Synthesis and Antibacterial Studies of Bio Based Polyacrylonitrile-g-kappa Carrageenan Copolymer via Heterogeneous Catalyst

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Synthesis and Antibacterial Studies of Bio Based Polyacrylonitrile-*g*-kappa Carrageenan Copolymer *via* Heterogeneous Catalyst

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Abstract: In this study, the formation of polyacrylonitrile (PAN) and carrageenan (κ) based graft copolymer formed by free radical polymerization with the help of heterogeneous catalyst (Propiophenonebutyldimethylammonium iodide) was investigated for its antibacterial activity against *E-Coli* and *Staphylococcus aureus* for potential use as coating on biomaterial surface. The polymerization kinetics with respect to the steady state approximation, effect of monomer and catalyst concentrations on the rate of polymerization is studied. The synthesized copolymer exhibited growth inhibition zone of 18 and 11 mm compared to streptomycin standard of 25 mm which successfully hindering the progression of the *S. aureus.*

Keywords: Polyacrylonitrile; Heterogeneous catalyst; Carrageenan; Antibacterial studies; Free radical polymerization

1. Introduction

Chemical industries have developed new catalysts recently to increase safety, efficiency, and lessen the environmental effect of chemical processes. It is well recognized that catalysis is essential to many facets of industrial processes in contemporary chemical technologies[1)] Catalysts have been utilized in industrial operations for the production of food items, petroleum products, and a variety of synthetic commodities by several industries worldwide. Even more difficult and complex issues confront modern catalytic science[2)]. Understanding the kinetics and mechanism of catalytic processes is crucial for the large-scale creation of innovative synthetic techniques that meet industrial needs and aims.

Phase transfer catalyst is one of the important industrial catalyst also called heterogeneous catalyst where an organic or inorganic salt is transported by phase transfer catalysis, from an water soluble segment to an water insoluble segment also called organic soluble and in this phase reaction occurs[3)]. With the utilization of a phase transfer catalyst, this method may be used to overlap two immiscible reagents: soluble organic reactant taken in hydrophobic medium and a salt comprising of complex medium from hydrophilic phase. The sensitive anions extracted from the water soluble medium and transferred to the hydrophobic medium containing the reactant by phase transfer catalyst[4)]. In the organic layer, there is an interaction between the non-transferred reactant and the transferred reagent.

An aqueous and an organic phase were used to carry out phase transfer catalyst reactions. It is an organic-aqueous two-phase system made up of two immiscible liquids: an organic phase containing a liquid reagent with or without an organic solvent, and an aqueous phase nucleophilic reagent M+ Nu-. A catalyst, such as quaternary salt, is partitioned between the two phases. Furthermore, polymers produced using phase transfer catalysts have a high molecular weight and a consistent polydispersity value even at high conversion rates[5)].

Sarina et al.[6)] reported the nanocomposites supported palladium nanoparticle pH activated phase transfer catalyst for the air induced respiration of alcohols. They found that the oxidation process is highly competent and chemo selective with the help of the catalyst. Mehrjardi et al.[7)] reported synthesized the magnetic nanoparticle supported ionic liquids as an efficient activator for various coupling reactions in water medium. The catalyst demonstrates high yield, shorter reaction time, reusability, recyclability and more acceptable reaction condition. Xu and coworkers[8)] recently reported eco – friendly phase transfer catalyst namely 2-amino-3-cyano-4-aryl-6-sulfane – pyrimidine for efficient green synthesis. Desai et al. produced new phosphonium-based ionic liquids as

a phase transfer catalyst in the ultrasonic aided oxidation and sulphur removal of liquid fuel[9] .The efficiency of various parameters including temperature, time and mass ratio of ionic liquids were discussed. They reviewed that the maximum efficiency for desulfurization using the reported phase transfer catalyst. Mori et al.[10] reported the preparation of 1-ethoxy 4-nitrobenzene utilizing 4-fluoro nitrobenzene in a repetitive flow micro-reactor using a phase transfer catalyst. At ambient pressure, the reaction somewhat accelerated but otherwise continued smoothly in the case of slug flow.

