

# 3D Architected Poly(acrylamide-co-azomethine-co-acrylic acid) Cogel: Synthesis, Characterization and Salinity Profile

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Herein, this innovative work; Poly(acrylamide-co-azomethine-co-acrylic acid) cogel is prepared in water as green solvent in order to study the effect of acrylamide content on swelling behaviour of hydrogels. It is found that hydrogels prepared in solution exhibited the highest swelling which probably extend its use in agricultural field as well as in marine industry. The hydrogels is characterized by fourier transform infrared, elemental analysis, differential scanning calorimetry, thermal gravimetric analysis and field emission scanning electron microscopy. From Morphology study, we can see the change in porosity of cogel which is responsible for the absorbance of cogel. The results also indicated that the stability of azomethine is increased by formation of co-gel with poly(acrylamide-co-acrylic acid). In this report, straight forward and efficient synthetic protocol for cogel formation is adopted without any environmental hazard. Swelling capacity of P(AM-co-AA) and cogel was studied by addition of different saline solutions including monovalent, divalent, and trivalent salts. Its applications can be extended in agricultural industries as a basis for super absorbent polymer, waste water treatment, and even in medical field. Hence, the synthesized materials can be biodegradable, environment-friendly, and biocompatible inspired by the green chemistry concept.

## Introduction

Super water-absorbent polymers are the most advance category of hydrogels that can define as cross-linked macromolecular networks that can absorb a large amount of water or solvent. However, during the absorption process, they retain their physical appearance by not getting dissolved when brought into contact with water [1]. These hydrogels are highly hydrophilic, non-toxic, biodegradable, and biocompatible [1,2]. Polymeric hydrogels are of great interest for biomaterials applications on account of their biocompatibility [3]. These are amongst the most attractive classes of "soft matters" with several established and many more possible applications. Conversely, swelling is limited to rubber-like behavior due to the presence of crosslink or strong physical interactions among the polymeric chains [4].

Few research groups have conducted studies on Schiff polymers, and a great diversity of structures is obtained [5]. Schiff base polymers like azomethine are high-performance polymers presenting good mechanical strength and semiconducting properties [5,6]. However, poor solubility of high-molecular-weight polymers makes it difficult for versatile applications and the determination of their structural and macromolecular features.

Most of the material scientist's research groups are engage to develop valuable products like waste water treatments and its environmental aspects [7]. Recent

trends are also work for combining the properties of organic and inorganic moieties with high surface areas and pore volumes offers endless possibilities to design materials adapted to a wide range of advanced applications [8]. This type of advance material can be prepared by number of technologies such as linking monomers, ionizing radiation, or physical interactions such as entanglements, electrostatics, and crystallite formation [9]. The mining industry is one of the growing industry which utilize densified tailings densification using thickeners sometimes proves unable to achieve the design target solids mass concentration. To overcome these, superabsorbent polymers (SAPs) seems to represent a promising alternative, owing to densified tailings higher water absorbent capacity [10]. Our research group D. S. Raghuvanshi *et. al.*, synthesized "3D architected polyazomethine gel" and determined its complexion ability. Still, these materials have very little stability, so to overcome this limitation, we integrate cogel of polyazomethine and poly(acrylamide-co-acrylic acid) [P(AM-co-AA)] [11,12].

The present context is mainly focusing on the synthesis of aliphatic 3D-structured azomethine polymer as per literature. Accordingly reports, this polyazomethine gel gets decompose after 5°C hence by intermolecular interactions with P(AM-co-AA)], the stability of polyazomethine is an increase, which is confirmed by

advance thermal techniques. The swelling capacity of P(AM-co-AA) and co-gel are studied by the addition of different saline solutions, including monovalent, divalent, and trivalent salts. Its applications may extend in marine water industries as a basis for antifouling coating, waste water treatment, and even in the medical field.

## Experimental

### Materials/chemicals details

Acrylamide (98%) is obtained from Spectrochem Pvt. Ltd., Mumbai, India. Glyoxal (40%) is purchased from Sigma Aldrich Chemicals. Triethylenetetramine (97%) (TETA) is purchased from Sisco Laboratory, Mumbai, India. Acrylic acid (98%), Potassium persulphate (KPS) was purchased from SD Fine Chemicals, Mumbai, India.

