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Synthesis, Characterization, and Swelling Behavior of Superabsorbent Hydrogel from Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder-*g*-PAN

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ABSTRACT: Polyacrylonitrile (PAN)-grafted sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP-*g*-PAN, %G = 413.76 and %GE = 96.48) was prepared using the established optimal reaction conditions for ceric-initiated graft copolymerization of acrylonitrile onto Na-PCMTKP ($\overline{DS}$ = 0.15) in a homogeneous medium. The graft copolymer was hydrolyzed by 0.7*N* KOH solution at 90–95°C to yield the superabsorbent hydrogel H-Na-PCMTKP-*g*-PAN. The nitrile groups of Na-PCMTKP-*g*-PAN were completely converted into a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, followed by in situ crosslinking of the grafted PAN chains. The products were characterized spectroscopically and morphologically. The swelling behavior of the unreported superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, was studied by carrying out its absorbency measurements in low-conductivity water, 0.15*M* salt (NaCl, $CaCl_2$, and $AlCl_3$) solutions, and simulated urine (SU) at different timings. The swelling behavior of the hydrogel in different swelling media followed the second-order kinetics. The values of the various swelling characteristics were reported. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1992–2003, 2013

KEYWORDS: grafting; swelling; gels

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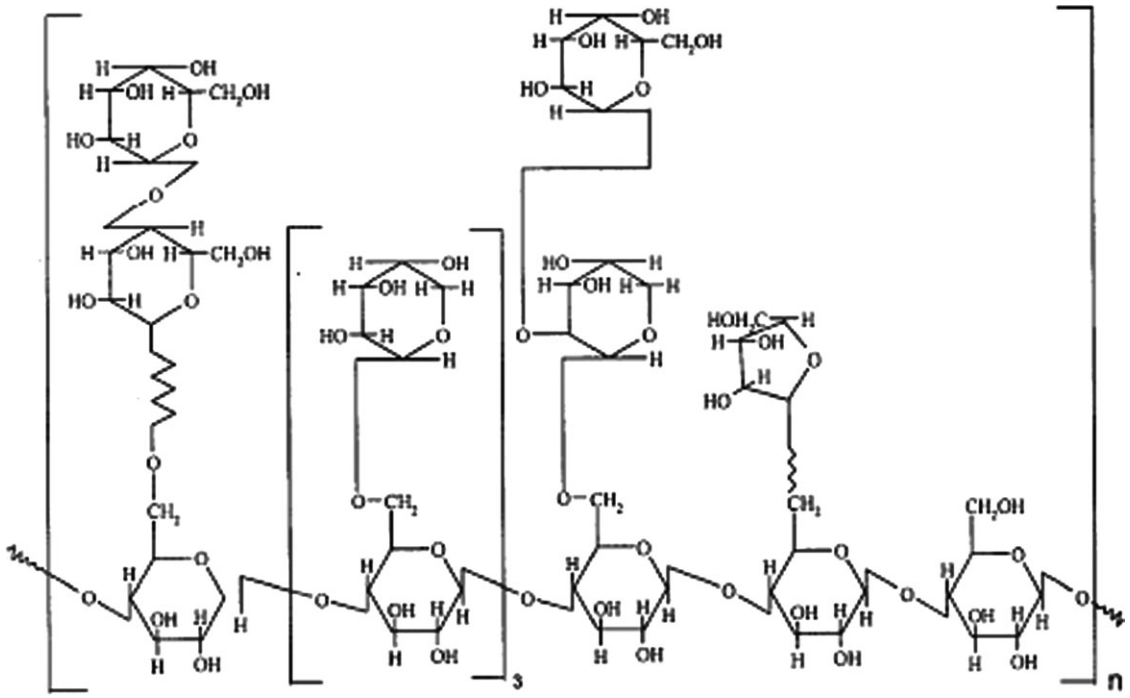
INTRODUCTION

