. Theorists also have

difficulties predicting characteristic gelation parameters, such as gel point and gelation time, with a single and simple equation. Gel point, the transition point from a polymer solution to gel, is a function of the extent of reaction or the fraction of functional groups reacted. Gelation time is the time interval between the onset of reaction– by heating, addition of catalyst into a liquid system, etc. – and gel point. Kinetic and statistical mathematical theories have had moderate success in predicting gelation parameters; a simple, accurate, and widely applicable theory has not yet been developed.

Application of Organogel

Organogels are useful in applications such as:

- Drug delivery mediums for topical and oral pharmaceuticals
- Organic application mediums for cosmetics
- Cleaning materials for art conservation
- As delivery mediums and/or nutrients in nutraceuticals (vitamins and supplements),
- Particles in personal care products (shampoo, conditioner, soap, toothpaste, etc.)
- A crystalline fat alternative in food processing.
- An undesirable example of organogel formation is wax crystallization in petroleum.

ROLE OF POLYMERIC GELS IN ENVIRONMENTAL REMEDIATION

Over the years, several effective treatment processes for dye removal such as photo-degradation (Lučić Škorić et al. 2016; Sharma and Singhal 2015), bio-degradation (Gajera et al. 2015; Ali 2010), membrane-based filtration), adsorption (Hassani et al. 2015), have been reported. Among these methods, dye removal by adsorption is advantageous due to its relatively simple adsorption mechanism, removal efficiency, economic feasibility, and flexibility in the process involved. Due to the three-dimensional network and its associated porosity and high surface area, gels can quickly and effectively adsorb dye molecules. Gel-based adsorption thus will have promising applications in dye removal from wastewater.

CHAPTER 2

LITERATURE SURVEY

GRAPHENE/NIO NANOWIRES: CONTROLLABLE ONE-POT SYNTHESIS AND ENHANCED PSEUDOCAPACITIVE BEHAVIOR

(Duc Tai Dam et al.,2014)

We present a simple and easy method for making a composite of mesoporous NiO nanowires and graphene nanosheets for supercapacitor applications in this paper. In a water/ethylene glycol mixture containing graphene oxide, a Ni precursor was produced using a one-pot solgel technique. The graphene oxide was thermally reduced to graphene and the Ni precursor was converted to NiO via heat treatment in the air. NiO nanowires have a rough surface, a diameter of around 60 nm, and are deposited uniformly on graphene sheets. In comparison to its equivalents, the NiO/ graphene nanocomposite exhibits superior pseudocapacitive qualities (high specific capacitance, outstanding cyclic performance, and excellent discharge rate capability). This behaviour, we hypothesised, occurred from the synergistic effect of adding graphene as elastic conductive channels, which resulted in improved charge transfer and more favourable ionic diffusion.

NITROGEN-DOPED HIERARCHICAL POROUS CARBON DERIVED FROM BLOCK COPOLYMER FOR SUPERCAPACITOR

(Yun-Xiao Tong et al.,2016)

A self-template approach was used to successfully synthesis nitrogen-doped hierarchical porous carbon using block copolymers as a precursor and subsequent KOH chemical activation. Polystyrene, the self-template agent, promotes the creation of mesopores, which are beneficial for the rapid movement of both electrons and electrolyte ions. After that, activation was used to further grow the micropores of nitrogen-doped hierarchical carbons, resulting in a significant electrochemical double-layer capacitance. The specific surface area of the materials grew considerably as the activation temperature increased from 600 to 900 degrees Celsius. As a result, the nitrogen-doped hierarchical carbon (NHPC-800) developed so far has a large surface area of up to 2104.5 m²/g with 5.79 percent nitrogen content for an electrochemical energy system with great performance. It has a maximum specific capacitance of 257 F/g in 6 M KOH aqueous electrolyte at a current density of 0.5 A/g, as measured in a three-electrode setup. Furthermore, the nitrogen-doped hierarchical carbon electrode has excellent rate capability, retaining 128 F/g at 20 A/g, and good cycling stability, with 90.38 percent retention over 100 cycles. In a two-electrode setup, 10,000 cycles are possible. The customizable porosity structure and effective nitrogen doping via block polymer precursor

have paved the way for the development of innovative electrode materials for high-performance electrochemical energy systems.

A GRAPHENE OXIDE SURFACE–MOLECULARLY IMPRINTED POLYMER AS A DISPERSIVE SOLID-PHASE EXTRACTION ADSORBENT FOR THE DETERMINATION OF CEFADROXIL IN WATER SAMPLES

(Xinwei Chen and Nengsheng Ye et al.,2017)

Using a non-covalent molecular imprinting approach, a graphene oxide (GO)–functionalized molecularly imprinted polymer (MIP) (GO–MIPs) was prepared and applied to dispersive solid-phase extraction (DSPE) coupled with ultra-high-performance liquid chromatography with photodiode array detection (UPLC-PDA) to sensitively detect cefadroxil (FAD) in aqueous solution. In methanol, 2-(trifluoromethyl) acrylic acid (TFMAA) and ethylene glycol dimethacrylate (EGDMA) were utilised as the monomer and cross-linker, respectively, to manufacture GO–MIPs. SEM, transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), and Raman spectroscopy were used to characterise the GO–MIPs, which were eluted using acetic acid–methanol (20/80, v/v). Using cefixime, cefoxitin sodium, and ceftiofur hydrochloride as structural analogues of FAD, the selectivity of the GO–MIPs versus a graphene oxide–functionalized non-imprinted polymer (GO–NIPs) was validated using selectivity factors (SFs). The proposed DSPE approach was used to evaluate the efficiency of the synthesised GO–MIPs. The analytical performance of the new DSPE-UPLC-PDA technique was assessed under optimum circumstances, including sample pH, extraction time, desorption reagents, and desorption time. Over the range of 0.04–6.0 mg mL⁻¹, good linearity ($R^2 = 0.9979$) was achieved, with a detection limit (S/N 3) of 0.01 mg mL⁻¹. Finally, the devised method was used to quantify the concentration of FAD in water samples, with average spiking recoveries ranging from 72.5 to 104.8 percent. The GO–MIPs were effective carriers for selective FAD adsorption and showed promise as a method for pre concentrating FAD in complicated materials.

BLOCK COPOLYMER-BASED POROUS CARBONS FOR SUPERCAPACITORS

(TianyuLiua et al.,2019)

Because of their outstanding electrical conductivity, high surface area, unique porous networks, and superior chemical inertness, porous carbons are interesting materials for supercapacitor electrodes. The recent development of block copolymer-based porous carbons for supercapacitor electrodes is summarised in this article. We first go through the basics of supercapacitors and block copolymers, then provide some examples of how block copolymers may be used to make porous carbons with topologies that aren't possible with conventional methods. Rather than a thorough assessment, the article focuses on studies that have been published in the last five years. Zero-dimensional powders, one-dimensional fibres, two-dimensional films, and three-dimensional monoliths are all examples of block copolymer-based porous carbons. Finally, the study discusses some of the obstacles and potential connected with using block copolymers in supercapacitors.

ELECTROCHEMICALLY ACTIVE NITROGEN-ENRICHED NANOCARBONS WITH WELLDEFINED MORPHOLOGY SYNTHESIZED BY PYROLYSIS OF SELF-ASSEMBLED BLOCK COPOLYMER

(MingjiangZhong et al.,2012)

A straightforward carbonization technique utilising well-defined block copolymer precursors containing the source of carbon, polyacrylonitrile (PAN), and a sacrificial block, poly(n-butyl acrylate) was used to create novel nanoporous nitrogen-enriched carbon materials (PBA). The high fidelity preservation of the original phase-separated nanostructure between two polymer blocks after carbonization enabled the synthesis of nitrogen-enriched nanocarbons with hierarchical pore structure. The generated carbons produced supercapacitors with very high capacitance per unit surface area ($>30 \text{ F/cm}^2$). which was attributed to the pseudocapacitance resulting from the PAN precursor's high nitrogen concentration. The findings of oxygen reduction studies revealed the nitrogen species' electrochemical availability. Such materials are particularly interesting for usage in supercapacitor and electrocatalyst applications because to their hierarchical pore structure and high nitrogen content.

ENHANCING PSEUDOCAPACITIVE CHARGE STORAGE IN POLYMER TEMPLATED MESOPOROUS MATERIALS

(IRIS E. RAUDA et al., 2012)

The need for renewable energy sources has grown as a result of rising global energy demands and environmental concerns. Energy storage devices will be required to make intermittent renewable energy sources such as solar and wind available on demand. The most common types of energy storage devices are batteries and supercapacitors, often known as electrochemical capacitors (ECs). Despite the fact that supercapacitors provide more power, faster response times, and longer cycle life than batteries, supercapacitors are typically neglected as an energy storage technology. Because ECs have a lower energy density than batteries, their potential uses have been limited.

This report summarises our recent work on customising the electrode architecture to improve pseudocapacitive energy storage performance. We present findings from research into mesoporous transition metal oxide structures that store charge via surface or nearsurface redox processes, a phenomenon known as pseudocapacitance. Pseudocapacitance's faradaic nature results in considerable gains in energy density, making it an attractive future direction for ECs. We show that when it comes to creating the optimum pseudocapacitor device, both material selection and electrode architecture are critical.

First, we'll go over the present status of pseudocapacitor electrode topologies, from slurry electrodes to carbon/metal oxide composites. The manufacture of mesoporous films using amphiphilic diblock copolymer templating agents is then described, with a focus on those that are suited for pseudocapacitive charge storage. Films built from nanoparticle building blocks and films made from standard battery materials are among them. We focus on adopting flexible architectures to decrease the strain associated with lithium intercalation, or the deposit of lithium ions or atoms between the layers of cathode or anode materials that occurs as batteries charge and discharge. By isolating capacitive contributions from typical diffusion-controlled intercalation processes, electrochemical study of these mesoporous films provides for a detailed understanding of the origin of charge storage. We also go over how to separate the two types of capacitance contributions: double-layer capacitance and pseudocapacitance. Understanding these contributions should allow for the selection of materials with an optimized architecture that maximize the contribution from pseudocapacitance.

