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# Synthesis and Conductivity Measurement of Polyacrylamide in Nano State

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Polyacrylamide was synthesized from its monomer by plasma polymerization technique. The polymer so formed is in nano state and was confirmed by IR, UV and SEM techniques. Conductivities were determined from 30 to 200 ºC with a frequency ranges from 42 Hz to 1 MHz in solid state. Observation indicates that the nano state showed better ionic conductivity than of the bulky one. SEM analysis indicates that the particle size of polyacrylamide prepared by plasma polymerization is within the range 60 to 100 nm. A possible mechanism for the formation of polyacrylamide by plasma technique is also explained.

**Key Words: Polyacrylamide, Plasma polymerization, Nano state, Conductivity.**

## INTRODUCTION

Plasma polymerization is gaining importance for last several years as a tool to modify material surfaces. Plasma polymerization can also be used to produce polymer film of organic compounds that do not polymerize under normal chemical polymerization conditions because such processes involve electron impact dissociation and ionization for chemical reactions[1]. Plasma processes provide a cost effective and environmentally friendly alternative to many important industrial processes because the method produces no unwanted waste products and in most cases expose operators to no significant hazards[2]. Plasma pre-treatment is a vital process used for improving lamination, printing and adhesion of polymeric materials. Most of the works of plasma polymerization were done for the deposition of polymeric materials on metal or glass surface[3-6]. Arefi *et al.*[7] suggested that plasma polymerization films are highly stable, chemically inert and mechanically tough.

Basically, polyacrylamide is a versatile synthetic water-soluble polymer and used worldwide in the various fields of engineering and technology[8,9]. One of the most promising applications of polyacrylamide is hydraulic resistance in turbulent flows. Other uses include flocculants in mining, papermaking, metallurgy, oil industries *etc*. The principal production method for polyacrylamide is free-radical polymerization in solution, emulsion or suspension from its monomer[10]. Due to commercial demand, the development of new methods and the perfection of existing methods are necessary. However, to develop an improved method, knowledge of the kinetic peculiarities and mechanism of polymerization, the properties of the medium, the influence of acrylamide as a monomer and several other factors are required. In this work, an attempt has been made to synthesize polyacrylamide from the monomer by plasma polymerization method. Various experimental techniques such as IR, UV, scanning electron microscopy and conductivity determination are employed to characterize the polymer that has been synthesized and to compare with the bulky one.

## EXPERIMENTAL

Acrylamide (Acros Organics) was used without further purification.

**Preparation of polyacrylamide by plasma polymerization method ($PAA_P$):** The experiment is performed in a direct current cylindrical magnetron device (CMD). The experimental arrangement for preparation of polyacrylamide by plasma polymerization method is shown in Fig. 1. The device (CMD) consists of a cylindrical stainless steel chamber of length 100 cm and diameter 20 cm. A small stainless steel cylinder with 1.5 cm in diameter and 15 cm in length is placed co-axially inside the chamber. This small cylinder acts as a cathode and the grounded plasma chamber itself is used as anode of the discharge system. An arrangement has been made for generation of axial magnetic field up to 500 Gauss by passing direct current through two solenoid coils wrapped around the body of the chamber. The magnetic field is axially uniform within a length of 18 cm at the central region of the chamber. Low pressure is created by using a combination of rotary and diffusion pumps. The base pressure of the chamber is usually $1 \times 10^{-5}$ mbar. The discharge power is supplied from a stabilized DC power supply (1500 V, 3 A) working in the voltage-regulated mode. The crystalline monomer acrylamide is kept the central region of the chamber in 8 cm glass petri-dish below the cathode as shown in Fig. 1. The amount of acrylamide taken is 0.71 g (0.01 mol) and covers around 12.56 $cm^2$ areas in the middle portion of the petri-dish. After the insertion of monomer the base pressure of the chamber comes down hardly up to $1 \times 10^{-4}$ mbar. This indicates the vapourization of the monomer. Direct current glow discharge plasma is produced by applying a high voltage between the central cylindrical cathode and grounded chamber in the argon gas environment. A cylindrical Langmuir probe ($L_p$) made of tungsten having 0.5 mm in diameter and 5 mm in length is used to measure plasma density ($n_e$) and temperature ($T_e$) from its I-V characteristics.