The modification of natural polymers by grafting of different vinyl monomers onto the polymers is a promising method for introducing some desirable properties into the polymers without affecting the architecture of the polymer backbone.[1] In recent years, natural-based especially polysaccharide-based superabsorbent hydrogels have attracted much attention because of their nontoxicity, hydrophilicity, biocompatibility, and biodegradability. The superabsorbent hydrogels are three-dimensional hydrophilic networks that can absorb, swell, and retain water or biological fluids from 10% up to thousands of times their own weight.[2] Due to their excellent characteristics, superabsorbent hydrogels exhibit potential applications in many fields such as hygienic products, agriculture and horticulture, pharmaceutics, and medicine.[3–5] Graft copolymerization of vinyl monomers onto polysaccharides followed by crosslinking of their chains is regarded as an efficient method for the synthesis of polysaccharide-based superabsorbent hydrogels. Many investigations have been carried out for the synthesis of superabsorbent hydrogels through graft copolymerization of vinyl monomers onto polysaccharides such as starch,[6–8] carboxymethyl starch,[9] carboxymethyl amylose,[10] cellulose,[11] carboxymethyl cellulose,[12] sodium alginate,[13] chitosan,[14] carrageenan,[15] protein,[16] tragacanth gum,[17] gelatin,[18] and konjac glucomannan.[19]

Tamarind kernel powder (TKP), food grade natural polysaccharide and one of the cheapest gums, is derived from the seeds of *Tamarindus indica* L., a common and most important tree of India and Southeast Asia. The polysaccharide is composed of D-galactose, D-xylose, and D-glucose in the molar ratio of 1 : 2 : 3.[20] It consists of a main chain of β-D-(1 → 4)linked glucopyranosyl units and that a side chain consisting of a single xylopyranosyl unit is attached to every second, third, and fourth D-glucopyranosyl unit through an α-D-(1 → 6)linkage. One D-galactopyranosyl unit is attached to one of the xylopyranosyl units through a β-D-(1 → 2)linkage. The structure of TKP is shown in Scheme 1. TKP has potential commercial applications in textile, explosives, plywood, and food industries. Even though TKP finds wide range of industrial applications, it also has some drawbacks like biodegradability,[21] which limits its uses considerably. These drawbacks can be improved through the grafting of vinyl monomers onto it. However, because of the low solubility of TKP in cold water, the poor solution clarity, and the desire for products with modified or special properties, we used carboxymethylated derivative of TKP, that is, sodium



Scheme 1. The structure of TKP.

salt of partially carboxymethylated TKP (Na-PCMTKP) in this work for its further modification via grafting. Recently, graft copolymerization of acrylamide[22] as well as acrylonitrile (AN)[23] onto TKP using ceric ammonium nitrate (CAN) as a redox initiator has been reported. The synthesis of carboxymethyl tamarind-*g*-acrylamide and its application as a novel polymeric flocculant has also been reported.[24]

However, to the best of the author's knowledge there is no published report regarding the synthesis of a superabsorbent hydrogel via alkaline hydrolysis of the graft copolymer of Na-PCMTKP-containing polyacrylonitrile (PAN). Therefore, in this work, we have carried out graft copolymerization of AN onto Na-PCMTKP ($\overline{DS} = 0.15$) using CAN as a redox initiator and evaluated the optimum reaction conditions for affording maximum percentage of grafting by varying various reaction parameters. The optimally synthesized Na-PCMTKP-*g*-PAN (%G = 413.76, %GE = 96.48) copolymer has been characterized and finally hydrolyzed in alkaline medium to form a superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN. Considering the great impact of external saline solutions on water absorbency of superabsorbents and extending their applications, especially for agriculture and hygienic products, the swelling behavior of the superabsorbent hydrogel H-Na-PCMTKP-*g*-PAN has been studied in low-conductivity water as well as different saline solutions. The swelling kinetics of the hydrogel has also been investigated.

EXPERIMENTAL

Materials

Sodium salt of partially carboxymethylated TKP (Na-PCMTKP, $\overline{DS} = 0.15$) sample was kindly supplied by Encore Natural Polymers (Ahmedabad, Gujarat, India). Analytical reagent grade CAN (Qualigens, Glaxo India, Mumbai, India) and potassium hydroxide (Samir Tech Chem, Baroda, Gujarat, India) were used as received. Acrylonitrile (Fluka, Switzerland and purity is $\geq$ 99.0%) was distilled out at atmospheric pressure and the middle fraction was collected and used. Sodium chloride and urea (Maruti Chemicals Corporation, Anand, Gujarat, India) of analytical reagent grade were used as received. Aluminum chloride (Loba Chemicals, Mumbai, India) as well as calcium chloride and magnesium sulfate (Samir Tech Chem) of analytical reagent grade were used as received. All other reagents and solvents used in this work were of reagent grade. Nitrogen gas was purified by passing through fresh pyrogallol solution. Low-conductivity water was used for the preparation of solutions as well as for graft copolymerization reactions.