Researchers[11] also described oxidizing N-phosphonomethyl-imidazolium acid with hydrogen peroxide and phosphate tungstate as a phase transfer catalyst. The catalyst was very efficient in bringing the activation energy 37 kJ/mol of the reaction for the temperature 343K. Statistical design analysis of isophorone electro catalytic hydrogenation using a cyclodextrin phase transfer catalyst was also reported. Marimuthu et al.[12] reported the ultrasonic polymerization of N-Vinyl carbazole using the novel PTC catalyst. The kinetics, efficiency of the catalyst, monomer concentration and temperature dependent on the polymerization rate were explained. Micronenko et al.[13] reported a crucial review regarding the water soluble restructuring of the compound furfural by the existence of solid support. The review explains the presence of various elements including palladium (Pd), nickel (Ni), cobalt (Co) and copper (Cu) containing catalyst in the significant hydrogenation of furfural

Because of their matrix structure and inability to degrade, polymers often lack inherent antibacterial characteristics. Antibacterial agents are frequently used in the production of polymer antibacterial materials to enhance the polymer's functionality using various techniques. Carrageenan is a particular sort of plant extract derived from red seaweed. Carrageenans are water-soluble, linear, and sulphated galactans with a wide range of biological uses[14]. The polymer made under this component will have anti-bacterial capabilities, which are more promising in contemporary times[15]. Carrageenans also have anticancer, antioxidant, and anticoagulant properties, making them an appealing component in biological research[16]. The literature has demonstrated the strong antibacterial activity of carrageenans, and as a result, the copolymer formed in the core of kappa carrageenan will carry out its antibacterial activity throughout the whole polymer[17]. There are several studies in the literature that describe how natural plant extract may be used to modify synthetic polymers, creating graft copolymers that have built-in antibacterial qualities[18]. Sadasivuni and coworkers[19] reported the glycine modified chitosan embedded silver nanoparticle via a green method of synthesis. The reported material exhibits high lead loading capacity of 270.2mg/g from aqueous solution with a efficiency of 93%. Yang et al.,[20] reported the sophisticated antibacterial material by loading silver nanoparticle to gelatin with enhanced mechanical, thermal and biodegradable nature which will be applied for wound healing and surface coating material. Ninan et al.,[21] reported the carboxylated agarose/tannic acid hydrogel with crosslinked zinc ions for controlled release of tannic acid. This reported compound has a proven application with good cytocompatibility and anti-inflammatory activities. Park and coworkers[22] reported highly active antibacterial agent to inhibit the growth of staphylococcus aureus and E.Coli using PEDOT based iron oxide material. High antibacterial activity against staphylococcus by utilizing soybean carrageenan and silver nanoparticle with a good food packaging application also reported[23]. High antibacterial inhibition zone is reported for polyaniline nanofibres with a value of 48.47 Scm^{-1} conductivity and 570 Fg^{-1} capacitance[24]. Photocatalytic degradation of methylene blue using carbon dot supported silver nanoparticle also reported recently[25].

Malik et al.[26] used a microwave-assisted approach to modify the graft of acrylamide on gum kondagogu. Gum kondagogu macro radicals combine with acrylamide free radicals to produce a sequence of free radical chain reactions that lead to the development of polyacrylamide and gum kondagogu-g-poly (acrylamide) graft copolymers rather than homopolymers. According to a recent research, plant extracts can be used because they have a higher affinity for binding with different polymers and have antibacterial capabilities. Their mode of action also includes material qualities that contribute to their antiviral activity[27]. A recent study highlights the application of porous polymeric gel as an antimicrobial substance, featuring a 3D, interpenetrating structure saturated with water or various liquid solvents that penetrate the bacterial cell[28]. Several natural polymers were chemically changed with synthetic polymers that are biocompatible, biodegradable, and nontoxic[29]. These nanofibres have shown to be effective materials for controlling the concentration of released chemicals and increasing antibacterial activity. Carrageenan[30] is a significant potential bioactive substance composed of linear polysaccharides. Yamashita et al. conducted a successful study of carrageenan's antibacterial activity utilizing foodborne pathogenic bacteria[31]. The results show that carrageenan is effective since it has the strongest inhibitory impact. In the present work, phase transfer catalyst assisted free radical polymerization is utilized for the polymerization of acrylonitrile which should yield a different range of molecular weight. Further, the homopolymers can be copolymerized with a bioactive compound kappa – carrageenan to yield a copolymer which should have wide range of biological applications including antibacterial and antifungal properties. In addition to that, the effects of variable concentration of monomer and PTC on the reaction rate were also studied. The antibacterial studies of the

synthesized copolymer were also investigated with various stains.