We show that nanocrystal-based nanoporous materials have a design that is optimised for high levels of redox or surface pseudocapacitance based on our research. Intercalation pseudocapacitance, which occurs when insertion processes become so kinetically simple that they appear capacitive, has been observed in some materials tailored to decrease the strain associated with lithium insertion.

Finally, we provide a summary of simple design criteria that should result in electrode topologies with high power and high energy density. To maximise electrode

surface area, these design rules include assembling small, nanoscale building blocks; maintaining an interconnected, open mesoporosity to facilitate solvent diffusion; seeking flexibility in electrode structure to facilitate volume expansion during lithium insertion; optimising crystalline domain size and orientation; and creating effective electron transport pathways.

CHAPTER 3

AIM AND SCOPE OF THE PRESENT INVESTIGATION

THE AIM AND OBJECTIVE OF THE RESEARCH

- ❖ Synthesize and elucidate the structure of the poly(4-vinylpyridine)(P4VP) polymer.
- ❖ Preparation of poly(4-vinylpyridine) polymeric organogel.
- ❖ Characterize the P4VP polymer and its organogel using proton NMR, FTIR, APC and Raman spectrophotometer.
- ❖ Demonstrate the application of the P4VP organogels for various anionic dyes from wastewater effluent.

SCOPE OF THE RESEARCH WORK

Over the past decades, there has been significant development in the field of soft materials based on polymeric gel materials such as hydrogels, organogels and Xerogel etc. These polymeric gels are used as the dye removal adsorbent, sensing materials, drug delivery etc. In this research work, the poly(4-vinylpyridine) was synthesized using free radical polymerization and characterized by ^1H NMR, and FTIR for structural confirmation, and the molecular properties were determined from advanced chromatography (APC). The chemically crosslinked organogels were prepared from poly(4-vinylpyridine) polymers using 1,12-dibromododecane. This organogel exhibited myriad applications such as superior dye removal and heavy metal adsorption. Our organogel is high performing than other reported gel-based absorbents. Comparing our work with the results with a mere 2 wt% of adsorbent used and much quicker times for dye removal, the organogel shows excellent potential for application in effluent water treatment. This organogel can be retained its remarkable adsorption characteristics with high removal efficiency.

CHAPTER 4

MATERIALS AND METHODS

4-VINYLPYRIDINE (VP)

4-Vinylpyridine is an organic compound with the formula $\text{CH}_2\text{CHC}_5\text{H}_4\text{N}$. It is a derivative of pyridine with a vinyl group in the 4-position. It is a colorless liquid, although impure samples are often brown. It is a monomeric precursor to specialty polymers. 4-Vinylpyridine is prepared by the condensation of 4-methylpyridine and formaldehyde.

Definition of VP

A vinyl polymer composed of repeating $-\text{CH}_2-\text{CR}-$ units where R is a 4-pyridyl group.

General Description of VP

(4-vinylpyridine) (VP) is a pyridine containing polymer that is used in the surface modification by immobilizing the atoms present on the surface.

4-Vinylpyridine Properties

- Melting point: 260°C (dec.)
- Boiling point: 225°C
- Density: 1.15 g/cm^3
- Flash point: 11°C
- Solubility: DMF, acetic acid and lower alcohols: soluble
- Specific Gravity: 1.15

Applications of VP

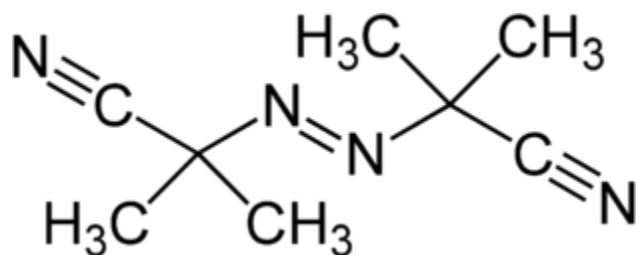
VP can be used in a variety of applications such as:

- Fabrication of antibacterial surfaces.
- Development of pH sensitive systems.
- 3D molecular level ordering systems.
- Anti-corrosive coatings.
- Dye sensitized solar cells (DSSCs)(90).

AZOBISISOBUTYRONITRILE

Azobisisobutyronitrile (abbreviated AIBN) is an organic compound with the formula $[(\text{CH}_3)_2\text{C}(\text{CN})]_2\text{N}_2$. This white powder is soluble in alcohols and common organic solvents but is insoluble in water. It is often used as a foamer in plastics and rubber and as a radical initiator.

As an azo initiator, radicals resulting from AIBN have multiple benefits over common organic peroxides. For example, they do not have oxygenated byproducts or much yellow discoloration. Additionally, they do not cause too much grafting and therefore are often used when making adhesives, acrylic fibers, detergents, etc.



Structure of AIBN

Why is AIBN a Good Radical Initiator?

When AIBN is used as an initiator, the compound decomposes partly because of the strong N-N triple bond that is formed, and partly because of the relatively stable radical that results. This radical is both tertiary and delocalized. Other initiators can also be used in radical polymerizations.

DIMETHYLFORMAMIDE

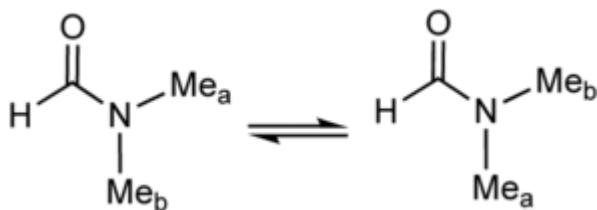
Dimethylformamide is an organic compound with the formula $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$. Commonly abbreviated as DMF (although this initialism is sometimes used for dimethylfuran, or dimethyl fumarate), this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions.

Dimethylformamide is odorless, but technical-grade or degraded samples often have a fishy smell due to impurity of dimethylamine. Dimethylamine degradation impurities can be removed by sparging samples with an inert gas such as argon or by sonicating the samples under reduced pressure. As its name indicates, it is structurally related to formamide. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as S_N2 reactions.

Structure and Properties of DMF

As for most amides, the spectroscopic evidence indicates partial double bond character for the C-N and C-O bonds. Thus, the infrared spectrum shows a C=O stretching frequency at only 1675 cm⁻¹, whereas a ketone would absorb near 1700 cm⁻¹.

DMF is a classic example of a fluxional molecule.



The ambient temperature ¹H NMR spectrum shows two methyl signals, indicative of hindered rotation about the (O)C-N bond. At temperatures near 100 °C, the 500 MHz NMR spectrum of this compound shows only one signal for the methyl groups.

DMF is miscible with water. The vapour pressure at 20 °C is 3.5 hPa. A Henry's law constant of 7.47 × 10⁻⁵ hPa m³ mol⁻¹ can be deduced from an experimentally determined equilibrium constant at 25 °C. The partition coefficient log P_{ow} is measured to -0.85. Since the density of DMF (0.95 g cm⁻³ at 20 °C) is similar to that of water, significant flotation or stratification in surface waters in case of accidental losses is not expected.

Production of DMF

- DMF was first prepared in 1893 by the French chemist Albert Verley (8 January 1867 – 27 November 1959), by distilling a mixture of dimethylamine hydrochloride and potassium formate.
- DMF is prepared by combining methyl formate and dimethylamine or by reaction of dimethylamine with carbon monoxide.
- Although currently impractical, DMF can be prepared from supercritical carbon dioxide using ruthenium-based catalysts.

Application of DMF

- The primary use of DMF is as a solvent with low evaporation rate.
- DMF is used in the production of acrylic fibers and plastics.
- It is also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings.

DMF uses in a Research Laboratory

- DMF can be utilized as a standard in proton NMR spectroscopy allowing for a quantitative determination of an unknown compound.
- In the synthesis of organometallic compounds, it is used as a source of carbon monoxide ligands.
- DMF is a common solvent used in electrospinning.
- DMF is commonly used in the solvothermal synthesis of Metal–Organic Frameworks.
- DMF- d_7 in the presence of a catalytic amount of KO t -Bu under microwave heating is a reagent for deuteration of polyaromatic hydrocarbons.

EXPERIMENTAL SECTION

4-vinylpyridine was purified by passing through an alumina column to remove the inhibitor. The initiator 2,2'-azobis(2-methylpropionitrile) and were recrystallized from

methanol before use. Dimethylformamide (DMF) Sigma-Aldrich, 98%) and Dibromododecane (DBD, Sigma-Aldrich, 98%) was used as the cross-linker. All chemicals used are purchased from Sigma Aldrich and the glasswares were pre-cleaned and dried before use.

The molecular weight of the P4VP polymer and their corresponding polydispersities were determined from advanced polymer chromatography (APC) (ACQUITY, Waters, USA) using DMF as the eluent at a flow rate of 0.5 mL/min. Fourier transform infrared (FTIR) spectrum of the polymers was recorded on a Bruker spectrophotometer using the KBr pellet technique. The ^1H NMR analysis was performed on a Bruker 400 MHz spectrometer using CDCl_3 as the solvent.

SYNTHESIS OF POLY 4-VINYLPYRIDINE (P4VP) POLYMER

P4VP polymer was synthesis by dissolving 50ml 4-vinylpyridine and 20 mg of initiator (AIBN) in 20 ml of DMF. The solutions were degassed by three freeze-pump-thaw cycles and reacted at 70°C for 24 hrs under an inert atmosphere. After the polymerization, the reaction mixtures were cooled to room temperature. P4VP polymer solution was precipitated using cold ether; the recovered powders of pure P4VP polymer had an orange in colour.