### Material synthesis /reactions

#### Scheme 1: Synthesis of Polyazomethine Gel

As per the literature [11], 10 mmol of glyoxal (40%) was subjected to slow stirring using a magnetic stirrer. Its temperature was brought down to 0-5°C. The gradual addition of (10 mmol) TETA into chilled glyoxal was executed through the addition funnel. In addition, an exothermic reaction occurs; so, the rate was adjusted such that the reaction temperature must not reach above the 5 °C; otherwise, the product gets degraded.

#### Scheme 2: Synthesis of Cogel

Cogels are prepared by free-radical polymerization of acrylamide and acrylic acid in water (**Fig. 1**). Acrylamide (5g) is dissolved in 20 mL of double distilled water in 250mL three-neck flask equipped with a stirrer, a condenser, and a thermometer. Acrylic acid (2mL) is added to the reaction mixture and stirred at room temperature for 10 min. polyazomethine gel is added to the reaction mixture when the temperature of reaction mass goes up to the 64°C with stirring. Potassium persulphate (0.2g) is added as a radical initiator into reaction mass for polymerization at constant stirring. The resulting cogel was cool at room temperature.

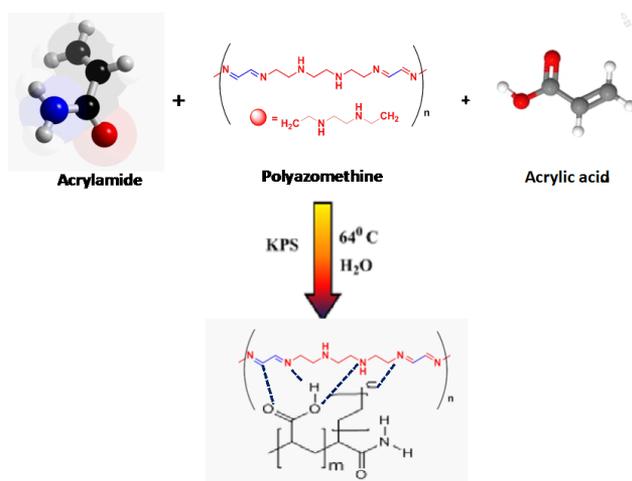


Fig. 1. Scheme for cogel synthesis.

## Analytical methods

The samples are tested with infrared spectra on a Shimadzu FT-IR 8400 frequency range from 400 to 4000  $\text{cm}^{-1}$  using KBr flakes. The scanning of the sample is done at a rate of 28 times before the final recording of spectra. Thermal Gravimetric Analysis is executed on TGA-4000 (Perkin Elmer) with the Nitrogen flow rate of 20 ml/minute and temperature increment rate of 15°C/minute. Differential Scanning Calorimetric analysis is executed on DSC-4000 (Perkin Elmer) with the Nitrogen flow rate of 20 ml/minute and temperature increment rate of 10°C/minute. FE-SEM images are taken on a Hitachi S4800 instrument after gold plating applied with the help of a Hitachi Ion Sputter E1010 instrument.

## Results and discussion

### FT-IR analysis

The infrared spectra of P(AM-co-AA) is given in **Fig. 2(a)**, The midrange peak in the range of 3633-3451  $\text{cm}^{-1}$  are results due to  $-\text{NH}_2$  from acrylamide, presence of water in hydrogel and acidic  $-\text{OH}$  of the polymer. The C-H stretching band is confirmed by the presence of a peak at 2950 $\text{cm}^{-1}$  due to asymmetric stretching vibrations of  $-\text{CH}_2$  groups in the polymer. Amide carbonyl is seen at 1683  $\text{cm}^{-1}$ , The peaks found in between 800- 400  $\text{cm}^{-1}$  are due to bending occurs from NH and OH groups [12,13].

FT-IR analysis is evident for the proper synthesis of polyazomethine shown in **Fig. 2(b)**. It shows a prominent peak at 1673  $\text{cm}^{-1}$  for C=N stretching. The broad peak at 3067  $\text{cm}^{-1}$  occurred due to the presence of secondary amine (N-H stretching) in the polymer repeating units. The peak at 2905  $\text{cm}^{-1}$  is for the methylene C-H stretching.