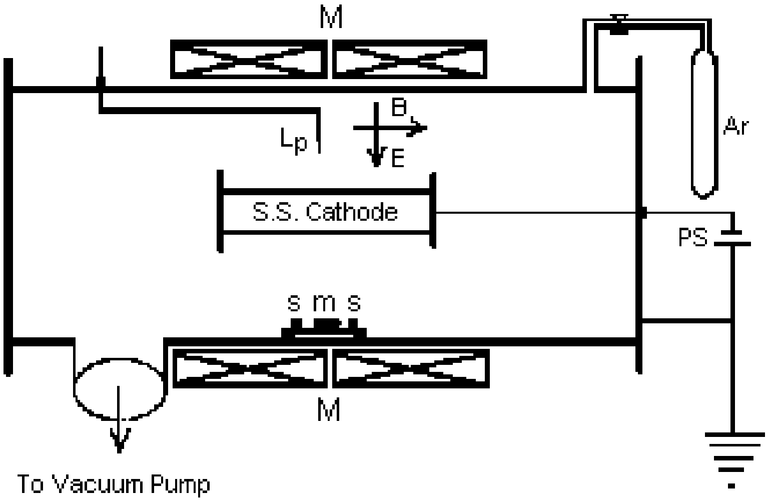


Fig. 1. Schematic diagram of the experimental set up: MM-Magnetic field coils, B-Magnetic field, E-Electric field, S.S. Cathode-Stainless steel cathode, PS-Discharge power supply (1500 V, 3 A), $L_P$-Langmuir probe, m-monomer, SS-Stainless steel or glass substrate

In this experiment, the control variables are magnetic field strength, gas pressure and discharge voltage. The control variables are optimized for preparation and deposition of polyacrylamide films on the substrates. The experiment is carried out at working argon pressure range of ($1 \times 10^{-3}$–$5 \times 10^{-2}$) mbar, applied voltage range of (500-1000) V and magnetic field range of (0-100) Gauss. The discharge current is varied within the range of 15 to 300 mA. It is found that the best condition for preparation of uniform, pinhole free and high percentage polyacrylamide film corresponds to the discharge voltage of 850 V, magnetic filed of 30 Gauss and gas pressure of $2 \times 10^{-2}$ mbar. The plasma density and electron temperature corresponding to this condition and measured with the help of the Langmuir probe are '$n_e$' = $2 \times 10^{10}$ cm$^{-3}$ and '$T_e$' = 0.5 eV, respectively. The discharge current is maintained at 60 mA. The processing time is 45 min. The polyacrylamide film is found to form in the inner wall of the chamber as well as on the glass, stainless steel (1 sq. cm) and other substrates placed around the monomer in the petri-dish. The polymerization of the crystalline acrylamide is initiated in vapour state and the polyacrylamide is deposited on the substrates.

**Preparation of polyacrylamide by thermal polymerization method ($PAA_T$):** The polyacrylamide is also prepared by heating the monomer at 60 ºC for 3 h. It is then dissolved in water and precipitated by acetone[11]. Reprecipitation was done to remove last traces of monomer. The product so obtained was then dried in an oven at 60 ºC for 12 h and stored over $P_2O_5$.

IR spectrum was recorded with a Bruker, Vector22 FTIR by reflectance method. The SEM of polyacrylamide was carried out in a scanning electron microscope (SEM, HITACHI: S3600N). Ultraviolet spectra were obtained on a Shimadzu UV-1601 spectrophotometer by reflectance method.