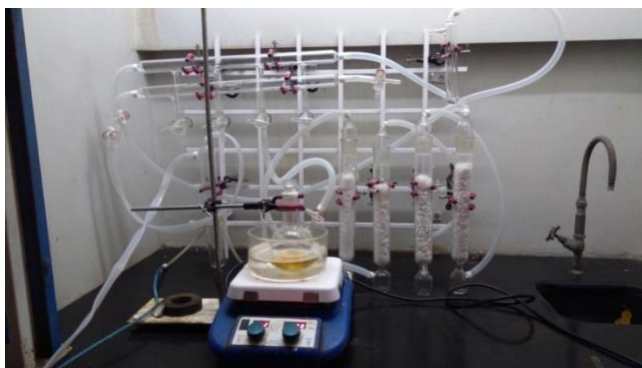




Fig 2: Synthesis of P4VP Polymer

PREPARATION OF P4VP ORGANOGEL

About 2 wt % P4VP polymer and 0.8 wt % DBD were dissolved in DMF and kept undisturbed at 70 °C for 4 h. The obtained organogel was washed with cold diethyl ether to remove the unreacted chemicals. The steps for synthesizing the P4VP polymer and its subsequent cross-linking with DBD to form the organogel are given in Scheme 1. The inset in the scheme shows the photograph of the P4VP block copolymer before and after gelation. It is also worth mentioning that leaving the diblock copolymer solution with 0.8 wt % DBD undisturbed for about two weeks resulted in gelation. However, heating at 70 °C was found to quicken the process of gelation.

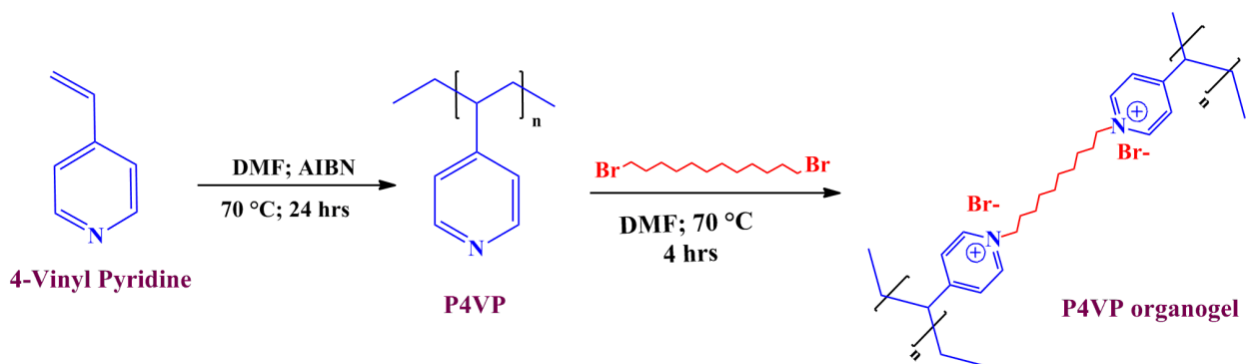


Fig 3: RAFT synthesis of P4VP Block Copolymer and its Cross-Linking with DBD to form the Quaternized Organogel

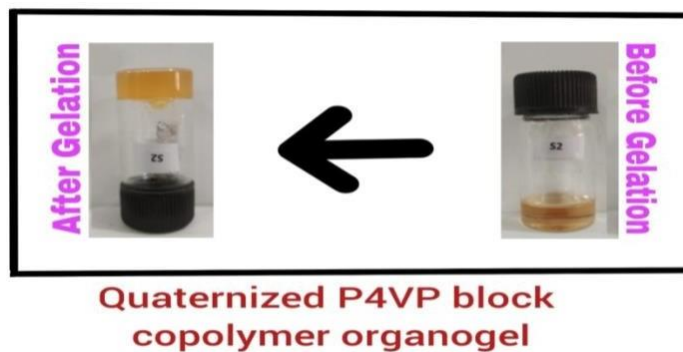


Fig 4: The photograph of the 2 wt % P4VP before and after gelation. Gelation is observed after 4 h heating the 2 wt % P4VP with 0.8 wt % DBD at 70 °C.

DYE ADSORPTION EXPERIMENTS

Dye adsorption studies have been carried out using 2 wt % pellets of the organogel in various anionic dye solutions. The molecular structure of the dyes is shown in Figure 1. The pellets of the organogel (weighing 20 mg) were obtained by cutting from the bulk of the organogel using a scalpel. Anionic dyes Congo red (CR), brilliant blue R-250 (BB), methyl orange (MO), and bromocresol green (BG) were used for the study. The concentration of the dyes used in the experiments was 0.1 g L⁻¹. The time evolution of the UV-vis absorption spectrum was monitored after 15 min of contact of the dye solution with the organogel. The residual dye concentration was estimated from the quantitative analysis of UV-vis absorption. Regeneration experiments were carried out by immersing the dye-adsorbed organogel into 5 ml of ethanol. After 10 min, the organogel was recovered, and after drying, the reusability of the organogel was ratified by repeating the dye adsorption and subsequent dye removal (desorption) cycles. The equilibrium adsorption capacity of the organogel is given by

$$Q_e = \frac{(C_0 - C_e)}{m} \times V$$

where C_0 and C_e are the initial and equilibrium dye concentrations, respectively, V is the volume of the dye solution, and m is the weight of the adsorbent.

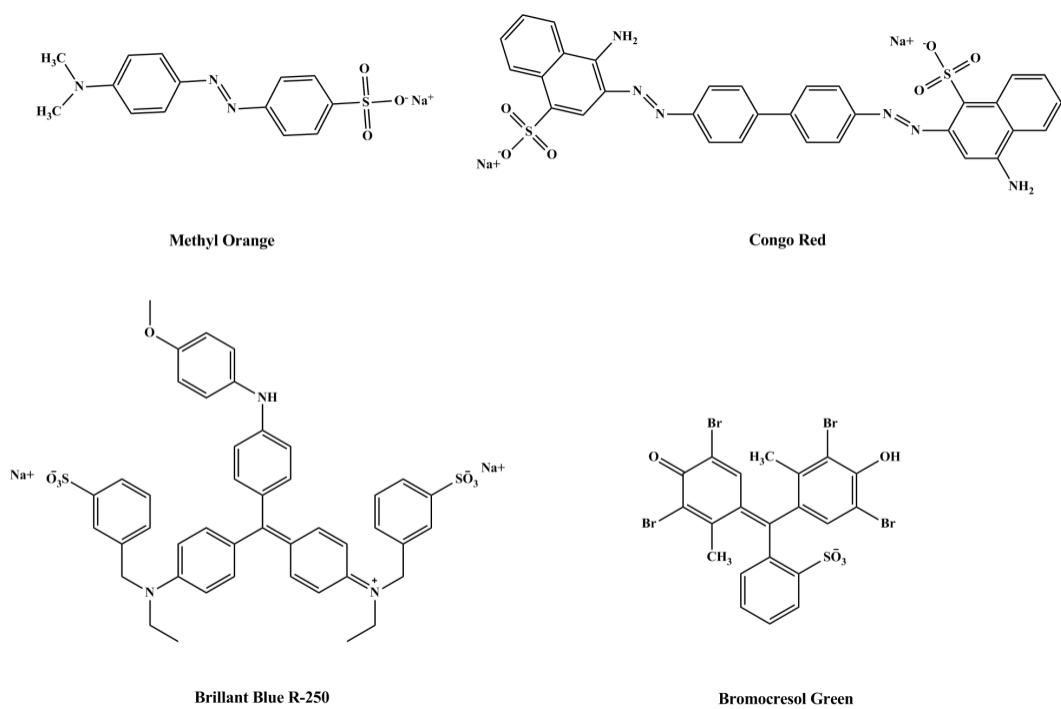


Fig 5: Molecular structure of the anionic and cationic dyes used in this study.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 DETERMINATION OF MOLECULAR WEIGHT

The molecular weight of P4VP was determined by APC analysis. The molecular weight of P4VP 14.5 KDa and the conversion rate from monomer to polymer is 82%. The obtained values were then compared with the theoretically calculated value, $M_{n,th}$ using equation

$$M_{n(theor)} = \frac{[M]_0}{[CTA]_0} \times M_m \times \text{conversion} + M_{CTA}$$

Where M_m and M_{CTA} are the molecular weights of the monomer and the CTA and $[M]_0$ and $[CTA]_0$ are the initial concentrations of the monomer and the CTA, respectively. Using equation and from the experimentally determined APC values,

FTIR SPECTROSCOPY

FTIR stands for “Fourier transform infrared” and it is the most common form of infrared spectroscopy. All infrared spectroscopies act on the principle that when infrared (IR) radiation passes through a sample, some of the radiation is absorbed. The radiation that passes through the sample is recorded. Because different molecules with their different structures produce different spectra, the spectra can be used to identify and distinguish among molecules.

FTIR is the preferred method of infrared spectroscopy for several reasons. First, it does not destroy the sample. Second, it is significantly faster than older techniques. Third, it is much more sensitive and precise.

FTIR Spectroscopy Uses

FTIR spectroscopy is used in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry and food analysis. In other words, it has a wide array of applications, from monitoring processes to identifying compounds to determining components in a mixture.

FTIR Working

A molecule's covalent bonds will selectively absorb radiation of specific wavelengths, which changes the vibrational energy in the bond. The type of vibration (stretching or bending) induced by the infrared radiation depends on the atoms in the bond. Because different bonds and functional groups absorb different frequencies, the transmittance pattern is different for different molecules. (Transmittance is the flipside of absorbance.) The spectrum is recorded on a graph with wavenumber (cm^{-1}) recorded on the X-axis and transmittance recorded on the Y-axis. (Wavenumber is $1/\text{wavelength}$ and corresponds to the energy of the vibration of the molecular bonds.)