Graft Copolymerization

The graft copolymerization reaction of AN onto Na-PCMTKP ($\overline{DS} = 0.15$) was carried out using CAN as a redox initiator in an aqueous medium under nitrogen atmosphere, and the optimum reaction conditions, for affording maximum percentage of grafting, were evaluated by successively varying various reaction conditions such as concentrations of nitric acid (nil to 1.0 mol/L), CAN (2.5×10^{-3} to 80×10^{-3} mol/L), AN (0.037 to 0.370 mol/L) as well as reaction time (0.5 to 10 h), temperature (15° to 55°C), and amount of substrate (0.5 to 3.0 g, dry basis).[25] In this work, using the optimum reaction conditions established in the case of grafting of AN onto Na-PCMTKP ($\overline{DS} = 0.15$), the graft copolymerization reaction was carried out as per the procedure reported earlier.[26] In a 500-mL three-necked flask, equipped with a mechanical stirrer, a reflux condenser, and a glass inlet system; 1.0 g of Na-PCMTKP ($\overline{DS} = 0.15$) was dissolved in a low-conductivity water (100 mL) with constant stirring and bubbling of a slow stream of nitrogen for 1 h at 40°C. Freshly prepared 10 mL solution of 20 $\times 10^{-3}M$ CAN in 0.20M

nitric acid was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled AN (0.222*M*) was added. The grafting reaction was carried out for 4 h. The zero time of the reaction was considered to be at the time of monomer addition. After completion of the reaction, the mixture was immediately poured into excess of methanol. The crude copolymer thus obtained was dried under vacuum at 40°C. The homopolymer, PAN, was separated from the crude graft copolymer by extraction with dimethyl formamide for 48 h. After complete removal of the homopolymer, the pure graft copolymer of Na-PCMTKP ($\overline{DS}$ = 0.15) containing PAN (Na-PCMTKP-*g*-PAN) was dried at 40°C under vacuum to a constant weight.

Grafting Parameters

Grafting parameters, namely percentage of grafting (%G), percentage of grafting efficiency (%GE), and homopolymer content (%H_p), were calculated by using the following expressions.[27]

$$\%\ G = \frac{\text{Wt. of polymer grafted}}{\text{Initial wt. of backbone}} \times 100$$

$$\%\ GE = \frac{\text{Wt. of polymer grafted}}{\text{Wt. of polymer grafted} + \text{Wt. of homopolymer}} \times 100$$

$$\%\ H_p = 100 - \%\ GE$$

Saponification or Alkaline Hydrolysis

The graft copolymer, Na-PCMTKP-*g*-PAN (%G = 413.76 and %GE = 96.48), sample synthesized under optimal reaction conditions was saponified by following the methanol precipitate method[28] for the formation of hydrogel, H-Na-PCMTKP-*g*-PAN. According to this method, in a loosely stoppered 500 mL flask, 10.0 g of the Na-PCMTKP-*g*-PAN was dispersed in 100 mL 0.7*N* potassium hydroxide solution and gently stirred in the base under atmospheric conditions (5 min). Then the dispersion was heated at 90–95°C with occasional stirring. The saponification was continued until the color of the mixture changed from deep orange-red to light yellow (~ 2.5 h). The pasty mixture was then allowed to cool to room temperature. Methanol (5 × 10 mL) was added portion-wise to the gelled product while mixing. After 1 h, 200 mL additional methanol was added to the yellow dispersion of the hydrogel (H-Na-PCMTKP-*g*-PAN) to complete the precipitation. The supernatant was decanted after 30 min; and 300 mL of fresh methanol was then further added to completely dewater the particles for 24 h. The yellow precipitate of the hydrogel (H-Na-PCMTKP-*g*-PAN) was filtered through sintered glass crucible (no. 3) using suction. Thus, the product of the hydrogel, H-Na-PCMTKP-*g*-PAN, obtained was thoroughly washed with fresh methanol and finally dried at 60°C and stored in a vacuum desiccator.