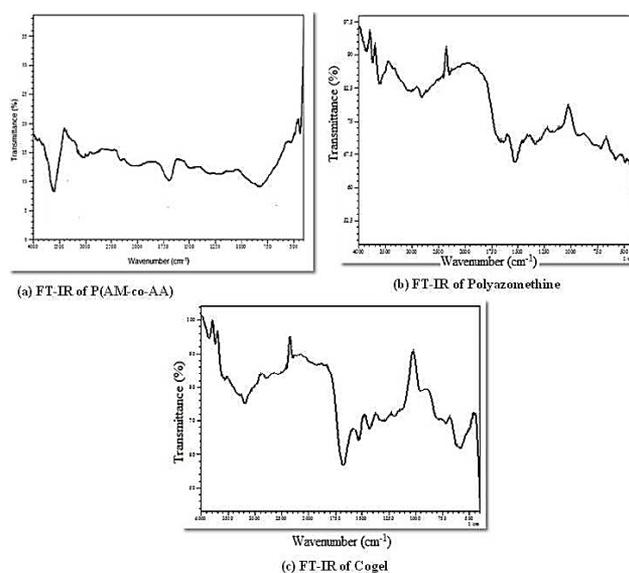


Fig. 2. Infrared spectra of (a) P(AM-co-AA) (b) Polyazomethine and (c) Cogel.

The infrared spectra of cogel are given in **Fig. 2(c)**, and from this spectra, we can see that the C-H stretching band at 2950  $\text{cm}^{-1}$  due to asymmetric stretching vibrations

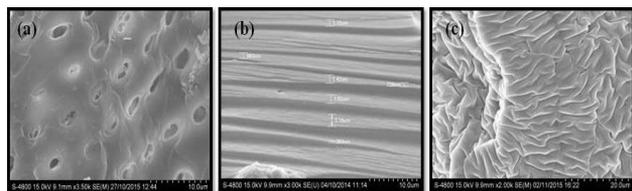
of  $-CH_2$  groups in co-gel. Amide carbonyl or  $C=N$  stretching is seen at  $1683\text{ cm}^{-1}$ , which is as per native polymers. The bands found in between  $800\text{--}400\text{ cm}^{-1}$  are due to bending occurs from NH and OH groups.

### Morphological Analysis (FE-SEM)

One of the most important properties that must be considered when studying hydrogel is its microstructure morphology. **Fig. 3(a)** shows the secondary electron images of P(AM-co-AA) in the water-saturated state are study. This finding verifies that the synthesized polymer structure of P(AM-co-AA) has a porous structure with an effective pore size  $150\text{--}250\text{ nm}$  range. It is supposed that these pores are a region of water permeation and interaction sites between external stimuli and the hydrophilic groups of the gel. These pores are produced from water evaporation at the time of hydrogel synthesis.

The sample morphological is studied with the help of FE-SEM images, as shown in **Fig. 3(b)** are showing the sheets like structures, which are separated by an average distance of  $1.5\text{ }\mu\text{m}$ . Thus, this is evident that the polymer was having three dimensional lamellar layered like morphology. The layers can be easily observed in an image. This can be concluded that the chains grow straight without any kind of branching in it.

The smooth structure of cogel is presented in **Fig. 3(c)**. It was clearly observed that the cogel exhibited homogeneous smooth with a layer like structure, resulting in higher swelling behaviour. It is supposed that these morphologies where the region of water permeation and interaction sites between external stimuli and the hydrophilic groups of the gel.