2. EXPERIMENTAL METHODS

2.1 MATERIALS

Chemicals such as Acetophenone, Paraformaldehyde, Sodium bicarbonate, Potassium peroxodisulphate etc. were purchased from SRL chemicals India Pvt. Ltd. K-Carrageenan, Dimethylaminohydrochloride, n-butyliodide and acrylonitrile were purchased from Aldrich chemicals are of AR grade and used as such. All the solvents used in this project are distilled before use.

2.2 POLYMERIZATION TECHNIQES

Polymerization took place in an argon environment at approximately 60°C with no agitation. The reaction blend comprised of 10 ml for both the water-soluble and insoluble phases. The aqueous phase contains the phase transfer (quaternary bet ammonium salt), whereas the initiator and organic phases include the monomer and solvent, which were blushed with pure nitrogen gas before the experiment began. By introducing an initiator to the reaction mixture at a specified concentration and starting the stop watch at the same time, the polymerization process was initiated in a nitrogen environment. After that, the reaction tubes were meticulously airtight with rubber linings to guarantee an inert environment the entire time.

The addition of an initiator to the reaction mixture resulted in the precipitation of the polymer, initiating the polymerization process. The polymerization process was halted by introducing the combination into ethanol solvent. The polymers underwent quantitative filtration using sintered glass crucible, purified by repeated washing with water followed by ethyl acetate and then a vacuum oven or desiccator was used to dry them at 40°C to constant weight. The aforementioned protocol was followed to conduct a polymerization experiment by varying the concentrations of different constituents. The polymerization rate Rp was determined by calculating the weight of the polymer generated during a designated polymerization timeframe through gravimetric measurement.

$$R_p = \frac{1000 \times W}{V.t.M}$$

where
W = polymer weight in gram; V = Volume; t = time (s); M=Mol. Wt. of the monomer.

2.3 Synthesis of PTC (Propiophenonebutyldimethylammonium iodide)

The PTC is synthesized in two states. In the first step, a Mannich base, Dimethylaminopropiophenonehydrochloride, was produced. In the second stage, this chemical was used to produce a quaternary ammonium salt, propiophenonebutyldimethyl ammonium iodide.

2.3.1 Preparation of Dimethylaminopropiophenonehydrochloride

Dimethylaminopropiophenonehydrochloride were prepared by adopting the following procedure[32]. In a typical synthesis, 26.5g (0.326 mole) of dry dimethylamine hydrochloride, 10 g (0.33 mole), of powdered paraformaldehyde and 30g (29.3 ml) (0.25 mole) of acetophenone were taken in a round bottom flask connected to a reflux condenser. It was mixed with estimated amount of pure ethanol and 0.5 milliliters of strong acid.

It was then heated to reflux for 2 hrs. A homogeneous yellow coloured solution was obtained. A hot water funnel was used to filter it after that. Acetone was used to get the filtrate. After bringing the mixture down to room temperature, it was refrigerated for a full day. After filtering and washing with 10 milliliters of acetone, the crystals were dried.

2.3.2 Synthesis of propiophenonebutyldimethylammoniumiodide

63.18 g (0.32 moles) of dimethylaminopropiophenone hydrochloride was taken in a 300 ml of distilled water and allowed to stir for complete dissolution. A 5% solution of sodium carbonate was added slowly to the solution with continuous stirring until fizziness terminated. The liberated amine was extracted with ether (50 ml) three times. The ether extract was transferred to a 250 ml separating funnel. It was washed thrice with distilled water and then the ether layer was separated and evaporated over water bath. To the resulting tertiary amine, 40 ml (0.035 mole) of n-butyliodide was added under cold conditions. Propiophenonebutyldimethyl ammonium iodide thus obtained was purified by recrystallization with acetone- alcohol mixture. IR Data: aromatic C-H (3150cm^{-1}); aliphatic C-H modes (2965 cm$^{-1)}$; -C=O (1680 cm^{-1}) Aromatic C-C stretch ring skeletal vibrations (1470, 1580 and 1620 cm^{-1}); Aliphatic C-H bending (1380 and 1450 cm^{-1}); -CN (1220 cm^{-1}). ^{1}H NMR spectral data: Aromatic protons of benzyl group are positioned at 7.2 to 7.4 ppm. A peak at 4.0-4.2 ppm is assigned to methylene protons of -$COCH_2$ and N-CH_2 group. A signal was created at 0.9 to 3.7 ppm, respectively, by the proton of the dimethylamino group and the methyl and –CH_2 protons of the butyl moiety. The supporting documentation displays the catalyst's ^{1}H NMR and infrared spectra.