**Conductivity measurement:** The bulk electrical conductivity of polyacrylamide was evaluated from the complex impedance-admittance plots recorded at different temperatures using a HIOKI 3520, frequency response analyzer. The plots were recorded in the frequency range from 42 Hz to 1 MHz keeping the signal amplitude of 20 mV. The geometry of the cell for the measurement of conductivity was SS|polymer film|SS, where SS stands for stainless steel were used as electrodes. The experiment was carried out under a relative humidity of 58 %[12].

## RESULTS AND DISCUSSION

The mechanism for the formation of polyacrylamide by plasma state energy (E) may be expressed as follows[13]

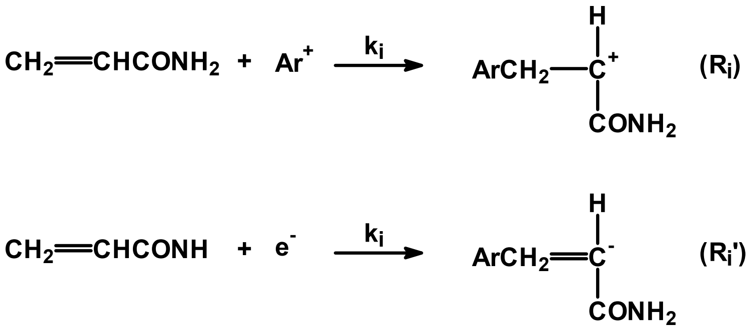
The primary process of an interaction between the ionizing radiation and argon is the ejection of an electron or pair producing the argon ion. Argon ion and electron are the initiating spices. The $Ar^+$ and the electron produce the carbonium ion and the carbanion, which can initiate the propagation

$$RH + Ar^+ \longrightarrow ArRH^+$$

$$RH + e^- \longrightarrow RH^-$$

where $Ar^+$ represents the ionized argon and e represents a high energy electron produced during the plasma state. The high energy electron will dissipate the energy during the successive electron molecule interaction. The termination is the head-to-head interaction between cationic and anionic species producing the polymer $P_{r+s}$ after rearrangement.

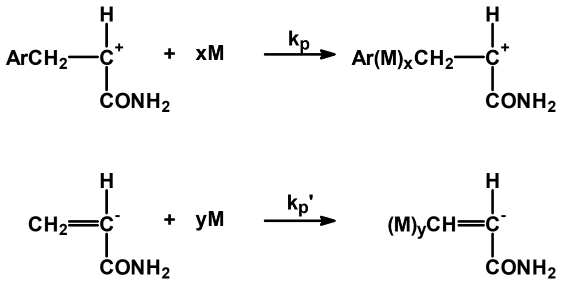
**Initiation:**



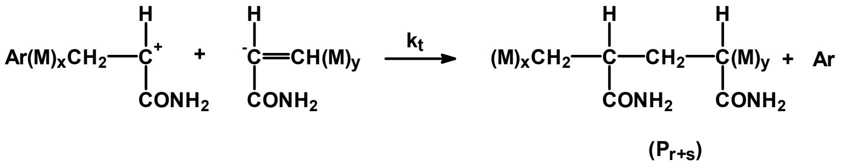
$$CH_2{=}CHCONH_2 + Ar^+ \xrightarrow{k_i} ArCH_2{-}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CONH_2}{|}}{C^+}} \qquad (R_i)$$

$$CH_2{=}CHCONH + e^- \xrightarrow{k_i} ArCH_2{=}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CONH_2}{|}}{C^-}} \qquad (R_i')$$

**Propagation:**



**Termination:**



The polymerization is a vapour phase reaction and the nano fine layer is deposited on the substrate glass, quartz or stainless steel. Since Ar is eliminated in the termination process its pattern of SEM is very regular.

The IR spectrum of polyacrylamide is showed the bands at 3372 and 3234 $cm^{-1}$ arise due to symmetrical and asymmetrical N-H stretching of PAA. The band at 1665 $cm^{-1}$ is due to C=O group[14]. The bands at 1636 to 1543 $cm^{-1}$ are recognized due to N-H deformation. These bands are confirmed the formation of polyacrylamide.