Swelling or Absorbency Measurements

In order to measure the swelling or absorbency capacity of the hydrogel, 0.1 g of the saponified Na-PCMTKP-*g*-PAN (i.e., H-Na-PCMTKP-*g*-PAN) powder, after passing through 100 mesh (150 μm) sieve, was put into a weighed tea bag. The tea bag then was immersed in 200 mL of low-conductivity water and allowed to soak for different timings (0.5–36 h) at room temperature. The equilibrated swollen gel was then allowed to drain by removing the tea bag from the water and was hung up until no more drops drained (~ 10 min). The bag was then weighed to determine the weight of the swollen gel.

By using the swelling or absorbency experimental weights of the hydrogel sample, the values of the swelling ratio (*S*) and the equilibrium water content (EWC%) of the hydrogel sample were calculated using the following equation:

$$S = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_s and W_d are the weights of the swollen gel and the dry gel, respectively. Thus, the swelling ratio (*S*) was calculated as grams of water per gram of hydrogel sample (g/g gel). The water absorption capacity was determined three repeats for each case and its average value was reported.

$$EWC\ (\%) = \frac{W_{eq} - W_d}{W_s} \times 100 \quad (2)$$

where W_{eq} is the weight of swollen gel at equilibrium.

Swelling in Salt Solutions

Absorbency measurements of the H-Na-PCMTKP-*g*-PAN hydrogel sample were also carried out in 0.15*M* solutions of NaCl, $CaCl_2$, and $AlCl_3$ as well as in simulated urine (SU; composition: 0.85 g $CaCl_2.2H_2O$, 1.14 g $MgSO_4.7H_2O$, 8.20 g NaCl, 20 g urea, and 1000 mL low-conductivity water) solution[29] for different timings (0.5–36 h) according to the method described above for absorbency measurements in low-conductivity water.

Swelling Kinetics

The swelling kinetics of the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, was studied by measuring the equilibrium swelling capacity of the hydrogel in low-conductivity water, different salt (NaCl, $CaCl_2$, and $AlCl_3$) solutions (0.15*M*), and SU solution (0.15*M*) at different time intervals according to the aforementioned method.

Infrared Spectroscopy

Infrared (IR) spectra of Na-PCMTKP ($\overline{DS}$ = 0.15), Na-PCMTKP-*g*-PAN (%G = 413.76), and the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, were taken in KBr pellets using Nicolet Impact 400D Fourier Transform Infra Red Spectrophotometer.