3. RESULTS AND DISCUSSIONS

To explore the antibacterial studies, the graft copolymer (PAN -*g*- Carrageenan) was prepared by

utilizing phase transfer catalyst. The detailed synthetic procedure are given in the experimental section The syntheiszed phase transfer catalyst was confirmed by means of various instrumentation techniques namely FT-IR and NMR which shows solid evidence for the formation of the expected structure and the confirmation of the functional moieties present in the same. The IR Spectrum of Propiophenonebutyldimethylammonium iodide exhibits the following stretching frequencies and is shown in Supporting Information (S. I. Fig. 1). At 3150 cm^{-1}, the aromatic C-H stretching modes have been observed. A distinct peak has been formed below 3000 cm-1 (i.e. 2965 cm-1) by the aliphatic C-H modes. The cause of the prominent peaks at 1680 cm-1 is carbonyl stretching. The positions of the aromatic C-C stretch ring structural vibrations are 1470, 1580, and 1620 cm-1. At 1380 and 1450 cm-1, aliphatic C-H bending modes are seen. The existence of two separate levels at 690 and 750 cm^{-1} indicates the existence of mono substitution on the core molecule. The cyano stretch is the cause of the peaks at 1220 cm^{-1}.

Similarly ^{1}H NMR spectrum exhibits the following signals and is shown in Supporting Information (S. I. Fig. 2). Aromatic protons of benzyl group are positioned at 7.2 to 7.4 ppm. Peaks at 4.0-4.2 ppm represent the presence of methylene protons of $-COCH_2$ and $N-CH_2$ groups. The signal resulting from the production of methyl and methylene protons in the butyl group and the proton of the $N-(CH_3)_2$ group at 0.9 to 3.7 ppm, respectively.

The findings of this characterization verify the creation of a phase transfer catalyst, which is then investigated further to learn more about the kinetics of PAN and grafted copolymer free radical polymerization. Through a number of optimization experiments, acrylonitrile was effectively homopolymerized from heterogeneous catalyst. The experimental part contains the whole synthetic protocol as well as the polymerization outcomes.

3.1 Kinetics of polymerization using the synthesized catalyst

The PTC-supported radical polymerization processes of acrylonitrile were carried out with the synthesized catalyst and PDS as initiator. The polymerization rate (Rp) was evaluated under several experimental conditions, including [monomer] and [PPBDMAI].

The various strength of acrylonitrile and the phase transfer catalyst were used for the polymerization reaction to observe and study the kinetics. Observations regarding polymerization included the following. The polymerization rate increased with increase in monomer concentration and the catalyst used. Further increase in polymerization rate results in saturation and it follows first order kinetics.

The polymerization reaction was quenched by expose to air. Change of cation from M^+ to NH_4^+, in initiator made no difference in polymerization dynamics which infers the transfer of anion from water soluble to insoluble layer depends only on the organic medium of the catalyst cation.

3.1.1 Polymerization rate using quasi constant State approximation.

Rate of polymerization using constant-state approximation was calculated using monomer at various time limits while keeping the other ingredients constant. The rate of polymerization increased sharply at first, then deviated, reached a peak, and finally remained constant. (See Fig. 1(a). It takes around 30 minutes to complete the SSA. Following that, the polymerization reaction rates were measured at a constant temperature of 60 ℃ for 30 minutes while altering the concentrations of the monomer, initiator, phase transfer catalyst, and so on.

3.1.2 The impact of different monomer strengths on the polymerization rate (R,)

The impact of various acrylonitrile strength on successful implementation of polymerization was monitored at various monomer concentrations ranging from 0.8 to 1.8 mol/dm while keeping other factors constant, representated in Fig. 1(b). Rp increased as the monomer strength increased. The slope of logarithm of polymerization rate vs monomer concentration will be applied to compute the reaction order in relation to monomer concentration, which was determined to be 2.2. As predicted, a plot of polymerization rate vs [AN]2.2 is linear and passes through the baseline, corroborating the previously stated fact.