Fig 6: FTIR Spectrum

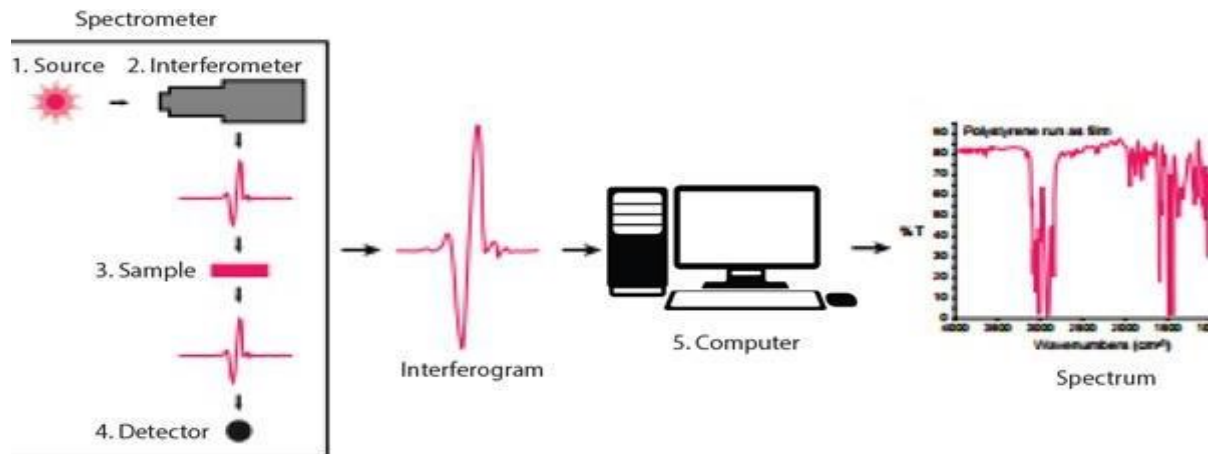


Fig 7: Schematic diagram of FTIR

NMR SPECTROSCOPY

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules due to the chemical shift of the resonance frequencies of the nuclear spins in the sample. Peak splittings due to J- or dipolar couplings between nuclei are also useful. NMR spectroscopy can provide detailed and quantitative information on the functional groups, topology, dynamics and three-dimensional structure of molecules in solution and the solid state. Since the area under an NMR peak is usually proportional to the number of spins involved, peak integrals can be used to determine composition quantitatively.

Structure and molecular dynamics can be studied (with or without "magic angle" spinning (MAS)) by NMR of quadrupolar nuclei even in the presence of magnetic "dipole-dipole" interaction broadening (or simply, dipolar broadening), which is always much smaller than the quadrupolar interaction strength because it is a magnetic vs. an electric interaction effect.

Additional structural and chemical information may be obtained by performing double-quantum NMR experiments for pairs of spins or quadrupolar nuclei such as ^2H

Furthermore, nuclear magnetic resonance is one of the techniques that has been used to design quantum automata, and also build elementary quantum computers.

NMR Working

- ❖ The sample is placed in a magnetic field and the NMR signal is produced by excitation of the nuclei sample with radio waves into nuclear magnetic resonance, which is detected with sensitive radio receivers.
- ❖ The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups.
- ❖ As the fields are unique or highly characteristic to individual compounds, NMR spectroscopy is the definitive method to identify monomolecular organic compounds.
- ❖ Besides identification, NMR spectroscopy provides detailed information about the structure, dynamics, reaction state, and chemical environment of molecules.
- ❖ The most common types of NMR are proton and carbon-13 NMR spectroscopy, but it is applicable to any kind of sample that contains nuclei possessing spin.

Application of NMR

- ❖ It is an analytical chemistry technique used in quality control.
- ❖ It is used in research for determining the content and purity of a sample as well as its molecular structure. For example, NMR can quantitatively analyze mixtures containing known compounds.
- ❖ NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Two-dimensional techniques are used to determine the structure of more complicated molecules.
- ❖ These techniques are replacing x-ray crystallography for the determination of protein structure.

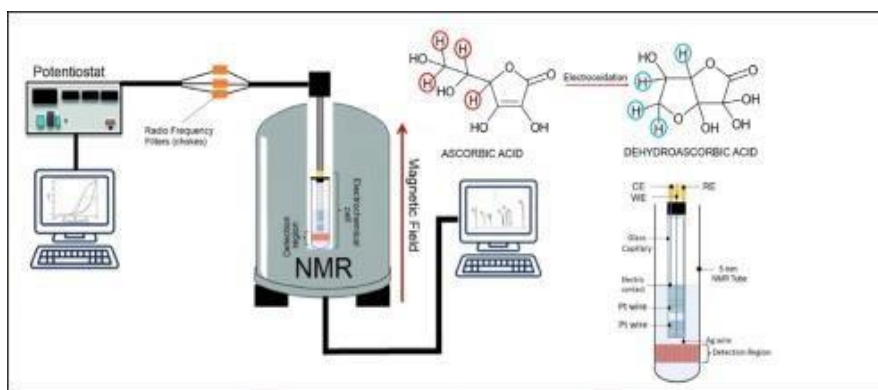


Fig 8: Schematic diagram of NMR

RAMAN SPECTROSCOPY

Raman spectroscopy belongs into the category of vibrational spectroscopy. This means that it analyzes a sample chemically, by using light to create (excite) molecular vibration, and interpreting this interaction afterwards.

It is based on the inelastic scattering of light that occurs when matter is irradiated by light. As the change of wavelength is very small compared to the wavelength of the irradiating light, the change of wavelength is most easily observed when using monochromatic light sources.

After this (monochromatic) light has interacted with the sample, a very small part of it has changed its wavelength. This change is called: the Raman effect. We can now collect that light and can use it gain information about the sample.

Raman Spectroscopy Principle

When light interacts with molecules in a gas, liquid, or solid, the vast majority of the photons are dispersed or scattered at the same energy as the incident photons. This is described as elastic scattering, or Rayleigh scattering. A small number of these photons, approximately 1 photon in 10 million will scatter at a different frequency than the incident photon. This process is called inelastic scattering, or the Raman effect, named after Sir C.V. Raman who discovered this and was awarded the 1930 Nobel Prize in Physics for his work. Since that time, Raman has been utilized for a vast array of applications from medical diagnostics to material science and reaction analysis. Raman allows the user to collect the vibrational signature of a molecule, giving insight into how it is put together, as well as how it interacts with other molecules around it

Information provided by Raman spectroscopy

Raman spectroscopy probes the chemical structure of a material and provides information about:

- ❖ Chemical structure and identity
- ❖ Phase and polymorphism
- ❖ Intrinsic stress/strain
- ❖ Contamination and impurity

Typically a Raman spectrum is a distinct chemical fingerprint for a particular molecule or material, and can be used to very quickly identify the material, or distinguish it from others. Raman spectral libraries are often used for identification of a material based on its Raman spectrum – libraries containing thousands of spectra are rapidly searched to find a match with the spectrum of the analyte.

Raman Spectroscopy Working

Unlike FTIR Spectroscopy that looks at changes in dipole moments, Raman looks at changes in a molecular bonds polarizability. Interaction of light with a molecule can induce a deformation of its electron cloud. This deformation is known as a change in polarizability. Molecular bonds have specific energy transitions in which a change of polarizability occurs, giving rise to Raman active modes. As an example, molecules that contain bonds between homonuclear atoms such as carbon-carbon, sulfur-sulfur, and nitrogen-nitrogen bonds undergo a change in polarizability when photons interact with them. These are examples of bonds that give rise to Raman active spectral bands, but would not be seen or difficult to see in FTIR.

Because Raman is an inherently weak effect, the optical components of a Raman Spectrometer must be well matched and optimized. Also, since organic molecules may have a greater tendency to fluoresce when shorter wavelength radiation is used, longer wavelength monochromatic excitation sources, such as solid state laser diodes that produces light at 785 nm, are typically used.

Raman Spectroscopy Applications

- Crystallization Processes
- Polymorphism Identification
- Polymerization Reactions
- Hydrogenation Reactions
- Chemical Synthesis
- Biocatalysis and Enzymatic Catalysis
- Flow Chemistry
- Bioprocess Monitoring

- Synthesis Reactions
- Quality by Design

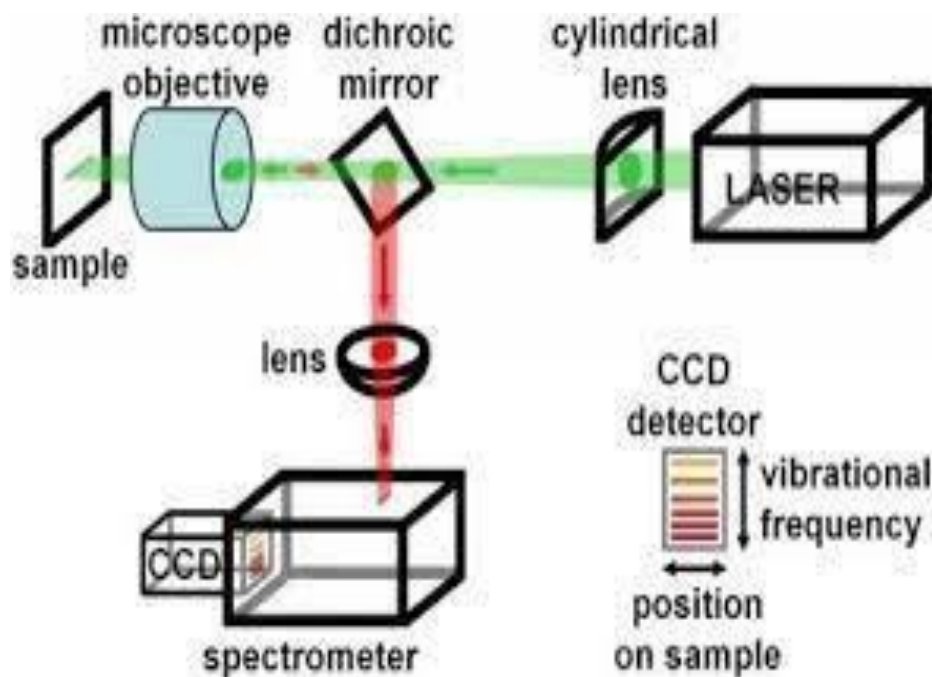


Fig 9: Schematic diagram of Raman Spectroscopy

SPECTRAL CHARACTERIZATION

The chemical shifts for the P4VP terminal exhibited a shift at $\delta = 8.0\text{--}8.6$ ppm (m, $-\text{CH}_2\text{CHC}_5\text{H}_4\text{N}$). Bridging between the two pyridine groups of the block copolymer with DBD is confirmed by the δ at 4.2–4.5 ppm. The FTIR spectrum exhibited the characteristic bands before and after gelation of P4VP. The sample before gelation showed peaks at $1600\text{--}2000\text{ cm}^{-1}$ corresponding to the aromatic C=C stretching; the peaks at 2950 and 3023 cm^{-1} correspond to the C–H asymmetric aliphatic stretching and C–H asymmetric stretching of the aromatic ring, respectively. Upon gelation (organogel), the sample exhibited an asymmetric aliphatic C–H stretching peak at 2923 cm^{-1} and a sharp aromatic symmetric stretching peak at 1644 cm^{-1} . Here, the conversion of pyridine to pyridinium ion is seen as a broad asymmetric $\text{N}^+ - \text{C}$ stretching peak at $810\text{--}1145\text{ cm}^{-1}$.