UV spectra (Fig. 2) show blue shift for $PAA_P$. The wavelength was 220 nm and 192 nm for the peaks of $PAA_T$ and $PAA_P$, respectively. So, it can be inferred that the $PAA_P$ particles are in nano fine state. The SEM photographs of $PAA_P$ and $PAA_T$ are presented in Figs. 3 and 4, respectively. The SEM analysis shows regularly spaced features, which is interesting and this might be due to the evolution of argon from the $PAA_P$ during the plasma polymerization process. Here the light areas are $PAA_P$ and the dark areas are the glass surface. This is confirmed by the SEM photograph (Fig. 5) which is done without monomer and an argon plasma treated surface. SEM analysis indicates that the particle size of $PAA_P$ is found within the range 60 to 100 nm and that for $PAA_T$ is 3 to 5 µm.

Conductivity data for $PAA_P$ and $PAA_T$ with respect to temperature showed that $PAA_P$ needs higher activation energy. The mechanism of conduction for the polymeric material is a mixture of ionic and electronic. The activation energy computed from Arrhenius plot (Fig. 6a & b) of log ($\sigma$T) *vs.* 1/T of the compounds $PAA_P$ and $PAA_T$ are 0.058 eV and 0.015 eV, respectively. The higher value of activation energy for $PAA_P$ indicates that