It is not rare to see Rp dependency on [M] values bigger than one. Such a high monomer order (1.6) was illustrated by Rasmussen et al., for PMMA in the presence of Aliqout-336 and $K_2S_2O_8$ catalyst system. The polymerization of styrene performed at higher temperature (80 ℃) shows an order ranging between 1.2 and 1.4 by using benzoyl peroxide as initiator. These findings will be attributed to the monomer concentration-dependent start rate. Because the main radicals have reduced mobility, the starting sequence determines the rate. It has been found that the homolytic fission of the hydroperoxide initiator proceeds at a rapid rate due to the presence of cyclic ring of vinylbenzene. The higher disintegration rate in the t-butyl hydroperoxidestyrene initiator system is due to a monomer-induced decomposition process, which results in a two-thirds order dependence of polymerization rate on the strength of monomer.

When the reaction doesn't end with a chain reaction of moving molecules, the order of the reactions is higher than unity. The second-order reliance of the polymerization on the monomer strength is greater for primary radical termination, leading to a diminished reaction relative to the initiator. Regarding [$K_2S_2O_8$], a reaction order of 0.68 excludes the possibility of primary

radical termination.

The departure from the first-order concentration of Rp on [M] might be due to an obstacle in the polymerization process. The low-temperature (60 °C) nature of the reaction renders interference unlikely, thereby explaining the significant monomer order dependence on Rp. As a result, the high monomer order seen in this study can be linked to the initiation rate's dependency on [M]. Variations in diffusion-controlled termination rate constant also have a considerable impact on monomer order, even at extremely low polymerization conversion rates. These reasons might have caused the 2.2 monomer exponent in the polymerization process of acrylonitrile.

3.1.3 Effect of variable catalyst strength on the polymerization rate

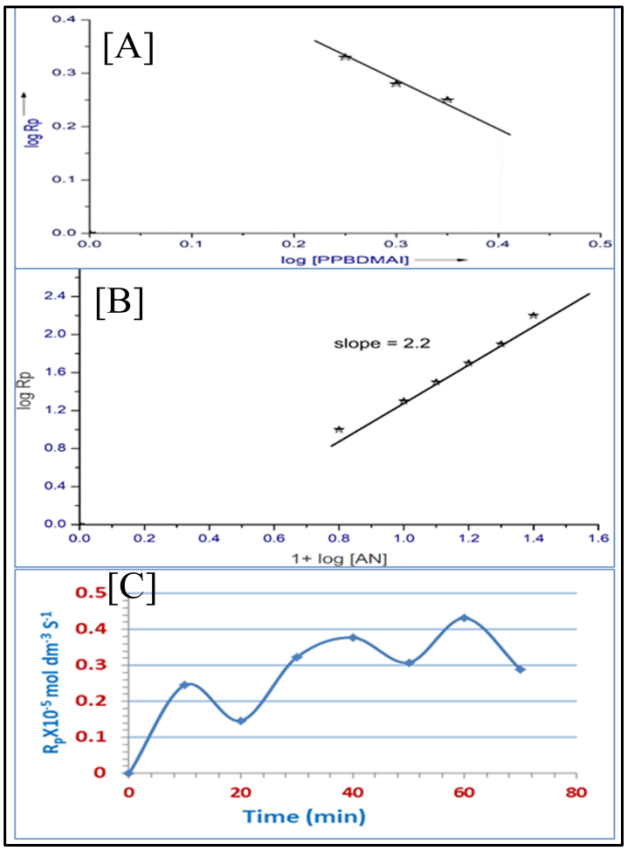


Fig. 1: (a)Kinetics representation for acrylonitrile – PPBDMAI – $K_2S_2O_8$ system. Variation of [PPBDMAI] (b)Kinetics representation for acrylonitrile – PPBDMAI – $K_2S_2O_8$ system. Variation of [AN] (c)Kinetics representation for acrylonitrile – PPBDMAI – $K_2S_2O_8$ steady state system.