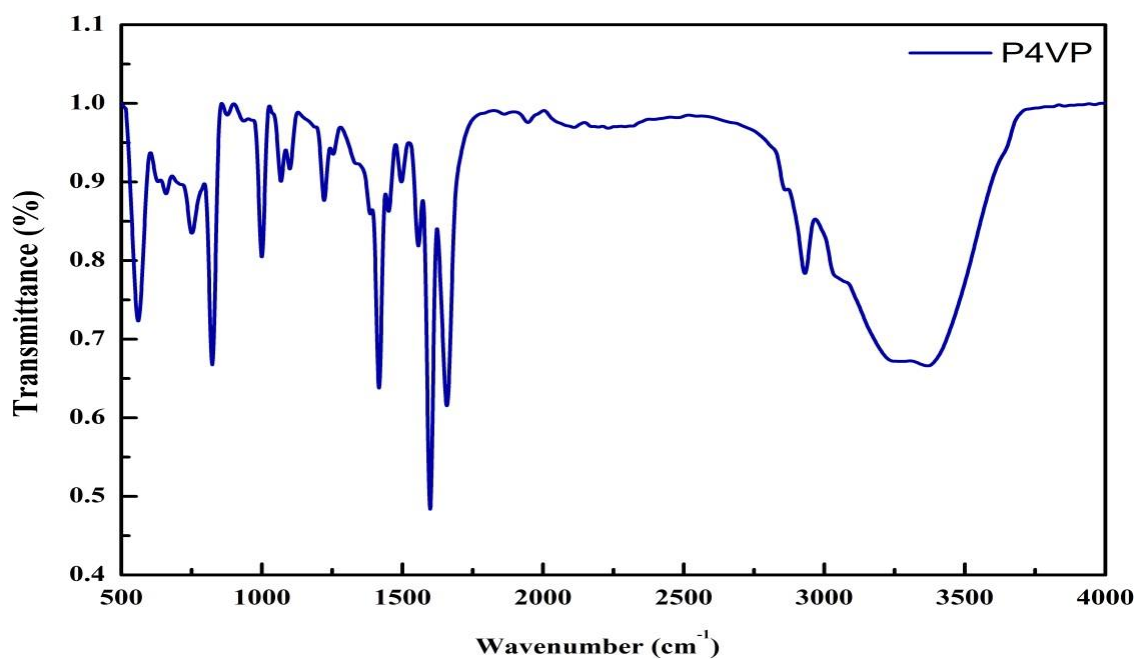


Fig 10: FTIR spectrophotometer of P4VP Polymer

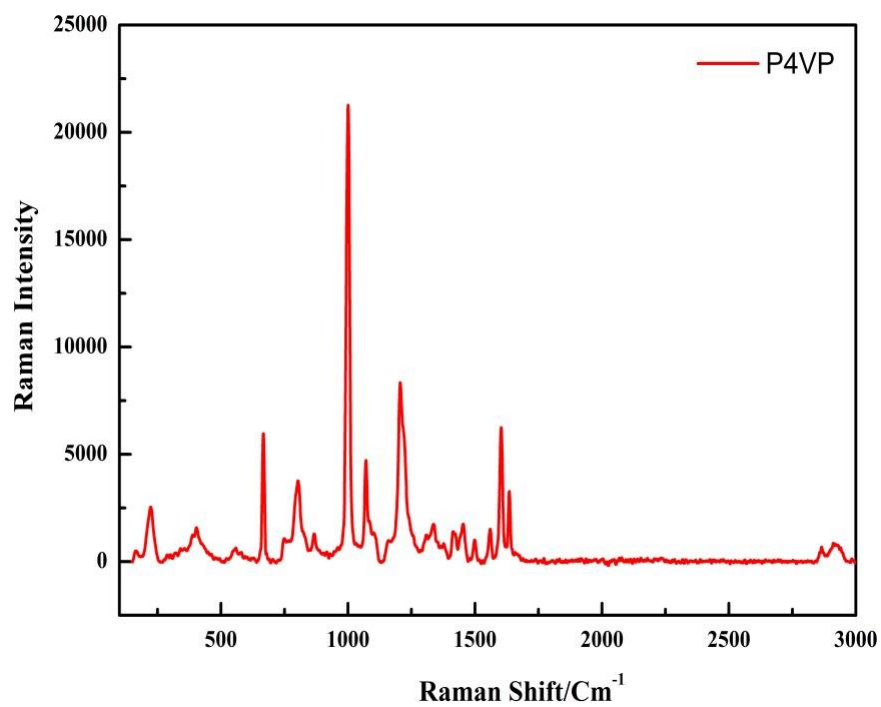


Fig 11: Raman spectrophotometer of P4VP Polymer

P4VP.....Sanjeevi

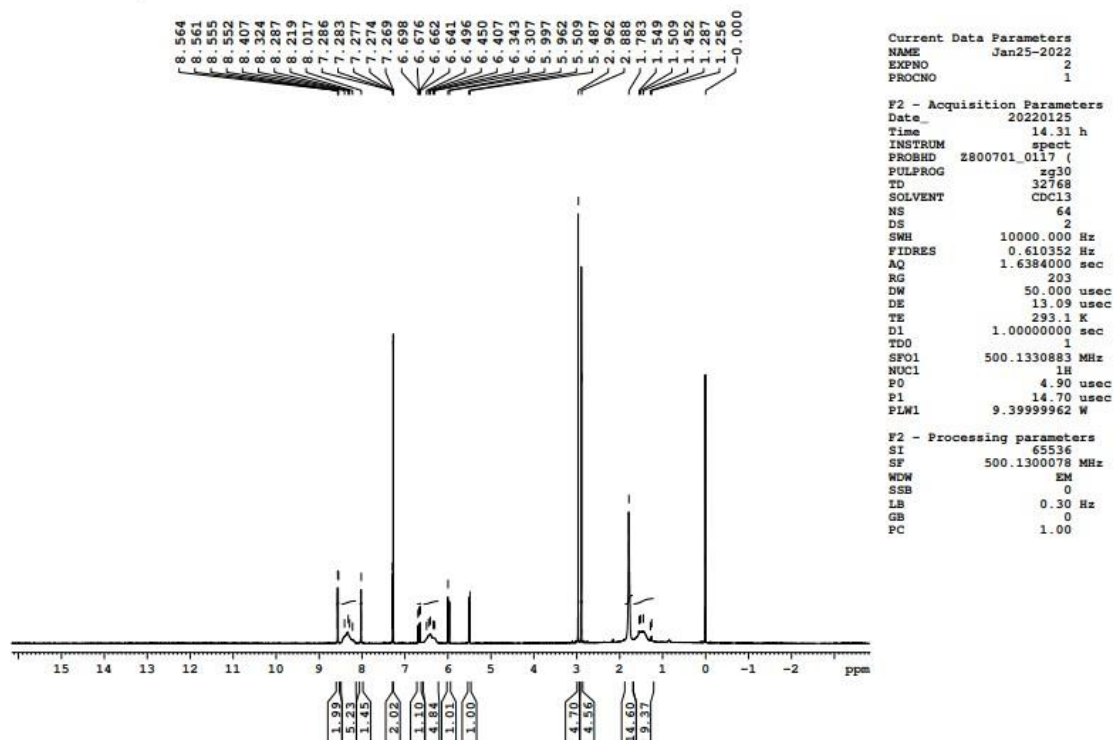
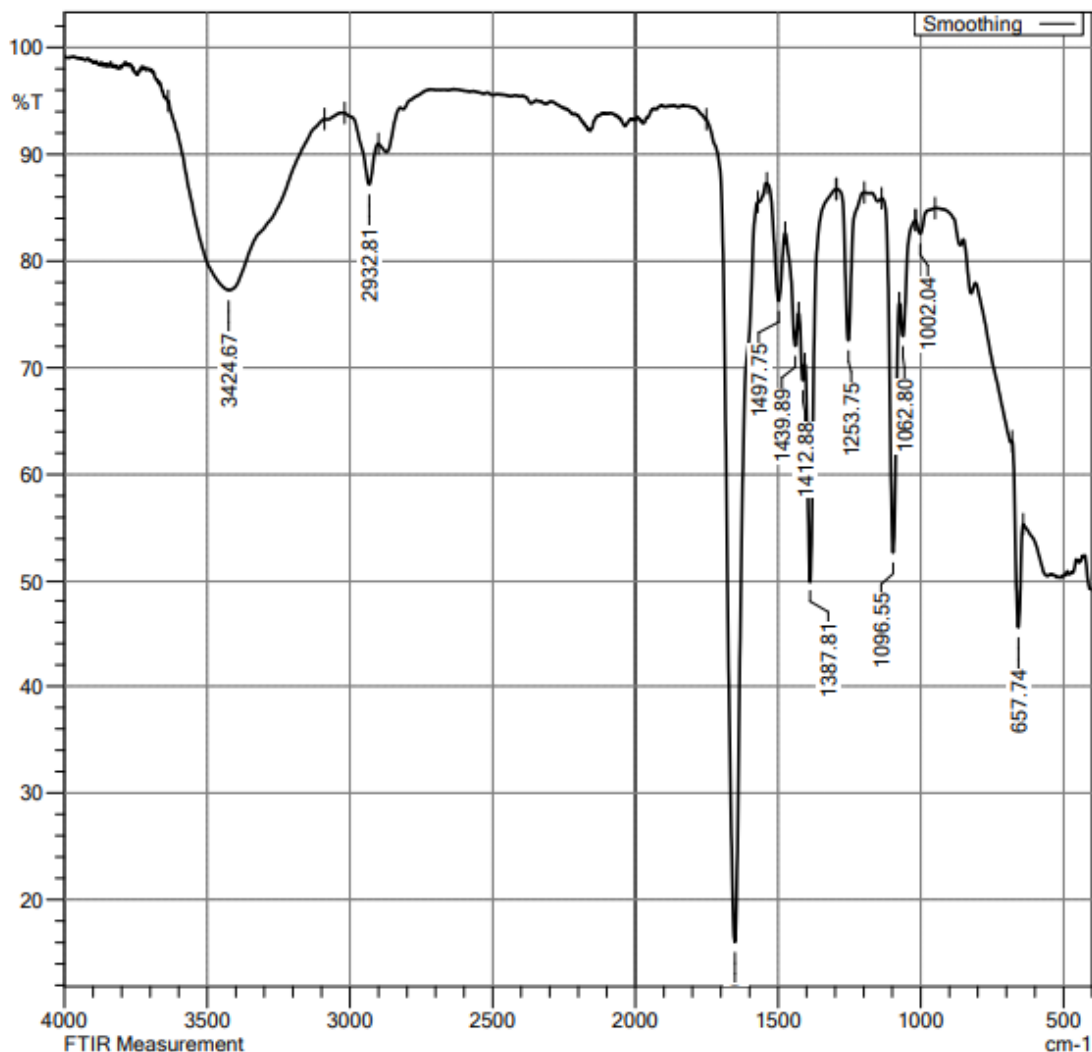