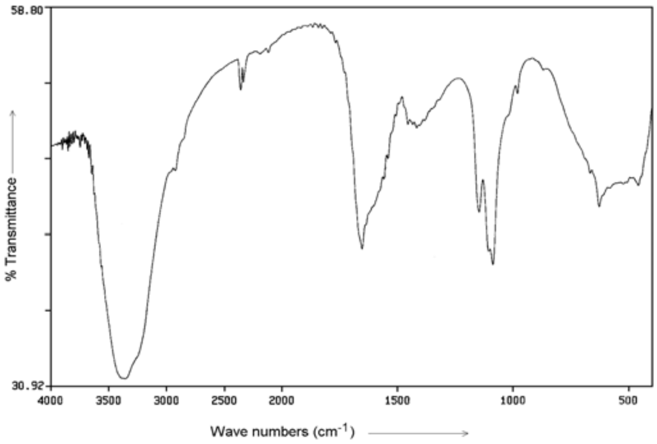


Fig. 2. IR spectra of polyacrylamide

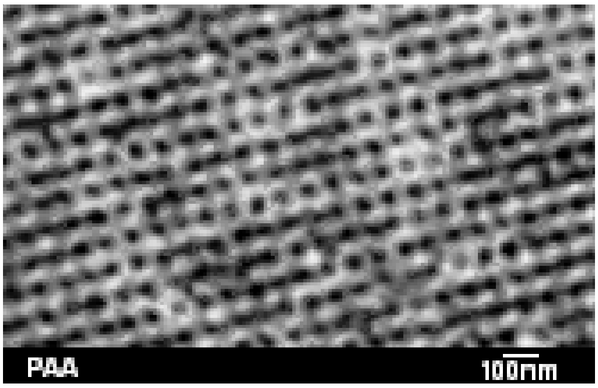


Fig. 3. SEM photograph of PAA$_P$

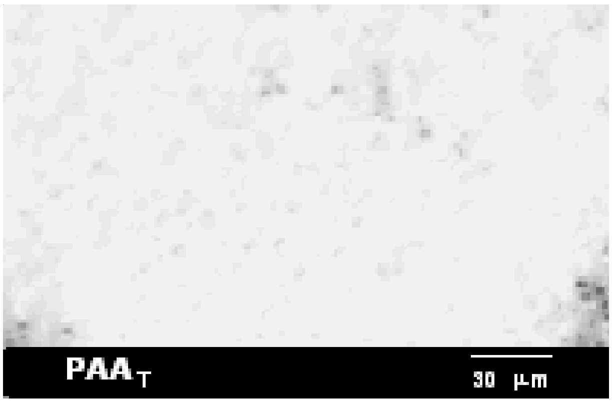


Fig. 4. SEM photograph of PAA$_T$

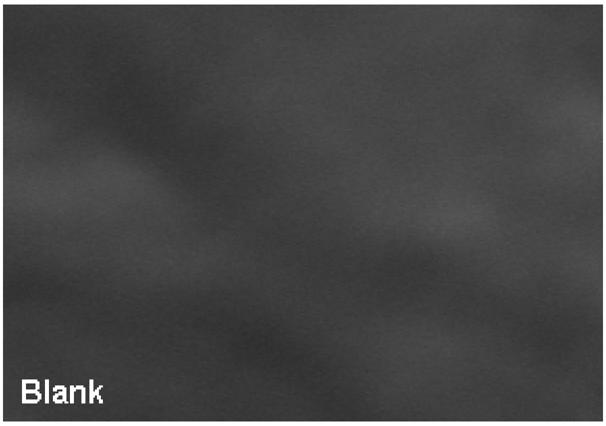


Fig. 5. SEM photograph of glass substrate treated with Ar plasma without monomer

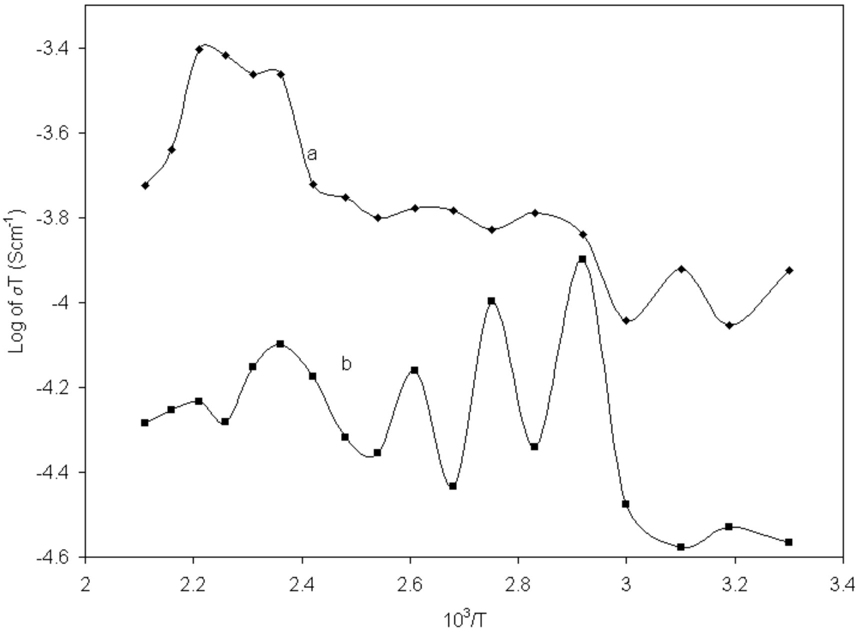


Fig. 6. log of σT *vs.* 1/T plot of polyacrylamide: a) $PAA_P$ b) $PAA_T$

the percentage of ionic conduction is predominant compared to $PAA_T$. The phenomenon is obvious since higher activation energy is necessary for the ionic conduction[15]. There was about ten-time increase of conductivity in the case of $PAA_P$ compare to $PAA_T$, which indicates the improvement of its conductance properties.

Conductivity *vs.* temperature curve of $PAA_T$ (Fig. 6b) shows a wavy character through out the entire temperature region, which is not so prominent in case of $PAA_P$. This may be due to the rearrangement of the molecules of polyacrylamide with the rise of temperature and this is an indication that $PAA_P$ is more neatly structured compared to $PAA_T$.

It is observed that the synthesis of polyacrylamide by plasma polymerization method is found to be in nano fine state and this improves its overall character compared to the bulky one. Therefore, plasma polymerization technique can be used for synthesis of nano polymeric materials in future research endeavours for a number of industrial applications.

## ACKNOWLEDGEMENT

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