The influence of rate, on the strength of the active catalyst was verified by different catalyst medium in the order 0.0023 to 0.0013 mol/dm^3 at reliably constant concentration of the acrylonitrile- and $K_2S_2O_8$. R_p falls with a steep rise in the concentration of the PTC (Fig. 1(c)). The rate of polymerization gradually increases with the increase in time which implements the efficiency of the catalyst with respect to the monomer. The time taken to carry out this analysis is usually from zero to 70 minutes. Between 50-70 minutes the rate of polymerization is almost same it increase and again decrease to the same value from 0.3 to 0.42 and again to 0.3 x 10^{-5} moldm^{-3} S^{-1}

3.2 Modification of Polyacrylonitrile (PAN) with carrageenan (κ) copolymer through grafting approach

Grafting to approach for the preparation of copolymers is one of the current frequently employed methods for polymer modification which yields the hybrid polymers from natural and synthetic polymers[33-35].

This happens when the polymer backbone chain and the polymer surface react, forming graft copolymers with different properties. Graft copolymerization has wider application in environmental field especially in modify the swelling, thermal pH responsiveness and releasing nature of natural gums[36].

0.2g of Polyacrylonitrile was dissolved in the 60:40 mixtures of tetrahydrofuran and water in the RB flask. 2 millilitres of 0.1 Normal sodium hydroxide followed by alkaline solution of k- carrageenan (50mg) were added to the flask. The reaction mixture was allowed to react for nearly 2 hours by sustaining the temperature at around 60°C. The grafted copolymer mixture was recovered and impurities was removed by filtration and then precipitated in hexane to get the final compound. The dried material is used for further characterization and application. The synthetic representation for the formation of PAN-g-k-Carrageenan is illustrated in Fig. 2.

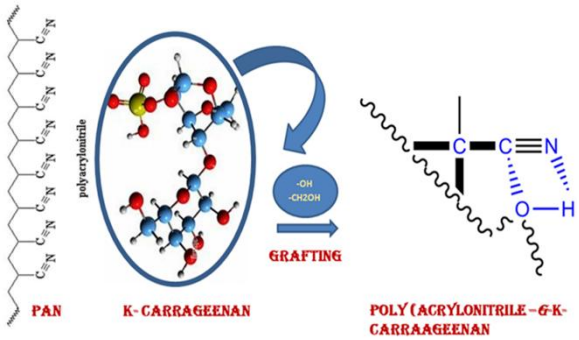


Fig. 2: Graphical representation for grafting approach for the preparation of PAN –g-carrageenan.

The Fourier transform infra-red spectra of κ-carrageenan is illustrated in Fig. 3. The carrageenan has special peaks around 3436, 2924, 1259, 925, and 847 cm^{-1}. The wide area around 3436 cm^{-1} is caused by stretching the hydroxyl moiety. The presence of peak around 2924 cm^{-1} is thought to be caused by a –C-H stretching vibration of –CH_2. Sulphur dioxide and C4-O-S of glycosidases vibrate in a symmetrical way. The presence of C-O-C of 3,6-anhydro-δ-galactose which is essentially monosaccharide of D-galactose in κ-carrageenan is shown by the peak at around 1200 cm^{-1}.

The subsistence of SO_2 and O-SO_3 stretching is confirmed by peaks around at 600 and 850 cm^{-1}.

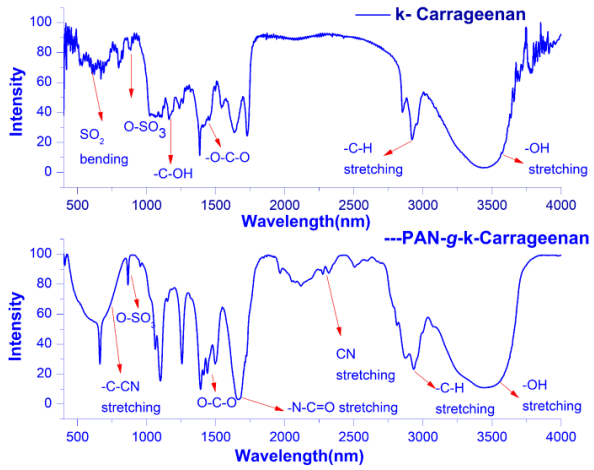


Fig. 3: The IR spectral comparison for the formation of PAN-g- carrageenan.