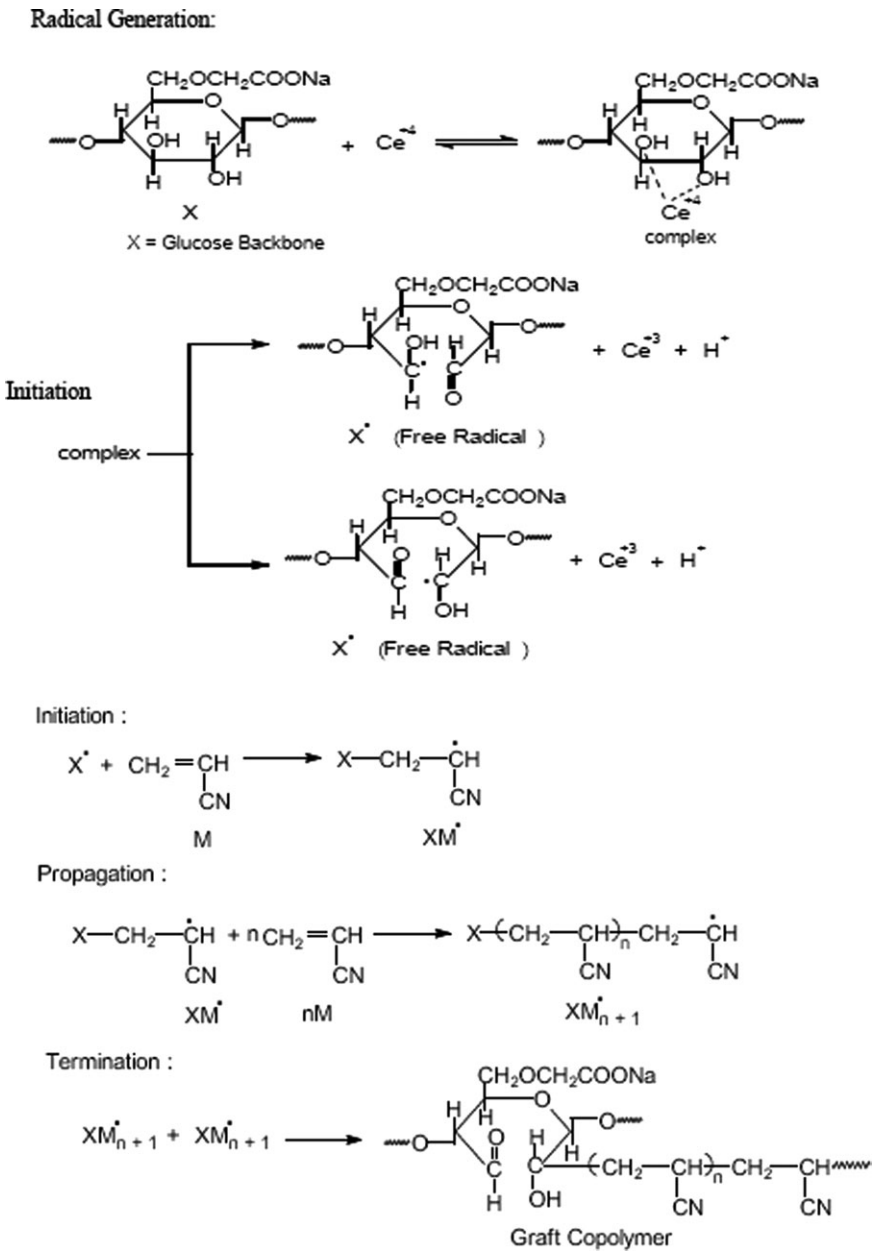
Scanning Electron Microscopy

Model ESEM TMP + EDAX (Philips, Netherlands (source: http://www.sicart.res.in/SEM.pdf) has been used to obtain the micrographs of Na-PCMTKP ($\overline{DS}$ = 0.15), Na-PCMTKP-*g*-PAN (%G = 413.76), and the superabsorbent hydrogel H-Na-PCMTKP-*g*-PAN.

RESULTS AND DISCUSSION

Synthesis and Mechanism Aspects

Synthesis of Na-PCMTKP-g-PAN. The mechanism of the graft copolymerization of AN onto Na-PCMTKP ($\overline{DS}$ = 0.15) was expected to follow according to Scheme 2.[30,31] The oxidation of Ce(IV) ion with Na-PCMTKP will occur preferably at the C_2–C_3 glucopyranosyl unit and to a lesser extent at the C_6 position



Scheme 2. Mechanistic pathway for synthesis of Na-PCMTKP-*g*-PAN.

as a result of single electron transfer process. The Ce(IV) ion initially, therefore, forms a complex with these hydroxyl groups, which is then reduced to produce Ce(III) ion with the formation of free radical at either C_2 or C_3 position as shown in Scheme 2. The free radicals (Na-PCMTKP macroradicals) so formed are responsible for the initiation of AN grafting onto Na-PCMTKP backbone. The grafting occurs mainly at C_2–C_3 glucopyranosyl unit leading to the formation of the graft copolymer Na-PCMTKP-*g*-PAN.

Synthesis of Superabsorbent Hydrogel (H-Na-PCMTKP-g-PAN). As discussed above, the saponification of Na-PCMTKP-*g*-PAN (%G=413.76) sample was carried out by treating it with aqueous 0.7*N* potassium hydroxide solution at 90–95°C. Scheme 3 represents the mechanism of crosslinking during conversion of nitrile groups of Na-PCMTKP-*g*-PAN into carboxamide and potassium carboxylate groups for the formation of the superabsorbent hydrogel H-Na-PCMTKP-*g*-PAN. As shown in the scheme 3, in the first step the hydroxide ions abstract hydrogen from the —OH group of Na-PCMTKP substrate to the formation of the corresponding alkoxide anions. Then, these Na-PCMTKP alkoxide anions (i.e., macroalkoxides) initiate crosslinking reaction between some adjacent PAN pendant chains leading to the formation of deep orange-red color intermediate with naphthyridine cyclic structures, including imine, —C=N—, conjugated bonds with evolution of ammonia.[32,33] Thus, the intermediate having a conjugated polyimine structure then gets further saponified with residual potassium hydroxide