Fig 12: NMR spectrophotometer of P4VP Polymer



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Fig 13: FTIR spectrophotometer of P4VP Organogel

DYE ADSORPTION STUDIES

The anionic dye adsorption potential of the P4VP polymer and its crosslinked organogel was demonstrated using four types of anionic dyes. A pre-weighed 20 mg pellet of the organogel was added to a solution containing the anionic dyes, and the

contact-time-dependent UV-vis absorption spectra were recorded (Fig11 & 12). In pure polymer P4VP there is no change in absorbance it clearly shows that no adsorption of dyes occurs in P4VP (Fig11). As can be seen from the spectra (Fig 12) there is a remarkable dye uptake by the organogel for all four anionic dyes. MO and BB had a single absorption maximum at 465 and 555 nm, whereas CR and BG exhibited two peaks: at 342, 500 nm and 437, 618 nm, respectively. An almost clear water-like solution is observed after 60 min of contact with the organogel. Generally, gel based selective adsorption occurs either via chemisorption or by electrostatic interaction between the reactive sites on the gel and the ionic groups on the dye molecules. In our study, the removal of the anionic dyes by the P4VP organogel can be justified by the high electrostatic attraction between the pyridinium cations in the organogel and the anionic sulfonate groups of MO, CR, BB, and BG. The photographs of the four dye solutions before and the color change of the organogel after 60 min of contact with the dye solution (bottom row) are shown as insets in Fig 10. Importantly, we have used only a meager amount of the organogel (2 wt %) for the adsorption studies; upscaling the quantity of the organogel can significantly shorten the adsorption time. The dye removal efficiency (R , %) of the organogel was calculated using the following equation

$$R = 100 \times \frac{C_i - C_f}{C_i}$$

where C_i and C_f are the initial and final concentrations (mg L^{-1}) of the dye after adsorption. Quantitative analysis of the UV-vis spectra was performed by monitoring the main peak intensity and from equation. From the peak intensity, about 90% MO, 72% CR, 76% BB, and 89% BG were removed within 60 min of contact with the organogel. Increasing the contact time to 120 min showed 98% MO, 90% CR, 88% BB, and 96% BG removal.

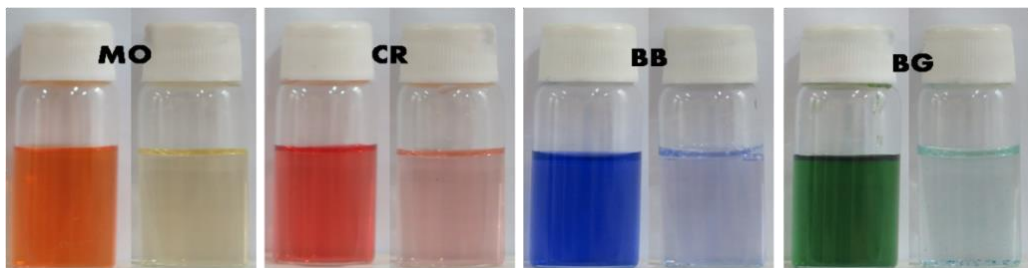


Fig 14: Insets in the figure show the photographs of the various dye solutions before and after the removal of the dyes by the organogel and the color change of the organogel after 60 min of contact with the dye solution.

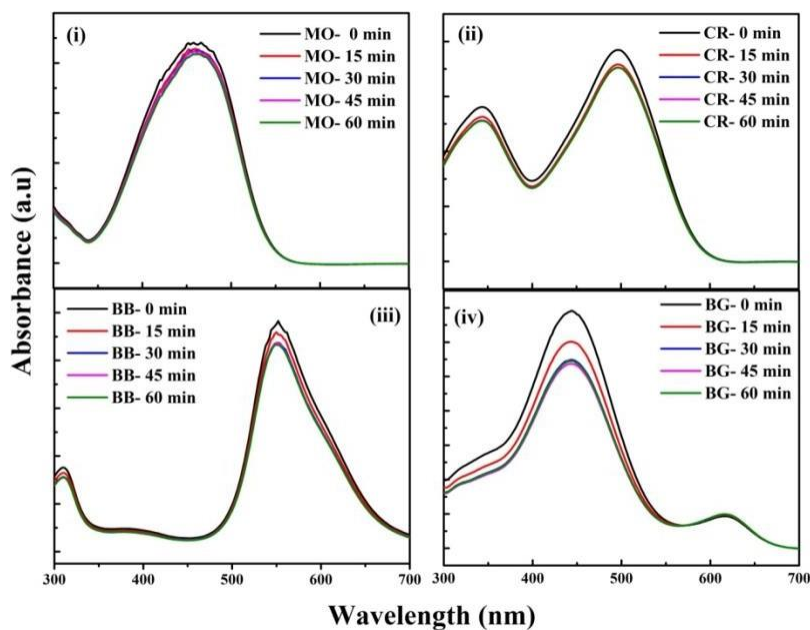


Fig 15: UV-visible spectral evolution with time of the various dye solutions in contact with the P4VP polymer: (a) methyl orange, (b) Congo red, (c) brilliant blue R-250, and (d) bromocresol green.

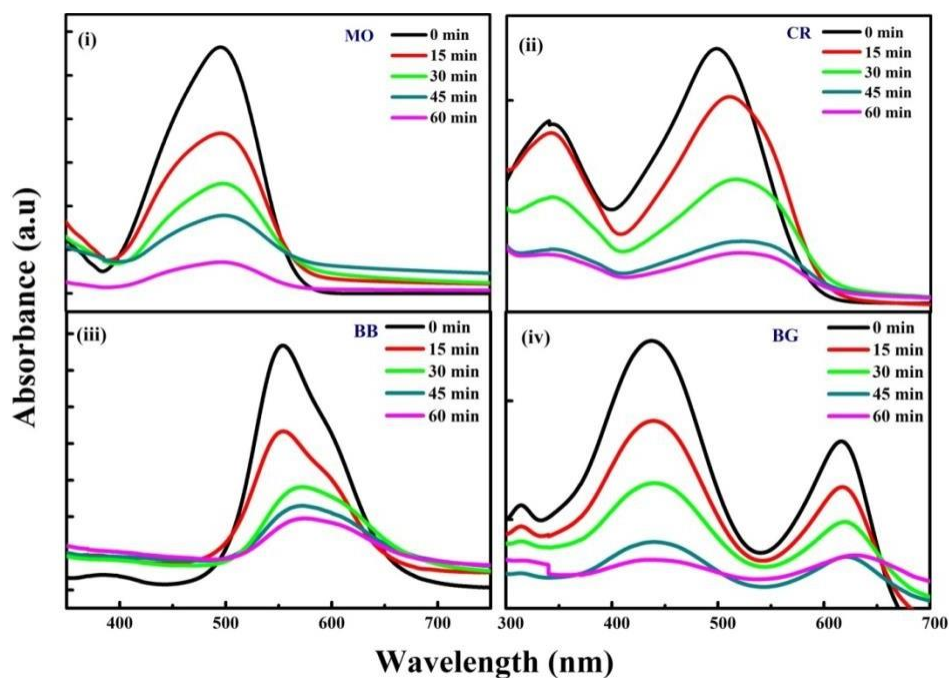


Fig 16: UV–visible spectral evolution with time of the various dye solutions in contact with the organogel: (a) methyl orange, (b) Congo red, (c) brilliant blue R-250, and (d) bromocresol green.