In the case of PAN-*g*-Carrageenan, the presence of peaks around 800, 1700, 2400 cm^{-1} confirms the presence of polyacrylonitrile repeating units in the graft copolymer. The presence of N-C=O stretching around 1700 cm^{-1} confirms the grafting of polymer to carrageenan. Similarly the peaks around 850 and 3436 cm^{-1} confirms the presence of carrageenan units in the grafted copolymer.

3.3 Morphological Studies

The morphological images of Carrageenan and PAN-*g*- Carrageenan are illustrated in Fig. 4. The appearance of Carrageenan in 1µm scale is represented in Fig. 4(a). The image illustrates the smooth surface of carrageenan whereas in the case of grafted copolymer, due to the grafting of PAN on the surface of carrageenan, clear spherical flower like morphology of PAN appeared on to the carrageenan surface in 3 µm scale is shown in image B confirms the grafting process. A clear morphological change from Fig. 4(a) to (b) is observed due to the hydrophilic nature of the carrageenan. Due to the amphiphilic nature of the graft copolymer, large macro voids are formed in the matrix. Hydrophilic additives are known to form pores and macrovoids in the graft copolymer membrane.

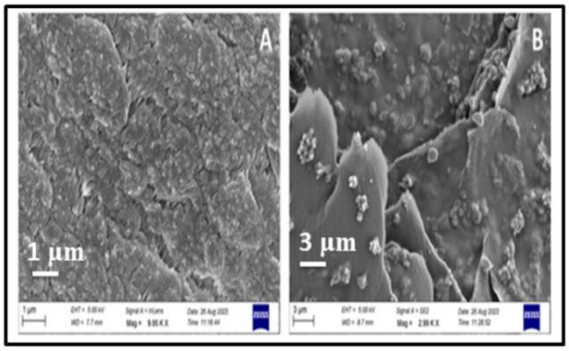


Fig. 4: SEM morphological images of (a) K-carrageenan (b) PAN-g-carrageenan.

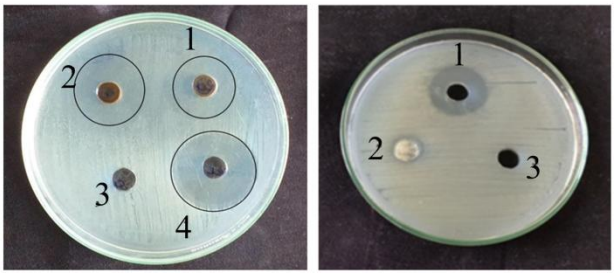
3.4 Antibacterial Studies

3.4.1 PREPARATION OF INOCULUM

The cultures were kept on plates made of agar at 4°C. To create viable cultures for research, cells were assembled from stock cultures to test tubes containing nutritious broth for bacteria[37].

These cells were then cultured for 24 hours at 37oC. The assay was done using the agar well dissemination method. The synthesized material's antibacterial effectiveness was evaluated using the Muller Hinton agar (MHA) medium and the well dissemination technique, the antibacterial efficiency of the synthesized material was assessed. Following the dissolution of 3.8 grams of Muller Hinton agar medium, one gram of agar was added to 100 millilitres of distilled water. The media is then stored for decontamination.

Following disinfection, the medium was transferred into cleaned Petri plates and kept aside for nearly an hour to solidify. Using a sterile swab dampened with the bacterial suspension, After the medium had set, the inoculums were incorporated to the plates with a sterile swab dampened with bacterial suspension. A cork crusher was used to create wells. . In their corresponding wells, the sample and positive control, streptomycin (1 milligram of sample in 1 mililitre of water) (20 µl), were added. These plates were incubated at 37ºC for a whole day. The inhibition zone diameter was measured to estimate microbial growth. Polyacrylonitrile-*g*-carrageenan was investigated to evaluate their antibacterial activity against staphylococcus and E-coli stain by utilising the methodology namely disc diffusion technique. Evaluation of antibacterial activity of this polymer was illustrated in Fig. 5 and Table 1.