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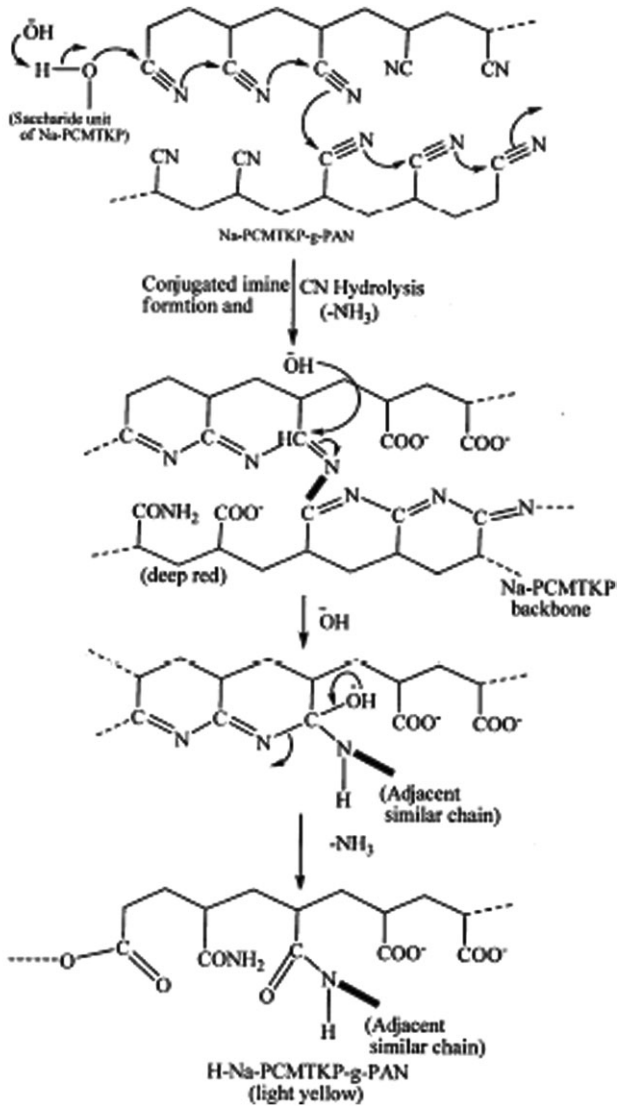

Scheme 3. Mechanism of crosslinking during conversion of nitrile groups of Na-PCMTKP-*g*-PAN into carboxamide and potassium carboxylate groups for the formation of superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN.

solution to form hydrophilic carboxamide (—$CONH_2$) and carboxylate (CO_2^-) groups. The disappearance of the conjugated system with formation of the hydrophilic groups was indicated when the color of the system changed from red to light yellow. This sharp change in color was used as a marker to halt the alkaline treatment. In this way, the starting hydrophobic graft copolymer (Na-PCMTKP-*g*-PAN) sample was converted into a hydrophilic gel, that is, superabsorbent hydrogel (H-Na-PCMTKP-*g*-PAN). The mechanism depicted in Scheme 3 is in accordance with the literature data.[15,34–46]

Characterization

Infrared Spectroscopy. Infrared spectroscopy was used to confirm the structures of the graft copolymer and the hydrogel. Figure 1(a) is the FTIR spectrum of Na-PCMTKP ($\overline{DS}$ = 0.15). A very strong and broad absorption band appearing at ~ 3435 cm^{-1} may be attributed to —OH stretching. Reasonably sharp absorption band appeared at ~ 2925 cm^{-1} may be attributed to —CH stretching. The asymmetric and symmetric vibrations of —COO— moiety are assigned to ~ 1662 cm^{-1} and ~ 1420 cm^{-1}, respectively. This can be attributed to the presence of the carboxymethyl groups incorporated during carboxymethylation of TKP. The IR spectrum of Na-PCMTKP-*g*-PAN is shown in Figure 1(b). The spectrum shows the absorption bands of Na-PCMTKP as well as an additional absorption band at ~ 2245 cm^{-1}, which can be attributed to —C≡N stretching mode. Figure 1(c) represents the IR spectrum of hydrogel, that is, H-Na-PCMTKP-*g*-PAN. The disappearance of the nitrile sharp peak at ~ 2245 cm^{-1} and appearance of the two distinct bands at ~ 1578 cm^{-1} and ~ 1409 cm^{-1}, indicating the respective presence of C=O asymmetric and symmetric stretching modes of the carboxylate anion and the absorption band appeared at ~ 1671 cm^{-1} indicating C=O stretching in carboxamide functional groups are the measure proofs for the conversion of the nitrile groups into carboxamide and carboxylate groups after alkaline hydrolysis of the graft copolymer. The presence of these highly