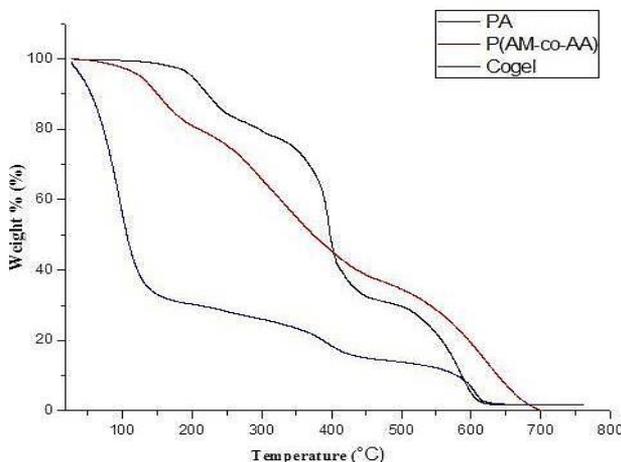


**Fig. 3.** FE-SEM images of (a) P(AM-co-AA) (b) Polyazomethine and (c) Cogel.

### Thermo gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) has been done on samples to identify the changes in weight percent concerning temperature change and given in **Fig. 4**. TGA was performed on P(AM-co-AA), polyazomethine, and cogel. TGA results plotted in **Fig. 4** in the temperature range of  $50\text{--}850^\circ\text{C}$  indicates P(AM-co-AA) exhibited weight losses at  $30\text{--}300^\circ\text{C}$  due to loss of water, second degradation due to decomposition of amide linkage at  $300\text{--}490^\circ\text{C}$ , remaining  $29.116\%$  weight loss at  $490\text{--}600^\circ\text{C}$  which are result of the degradation of acrylic acid group in polymer [13]. Thermal Gravimetric curves are showing three-step degradation of polyazomethine comprising TETA as a repeating unit. The first step degradation starts from  $60^\circ\text{C}$  up to  $\sim 200^\circ\text{C}$  due to the evaporation of the

water of crystallization introduced through  $40\%$  glyoxal. During the first step degradation of the polymer,  $20\%$  weight loss is observed. The second step degradation starts from  $220^\circ\text{C}$  up to  $470^\circ\text{C}$ , due to breaking of polymer linkages and generation small organic molecules. Third step degradation at  $470^\circ\text{C}$ , which renders up to  $700^\circ\text{C}$ , which is because of the total decomposition of materials into carbon residue and gasses. Nearly  $40\%$  of weight loss observed during the second step degradation of polymer while again  $40\%$  weight loss observed during third step degradation.



**Fig. 4.** TGA curves of P(AM-co-AA), Polyazomethine (PA) and Cogel.

Thermal gravimetric analysis is used for the recognition and thermal stability of gel. The cogel underwent weight loss in three stages and  $97.393\%$  of its original weight loss at  $650^\circ\text{C}$ . The first degradation due to dehydration of water molecule, the second degradation is due to the decomposition of the acrylic polymeric chain, and third stage degradation is due to decomposition azomethine linkage present in the gel. Cogel show three-step degradation in-between temperature  $20\text{--}650^\circ\text{C}$  in which the first degradation occurs at a temperature between  $29\text{--}200^\circ\text{C}$  at this maximum temperature amount of polymer chain get break and  $68.88\%$  weight loss occurs, Second step degradation starts from  $200\text{--}480^\circ\text{C}$  near about  $15.57\%$  weight loss due to degradation of residues, Third step degradation starts from  $480\text{--}620^\circ\text{C}$  concerning  $12.931\%$  weight loss occurs.

### Differential Scanning Calorimetry (DSC)

The DSC curves for polyazomethine, P(AM-co-AA), and cogel are represented in **Fig. 5**. The curve of P(AM-co-AA) showed a characteristic endothermic peak at  $240^\circ\text{C}$ , corresponding to its decomposition. In comparison, polyazomethine showed the exothermic peak at  $150^\circ\text{C}$  for evaporation of water crystallization introduced through  $40\%$  glyoxal. As regards the analysis of cogel, the peak for the decomposition of P(AM-co-AA) shifted to  $180^\circ\text{C}$ , and peak for polyazomethine to  $130^\circ\text{C}$  indicated there is the presence of interactions between polyazomethine and P(AM-co-AA). This concludes lowering of melting of

P(AM-co-AA) in the complex state may be due to a variation of intermolecular forces between P(AM-co-AA) by polyazomethine and introduces intermolecular interactions, which also supports the formation of cogel [14].

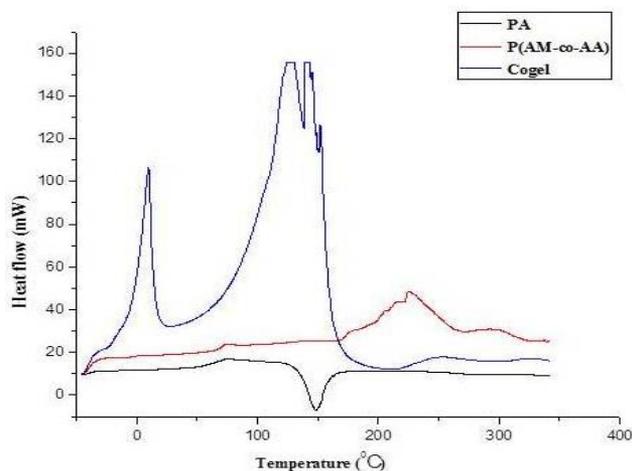


Fig. 5. DSC curves of P(AM-co-AA), Polyazomethine (PA) and Cogel.