(a) (b)

Fig. 5: Antibacterial activity of the polymer against microorganism (a) Staphylococcus stain (b) E-coli stain

The results revealed that the polymer which is grafted to a biologically active material carrageenan can potentially effective in suppressing microbial growth with variable potency. The Figure 5 illustrates the maximum zone of inhibition by standard streptomycin (25mm). Carrageenan imparts its antibacterial efficiency to the polymer which in whole effective in retarding microbial growth of all tested pathogenic bacteria. The zone of inhibition of staphylococcus is 11 mm for solid whereas for E-coli, both solid and liquid imparts the zone of inhibition around 18 and 22 mm in compared to the standard streptomycin (25 mm) as evident from Table 1. This study clearly shows that the grafted polymers almost have better antibacterial activity for E-coli and somewhat lower activity for staphylococcus. Further in future by monitoring the effect of different degree of polymerization of PAN in antibacterial activity will produce some interesting results.

Table 1. Antibacterial activity of the PAN-g-Carrageenan in the presence of microorganism staphylococcus1= Standard (streptomycin); 2= Solid (disc); 3= Liquid. For E-Coli 4= Standard (streptomycin); 1= Solid (disc); 2= Liquid

Sample/ Microorganisms		**Zone of Inhibition in mm**	
		sample	**Streptomycin (20µl)**
Staphylococcus aureus	**Solid (disc)**	11	25
	Liquid (80µl)	-	
Escherichia coli	**Solid (disc)**	18	29
	Liquid (80µl)	22	

The inclusion of carboxylate and sulfate groups present in PAN-g-k-Carrageenan may be the cause of its antibacterial activity which will create an acidic pH environment and in addition, the long polymer chain in the graft copolymer imparts interaction with enzymes and proteins of microbial cell membrane and inhibits the dispersion of protons towards cell exterior to induce cell death[38-42]. Furthermore, the presence of carboxylate groups may enhance the polymer's nucleophilicity, causing Polyacrylonitrile-g-carrageenan's amphiphilic properties to react with microbial cell membrane proteins, disrupting their structure and altering their permeability.

4. Conclusions

In the present work, polymerization of acrylonitrile was carried out using heterogeneous catalyst which is one of the potential phase transfer catalysts consisting of quaternary ammonium salt. The synthesized polymer was characterized and optimized using various kinetic studies. The necessity of polymerization ratio on numerous investigational circumstances such as varying degree of monomer and catalyst was discussed. Polymerization of acrylonitrile with activation energy was computed using the slope of logarithm of polymerization rate vs 1/T between varying degree of temperature 50 and 65°C. The optimized PAN was grafted with a natural polymer k-carrageenan which is a potential antibacterial material. The grafting to approach was followed by incorporating k-carrageenan to the Polyacrylonitrile by base catalyzed reaction at moderate temperature. Morphological images confirm the formation of graft copolymer by means of large macro voids in the matrix due to the amphiphilic nature of the graft copolymer. The synthesized graft copolymer was analyzed for its antibacterial activity with bacterial stain streptococcus aureus and E-coli. Carrageenan imparts its antibacterial efficiency to the polymer which in whole effective in retarding microbial growth of all tested pathogenic bacteria at zone inhibition of 11 and 18 mm for streptococcus and E-coli compared to streptomycin standard of 25 mm, which may due to the enhanced biological activity and amphiphilic nature of the proposed material.

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Author Contributions

Material preparation, data collection and analysis were performed by (Haridharan). Antibacterial studies were performed by (Malarvizhi) and (Haridharan). The first draft of the manuscript was written by (Haridharan). Both the authors read and approved the final manuscript.

Nomenclature

PAN – Poly (acrylonitrile)
κ – kappa
M+ Nu^- - metal ion and nucleophile
kJ/mol – Kilojoule/mole

K – kelvin
PTC – Phase Transfer Catalyst
3D – 3 dimensional
g – grafted
AR – Analytical reagent
°C – Celsius
Rp – rate of polymerization
W = Wt. of the polymer in gram
V = Volume of the reaction mixture
t = time in sec
M=Mol. Wt. of the monomer.
g – gram
hrs – hours
ml – millilitre
cm^{-1} – Centimetre
ppm – parts per million
FT-IR – Fourier transform
NMR – nuclear magnetic resonance
SSA – steady state approximation
[PPBDMAI]propiophenonebutyldimethylammoniumiodide
[PDS] – peroxodisulphide
[AN] - Acrylonitrile
$K_2S_2O_8$ – Potassium peroxodisulphide
Mg/ml – milligram/millilitre
mm – millimetre
µl – microliter
$K_2S_2O_8$: Potassium Persulfate

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