Table 1. % Removal efficiency reported by various research groups for a few dyes using gel-based materials

Type of gels	Dyes	Dye removal (%)	References
Poly(N-isopropylacrylamide) microgels	Orange II	73.1	(Parasuraman and Serpe 2011)
Methylacryloyloxyethyltrimethyl ammoniumchloride zwitterionic hydrogel	Acid red	95	(Wei et al. 2018)
	Quinoline yellow	95	

	Methyl violet	10	
	Methylene blue	10	
Metal-organic gels	Congo Red	95	(Hong et al. 2018)
	Rhodamine B	92	
	Methylene blue	85	
	Chrome azurol S	97	
	Methyl violet	94	
	Amido black 10B	67	
Imidazolium-based supramolecular gels	Eosin yellow	80	(Cheng et al. 2015)
Supramolecular ionic liquid gels	Rhodamine B	95	(Rizzo et al. 2018)
Poly(acrylic acid)-nanocomposites hydrogel	Methylene blue	98	(Hu et al. 2015)
Poly-epichlorohydrin-ethylenediamine hydrogel	DR 23	99	(Li et al. 2017)
	AR1	99	
	AO7	98	
	AY36	99.8	
	DB15	100	
Folic Acid-polyaniline hybrid hydrogel	Eosin yellow	98	(Das et al. 2017)
Poly(acrylic acid)-kaolin hydrogel	Brilliant green	99.3	(Shirsath et al. 2013)
Tripeptide based hydrogels	Rhodamine B		(Adhikari et al. 2009)
	Direct red 80		

	Reactive blue 4	~95	
Alginate/polyaspartate hydrogel	Methylene blue	97	(Jeon et al. 2008)

CHAPTER 6

SUMMARY AND CONCLUSION

This work describes the synthesis of an organogel of a poly(4-vinylpyridine) polymer using dibromododecane as the cross-linker. From the protonNMR and FTIR, the cross-linking of the block copolymer into a gel is confirmed. Due to the presence of N⁺ ions, the organogel acts as an adsorbent for anionic dyes and also exhibits anion selectivity in a mixture of cationic and anionic dyes, which is driven by electrostatic attraction between the positively charged gel and negatively charged dye molecules. This organogel is highly cost-effective as it can be recycled, reused, and regenerated with a very high throughput removal of anionic dyes within a short period – the performance of the organogel is expected to remain unaltered for long-term water treatment applications. The P4VP organogel is high performing as compared with other reported gel-based absorbents. In Table 1, we have shown the removal efficiency of several gel-based adsorbents. Comparing our work with the results summarized in Table 1, with a mere 2 wt % adsorbent used and much quicker times for dye removal, the organogel of P4VP shows excellent potential for applications in effluent water treatment. We strongly believe that the adsorption performance of the organogel will not deteriorate with time and remain unaltered for long-term effluent water treatment applications.

References

- (1) Abramian, L.; El-Rassy, H. Adsorption Kinetics and Thermodynamics of Azo-Dye Orange II onto Highly Porous Titania Aerogel. *Chem. Eng. J.* 2009, 150, 403–410.
- (2) Adhikari, B.; Palui, G.; Banerjee, A. Self-Assembling Tripeptide Based Hydrogels and Their Use in Removal of Dyes from WasteWater. *Soft Matter* 2009, 5, 3452–3460.
- (3) Ali, H. Biodegradation of Synthetic Dyes - A Review. *Water. Air. Soil Pollut.* 2010, 213, 251–273.
- (4) Amini, M.; Arami, M.; Mahmoodi, N. M.; Akbari, A. Dye Removal from Colored Textile Wastewater Using Acrylic Grafted Nanomembrane. *Desalination* 2011, 267, 107–113.
- (5) Aouni, A.; Fersi, C.; Cuartas-Urbe, B.; Bes-Pía, A.; AlcainaMiranda, M. I.; Dhahbi, M. Reactive Dyes Rejection and Textile Effluent Treatment Study Using Ultrafiltration and Nanofiltration Processes. *Desalination* 2012, 297, 87–96.
- (6) Cheng, N.; Hu, Q.; Guo, Y.; Wang, Y.; Yu, L. Efficient and Selective Removal of Dyes Using Imidazolium-Based Supramolecular Gels. *ACS Appl. Mater. Interfaces* 2015, 7, 10258–10265.
- (7) Chinoune, K.; Bentaleb, K.; Bouberka, Z.; Nadim, A.; Maschke, U. Adsorption of Reactive Dyes from Aqueous Solution by Dirty Bentonite. *Appl. Clay Sci.* 2016, 123, 64–75.
- (8) Daassi, D.; Rodríguez-Couto, S.; Nasri, M.; Mechichi, T. Biodegradation of Textile Dyes by Immobilized Laccase from *Coriolopsis Gallica* into Ca-Alginate Beads. *Int. Biodeterior. Biodegrad.* 2014, 90, 71–78.
- (9) Das, S.; Chakraborty, P.; Ghosh, R.; Paul, S.; Mondal, S.; Panja, A.; Nandi, A. K. Folic Acid-Polyaniline Hybrid Hydrogel for Adsorption/Reduction of Chromium(VI) and Selective Adsorption of Anionic Dye from Water. *ACS Sustainable Chem. Eng.* 2017, 5, 9325–9337.

- (10) Dai, M.; Li, H. X.; Lang, J. P. New Approaches to the Degradation of Organic Dyes, and Nitro- and Chloroaromatics Using Coordination Polymers as Photocatalysts. *CrystEngComm* 2015, 17, 4741–4753.
- (11) Gajera, H. P.; Bambharolia, R. P.; Hirpara, D. G.; Patel, S. V.; Golakiya, B. A. Molecular Identification and Characterization of Novel Hypocrea Koningii Associated with Azo Dyes Decolorization and Biodegradation of Textile Dye Effluents. *Process Saf. Environ. Prot.* 2015, 98, 406–416.
- (12) Ghosh, A.; Mondal, A. Fabrication of Stable, Efficient and Recyclable p-CuO/n-ZnO Thin Film Heterojunction for Visible Light Driven Photocatalytic Degradation of Organic Dyes. *Mater. Lett.* 2016, 164, 221–224.
- (13) Gök, Ö .; Özcan, A. S.; Özcan, A. Adsorption Behavior of a Textile Dye of Reactive Blue 19 from Aqueous Solutions onto Modified Bentonite. *Appl. Surf. Sci.* 2010, 256, 5439–5443.
- (14) Hassani, A.; Khataee, A.; Karaca, S.; Karaca, M.; Kiransan, M. , Adsorption of Two Cationic Textile Dyes from Water with Modified Nanoclay: A Comparative Study by Using Central Composite Design. *J. Environ. Chem. Eng.* 2015, 3, 2738–2749.
- (15) Hassani, A.; Soltani, R. D. C.; Karaca, S.; Khataee, A. Preparation of Montmorillonite-Alginate Nanobiocomposite for Adsorption of a Textile Dye in Aqueous Phase: Isotherm, Kinetic and Experimental Design Approaches. *J. Ind. Eng. Chem.* 2015, 21, 1197–1207.
- (16) Hong, Y.; Gao, Z.; Chen, M.; Hao, J.; Dong, S. Metal-Organic Gels of Catechol-Based Ligands with Ni(II) Acetate for Dye Adsorption. *Langmuir* 2018, 34, 9435–9441.
- (17) Hu, X.-S.; Liang, R.; Sun, G. Super-Adsorbent Hydrogel for Removal of Methylene Blue Dye from Aqueous Solution. *J. Mater. Chem. A* 2018, 6, 17612–17624.
- (18) Huang, P.; Xia, D.; Kazlauciusas, A.; Thornton, P.; Lin, L.; Menzel, R. Dye-Mediated Interactions in Chitosan-Based Polyelectrolyte/Organoclay Hybrids for Enhanced Adsorption of Industrial Dyes. *ACS Appl. Mater. Interfaces* 2019, 11, 11961–11969.

- (19) Jagur-Grodzinski J (2010), "Polymeric gels and hydrogels for biomedical and pharmaceutical applications", Vol. 21, No. (1). pp. 27-47
- (20) Jeon, Y. S.; Lei, J.; Kim, J. H. Dye Adsorption Characteristics of Alginate/Polyaspartate Hydrogels. *J. Ind. Eng. Chem.* 2008, 14, 726– 731.
- (21) Jia, L.; Zhou, T.; Xu, J.; Li, X.; Dong, K.; Huang, J.; Xu, Z. The Enhanced Catalytic Activities of Asymmetric Au-Ni Nanoparticle Decorated Halloysite-Based Nanocomposite for the Degradation of Organic Dyes. *Nanoscale Res. Lett.* 2016, 11, No. 72.
- (22) Kang, J. K.; Cho, E. J.; Han, W. S.; Jeong, I. Y.; Jung, J. H.; Lee, S. J. Terpyridine-Based Smart Organic-Inorganic Hybrid Gel as Potential Dye-Adsorbing Agent for Water Purification. *Tetrahedron Lett.* 2007, 49, 1076–1079.
- (23) Kar, T.; Debnath, S.; Das, D.; Shome, A.; Das, P. K. Organogelation and Hydrogelation of Low-Molecular-Weight Amphiphilic Dipeptides: PH Responsiveness in Phase-Selective Gelation and Dye Removal. *Langmuir* 2009, 25, 8639–8648.
- (24) Karan, C. K.; Bhattacharjee, M. Self-Healing and Moldable Metallogels as the Recyclable Materials for Selective Dye Adsorption and Separation. *ACS Appl. Mater. Interfaces* 2016, 8, 5526–5535.
- (25) Kuddushi, M.; Rajput, S.; Shah, A.; Mata, J.; Aswal, V. K.; El Seoud, O.; Kumar, A.; Malek, N. I. Stimuli Responsive, SelfSustainable, and Self-Healable Functionalized Hydrogel with Dual Gelation, Load-Bearing, and Dye-Absorbing Properties. *ACS Appl. Mater. Interfaces* 2019, 11, 19572–19583.
- (26) Kuddushi, M.; Mata, J.; Malek, N. Self-Sustainable, SelfHealable, Load Bearable and Moldable Stimuli Responsive Ionogel for the Selective Removal of Anionic Dyes from Aqueous Medium. *J. Mol. Liq.* 2020, 298, No. 112048.
- (27) Kuddushi, M.; Patel, N. K.; Rajput, S.; Shah, A.; El Seoud, O. A.; Malek, N. I. Thermo-Switchable de Novo Ionic Liquid-Based Gelators with Dye-Absorbing and Drug-Encapsulating Characteristics. *ACS Omega* 2018, 3, 12068–12078.