### Effect of salt solution on water absorbency

The influence of ions (cations and anions) on the swelling ability of cogel was experienced by the addition of different saline solutions, including monovalent (NaCl), divalent (CaCl<sub>2</sub>), and trivalent (AlCl<sub>3</sub>) solutions at the rate of 0.15 mol L<sup>-1</sup> at 25°C. Multivalent cations can neutralize several charges inside the cogel by complex formation with hydroxyl and amide groups, including intramolecular and intermolecular interactions leading to an increased ionic crosslinking degree and consequently loss of swelling. Therefore, the absorbency for the cogel in studied salt solutions is in order of monovalent > divalent > trivalent. From Fig. 6, it can be concluded that the higher the cation charge, the smaller is the swelling value. Consequently, the crosslinking density of the network increases while water absorption capacity decreases [15,16].

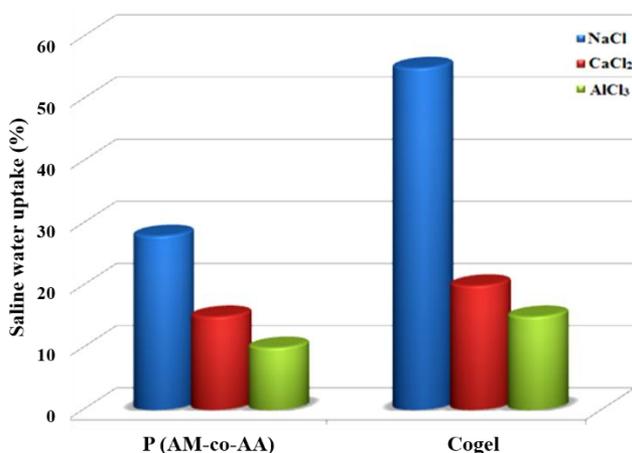


Fig. 6. Swelling ability of P(AM-co-AA) and Cogel.

### Conclusion

This innovation is straight forward, and efficient synthetic protocol for cogel formation responds without any environmental hazard. The present study demonstrated the formation of cogel between P(AM-co-AA) and polyazomethine. Cogel of P(AM-co-AA) and polyazomethine showed responsive behaviour concerning the salt solution presenting the excellent potential of the application as devices for the controlled release of solutes. The results indicate that the order of water uptake decreases with increases in valency of salts. Hence, simple operations and eco-friendly protocol for the synthesis of cogel is developed.

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### Conflicts of interest

There are no conflicts to declare.

### Keywords

Poly(acrylamide-co-azomethine-co-acrylic acid), polyazomethine, swelling behaviour, salinity profile.

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### Authors biography



Prof. Jyotsna Meshram is presently heading the Department of Chemistry at Rashtrasant Tukdoji Maharaj Nagpur University, Nagpur. She had all most 25 year teaching and research experience. She was the member of several national committee bodies. She had published more than 120 research articles in national and internationally reputed journals including RSC Advances, Journal of Toxicology and Luminescence etc. More than 20 students had persude their doctoral degree under her guidance.



Dr. Nandkishor B. Shirsath serves as an Assistant Professor at the Department of Chemistry, M.S.G. College, Malegaon, Dist. Nashik under Pune University. Dr. Shirsath has been actively engaged in material science research, especially composite, dendrimers, polymer degradation, fly ash, hydrogels, and ionic liquids. With this he has number of research paper at National and International reputed journals and life member of SMC, BARC and ISC. He Handle critical challenges in medical, agricultural, energy, and

environmental issues realized by the integration of artificial intelligence and smart strategies..



Dr. Devendra Raghuvanshi is currently working as Team Leader, Research and Development Department, Shiva Pharmachem Pvt. Ltd., Luna, Padra, Vadodara. He has published 5 papers and 1 book chapter in internationally and nationally reputed journals. He has 4 year institutional and 4.5 year industrial research experience. He had presented in more than 12 national/international conferences and workshops and achieved 4 awards on credit including RSC Fellowship Awards. He has delivered lectures and taken practicles of post graduate students. Some lectures are available online on his personal you tube channel "Dr. Devendra Raghuvanshi".

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### Graphical Abstract