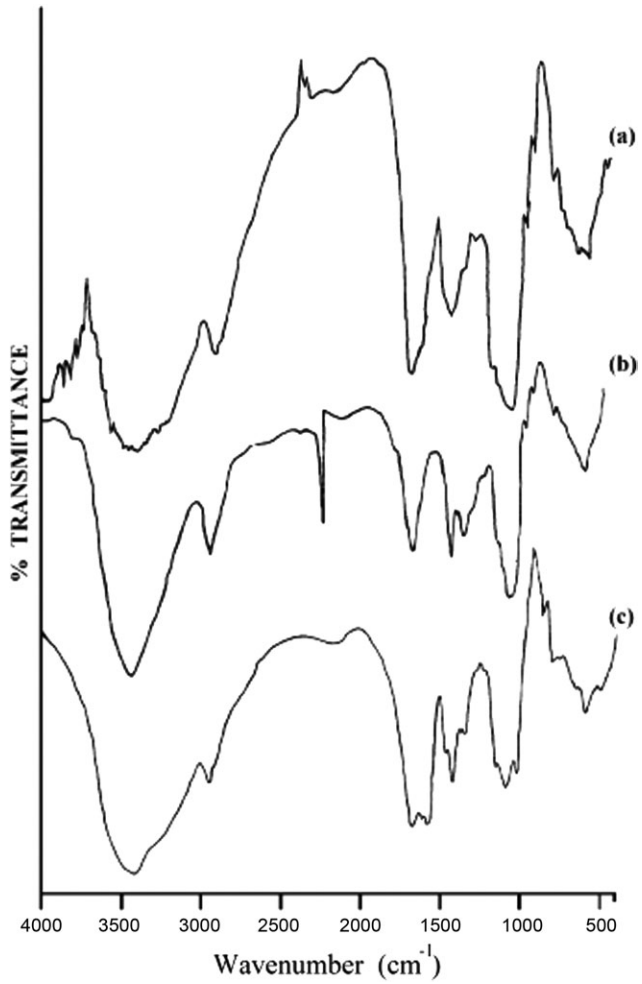

Figure 1. FTIR spectra of (a) sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, $\overline{DS}$ = 0.15), (b) Na-PCMTKP-*g*-PAN (%G = 413.76), and (c) the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN.