- (28) Li, D.; Li, Q.; Bai, N.; Dong, H.; Mao, D. One-Step Synthesis of Cationic Hydrogel for Efficient Dye Adsorption and Its Second Use for Emulsified Oil Separation. *ACS Sustainable Chem. Eng.* 2017, 5, 5598–5607.
- (29) Lonč arevic, D.; Dostanić , J.; Radonjić , V.; Z ´ ´ ivkovic, L.; Jovanovic, D M. Simultaneous Photodegradation of Two Textile ´ Dyes Using TiO₂ as a Catalyst. *React. Kinet., Mech. Catal.* 2016, 118, 153–164.
- (30) Lucić Š koric, M.; Terzić , I.; Milosavljević , N.; Radetić , M.; Š aponjic, Z Radoić ić , M.; Kalagaidis Krus´ ić , M. Chitosan-Based ´ Microparticles for Immobilization of TiO₂nanoparticles and Their Application for Photodegradation of Textile Dyes. *Eur. Polym. J.* 2016, 82, 57–70.
- (31) Maatar, W.; Alila, S.; Boufi, S. Cellulose Based Organogel as an Adsorbent for Dissolved Organic Compounds. *Ind. Crop. Prod.* 2013, 49, 33–42.
- (32) Mandal, B.; Ray, S. K. Synthesis of Interpenetrating Network Hydrogel from Poly(Acrylic Acid-Co-Hydroxyethyl Methacrylate) and Sodium Alginate: Modeling and Kinetics Study for Removal of Synthetic Dyes from Water. *Carbohydr. Polym.* 2013, 98, 257–269.
- (33) Mohar, M.; Das, T. Phenylalanine-Based Low-MolecularWeight Gelator for the Removal of Metal Ions and Dyes from Wastewater. *Soft Mater.* 2019, 17, 328–341.
- (34) Pal K and Banerjee I: "Polymeric Gels: Characterization, Properties, and Biomedical Applications", Elsevier Science 2018
- (35) Parasuraman, D.; Serpe, M. J. Poly (N-Isopropylacrylamide) Microgel-Based Assemblies for Organic Dye Removal from Water. *ACS Appl. Mater. Interfaces* 2011, 3, 4714–4721.
- (36) Pourjavadi, A.; Doulabi, M.; Soleyman, R. Novel CarbonNanotube-Based Organogels as Candidates for Oil Recovery. *Polym. Int.* 2013, 62, 179–183.

- (37) Riera-Torres, M.; Gutiérrez-Bouzán, C.; Crespi, M. Combination of Coagulation-Flocculation and Nanofiltration Techniques for Dye Removal and Water Reuse in Textile Effluents. *Desalination* 2010, 252, 53–59.
- (38) Rizzo, C.; Marullo, S.; Campodonico, P. R.; Pibiri, I.; Dintcheva, N. T.; Noto, R.; Millan, D.; D'Anna, F. Self-Sustaining Supramolecular Ionic Liquid Gels for Dye Adsorption. *ACS Sustainable Chem. Eng.* 2018, 6, 12453–12462.
- (39) Rizzo, C.; Marullo, S.; D'Anna, F. Carbon-Based Ionic Liquid Gels: Alternative Adsorbents for Pharmaceutically Active Compounds in Wastewater. *Environ. Sci. Nano* 2021, 8, 131–145.
- (40) Rizzo, C.; Marullo, S.; Dintcheva, N. T.; Gambarotti, C.; Billeci, F.; D'Anna, F. Ionic Liquid Gels and Antioxidant Carbon Nanotubes: Hybrid Soft Materials with Improved Radical Scavenging Activity. *J. Colloid Interface Sci.* 2019, 556, 628–639.
- (41) Rogovina L Z, Vasil'ev V G, and Braudo E E (2008), "Definition of the concept of polymer gel", *Polymer Science Series C*, Vol. 50, No. (1). pp. 85-92.
- (42) Sar, P.; Roy, S. G.; De, P.; Ghosh, S. Synthesis of Glutamic Acid Derived Organogels and Their Applications in Dye Removal from Aqueous Medium. *Macromol. Mater. Eng.* 2020, 305, No. 1900809.
- (43) Saravanakumar, K.; Muthuraj, V.; Jeyaraj, M. The Design of v Visible Light Driven Ag/CdO as Smart Nanocomposite for Photodegradation of Different Dye Contaminants. *Spectrochim. Acta, Part A* 2018, 188, 291–300.
- (44) Sengupta, S.; Mondal, R. A Novel Gel-Based Approach to Wastewater Treatment-Unique One-Shot Solution to Potentially Toxic Metal and Dye Removal Problems. *J. Mater. Chem. A* 2014, 2, 16373–16377.
- (45) Sharma, R.; Singhal, S. Photodegradation of Textile Dye Using Magnetically Recyclable Heterogeneous Spinel Ferrites. *J. Chem. Technol. Biotechnol.* 2015, 90, 955–962.

- (46) Sharma, R.; Kaith, B. S.; Kalia, S.; Pathania, D.; Kumar, A.; Sharma, N.; Street, R. M.; Schauer, C. Biodegradable and Conducting Hydrogels Based on Guar Gum Polysaccharide for Antibacterial and Dye Removal Applications. *J. Environ. Manage.* 2015, 162, 37–45.
- (47) Shirsath, S. R.; Patil, A. P.; Patil, R.; Naik, J. B.; Gogate, P. R.; Sonawane, S. H. Removal of Brilliant Green from Wastewater Using Conventional and Ultrasonically Prepared Poly(Acrylic Acid) Hydrogel Loaded with Kaolin Clay: A Comparative Study. *Ultrason. Sonochem.* 2013, 20, 914–923.
- (48) Sreedhar, M.; Brijitta, J.; Reddy, I. N.; Cho, M.; Shim, J.; Bera, P.; Joshi, B. N.; Yoon, S. S. Dye Degradation Studies of Mo-Doped TiO₂ thin Films Developed by Reactive Sputtering. *Surf. Interface Anal.* 2018, 50, 171–179.
- (49) Sreedhar, M.; Neelakanta Reddy, I.; Reddy, C. V.; Shim, J.; Brijitta, J. Highly Photostable Zn-Doped TiO₂ Thin Film Nanostructures for Enhanced Dye Degradation Deposited by Sputtering Method. *Mater. Sci. Semicond. Process.* 2018, 85, 113–121.
- (50) Sridhar, Sanjeevi Prasath, Jacob John, Rajan Kumar, Raja Shunmugam, Chandran Saravanan, and Brijitta Joseph. "Chemically crosslinked poly (N- isopropylacrylamide-block-4-vinylpyridine) organogel with myriad applications". *Materials Letters* 272 (2020): 127854.
- (51) Sridhar, Sanjeevi Prasath, Jacob John, Peter Holmqvist, Ulf Olsson, Saravanan Chandran, and Brijitta Joseph. "Adsorption of Anionic Dyes Using a Poly (styrene- block-4-vinylpyridine) Block Copolymer Organogel". *Langmuir* 37, no. 13 (2021): 3996-4006.
- (52) Song, S.; Feng, L.; Song, A.; Hao, J. Room-Temperature Super Hydrogel as Dye Adsorption Agent. *J. Phys. Chem. B* 2012, 116, 12850–12856.
- (53) Van Hoa, N.; Khong, T. T.; Thi Hoang Quyen, T.; Si Trung, T. One-Step Facile Synthesis of Mesoporous Graphene/Fe₃O₄/ Chitosan Nanocomposite and Its Adsorption Capacity for a Textile Dye. *J. Water Process Eng.* 2016, 9, 170–178.

- (54) Vintiloiu, A.; Leroux, J. C. Organogels and Their Use in Drug Delivery - A Review. *J. Control. Release* 2008, 125, 179–192.
- (55) Wang, F.; Li, F. L.; Xu, M. M.; Yu, H.; Zhang, J. G.; Xia, H. T.; Lang, J. P. Facile Synthesis of a Ag(i)-Doped Coordination Polymer with Enhanced Catalytic Performance in the Photodegradation of Azo Dyes in Water. *J. Mater. Chem. A* 2015, 3, 5908–5916.
- (56) Wei, R.; Song, W.; Yang, F.; Zhou, J.; Zhang, M.; Zhang, X.; Zhao, W.; Zhao, C. Bidirectionally PH-Responsive Zwitterionic Polymer Hydrogels with Switchable Selective Adsorption Capacities for Anionic and Cationic Dyes. *Ind. Eng. Chem. Res.* 2018, 57, 8209– 8219.
- (57) Yang, X.; Liu, H. Diphenylphosphine-Substituted Ferrocene/ Silsesquioxane-Based Hybrid Porous Polymers as Highly Efficient Adsorbents for Water Treatment. *ACS Appl. Mater. Interfaces* 2019, 11, 26474–26482.
- (58) Zheng, Y.; Yao, G.; Cheng, Q.; Yu, S.; Liu, M.; Gao, C. Positively Charged Thin-Film Composite Hollow Fiber Nanofiltration Membrane for the Removal of Cationic Dyes through Submerged Filtration. *Desalination* 2013, 328, 42–50.