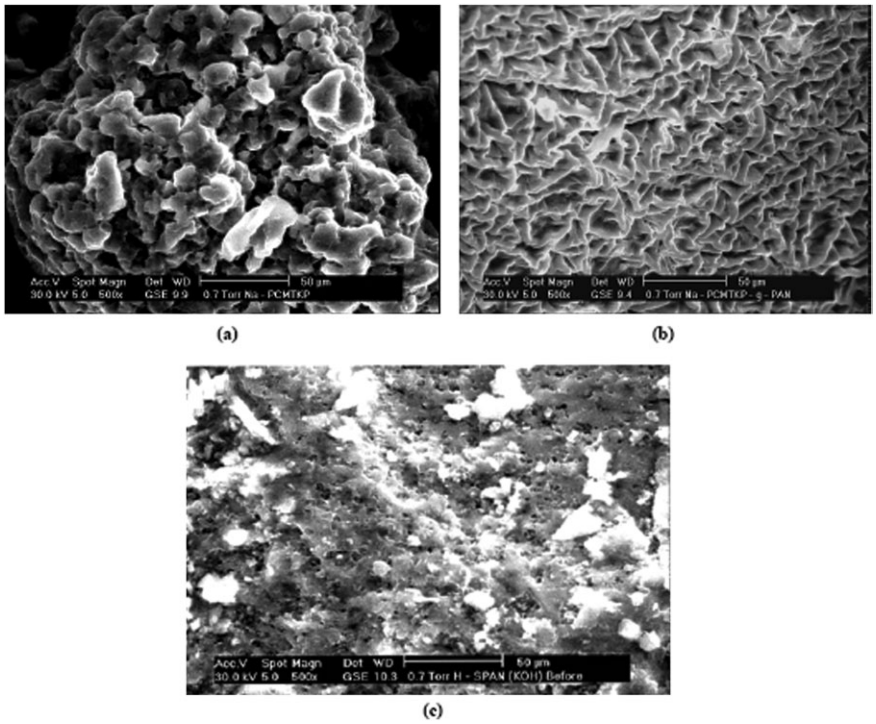

Figure 2. Scanning electron micrographs of (a) sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, $\overline{DS} = 0.15$) (500×), (b) Na-PCMTKP-*g*-PAN (%G = 413.76) (500×), and (c) the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN (500×).

hydrophilic groups is the main responsible factor for imparting super swelling behavior of the saponified graft copolymer, that is, hydrogel (H-Na-PCMTKP-*g*-PAN).

Scanning Electron Microscopy. As the textural characterization of a superabsorbent polymer is important to understand its swelling behavior, the surface appearance and structure of Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-*g*-PAN (%G = 413.76), and the hydrogel (H-Na-PCMTKP-*g*-PAN) were observed using scanning electron microscopy (SEM). These micrographs are shown in Figure 2(a–c). Figure 2(a) is the SEM of the Na-PCMTKP ($\overline{DS} = 0.15$). The observed surface morphology showing the clustered granular structure is due to its branched structure and interactions of the hydrophilic or ionic groups present in it. In figure 2(b), after grafting with PAN, a hydrophobic polymer, the surface of the resultant Na-PCMTKP-*g*-PAN (%G = 413.76) exhibits contrastingly different morphology compared to that of the Na-PCMTKP ($\overline{DS} = 0.15$) [Figure 2(a)], because of the hydrophobic–hydrophobic interactions taking place between the grafted PAN chains that assemble on the surface of the polymer backbone. Thus, the surface evidence supports the grafting of PAN onto the Na-PCMTKP ($\overline{DS} = 0.15$).

The morphology of the graft copolymer, Na-PCMTKP-*g*-PAN (%G = 413.76) [Figure 2(b)], was converted to a totally different morphology [Figure 2(c)] as the graft copolymer was treated in the alkaline medium to yield the superabsorbing hydrogel (H-Na-PCMTKP-*g*-PAN) [Figure 2(c)]. The hydrogel [Figure 2(c)] exhibits porous structure. It is supposed that these pores are the regions for the permeation of water into the polymeric network, and ultimately it helps in enhancing the water absorbency of the hydrogel.

Swelling Behavior in Water and Salt Solutions. The swelling behavior of the superabsorbent hydrogel could be significantly affected by various factors of the external solutions such as its valences and ionic strength. The presence of ions in the swelling medium has a profound effect on the swelling behavior of the superabsorbent hydrogels. The underlying principle behind the ionic dependence of swelling is well explained by the Donnan Equilibrium theory (Scheme 4). According to the Donnan Equilibrium theory, the balance between the osmotic pressure of the swelling system and elastic response of the polymeric network that controls the extent of swelling. The osmotic pressure results from the difference in concentration of mobile ions between the interior of the hydrogel network and the external solution. The fundamental feature within the hydrogel, bringing about the unequal distribution, in the present case, is the presence of the ionizable carboxylate groups (anionic sites) attached to the polymeric network.

In the present work, the swelling behavior of the "anionic" superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, has been studied by carrying out its absorbency measurements in low-conductivity water, 0.15*M* salt (NaCl, $CaCl_2$, and $AlCl_3$) solutions, and SU at different timings. The results obtained are shown in Figure 3(a–e). The swelling of the anionic hydrogel is found to be increased steadily and continuously with time in low-conductivity water up to 12 h beyond which it almost levels off. The hydrophilic groups such as carboxylate and carboxamide groups absorb the penetrating water through the

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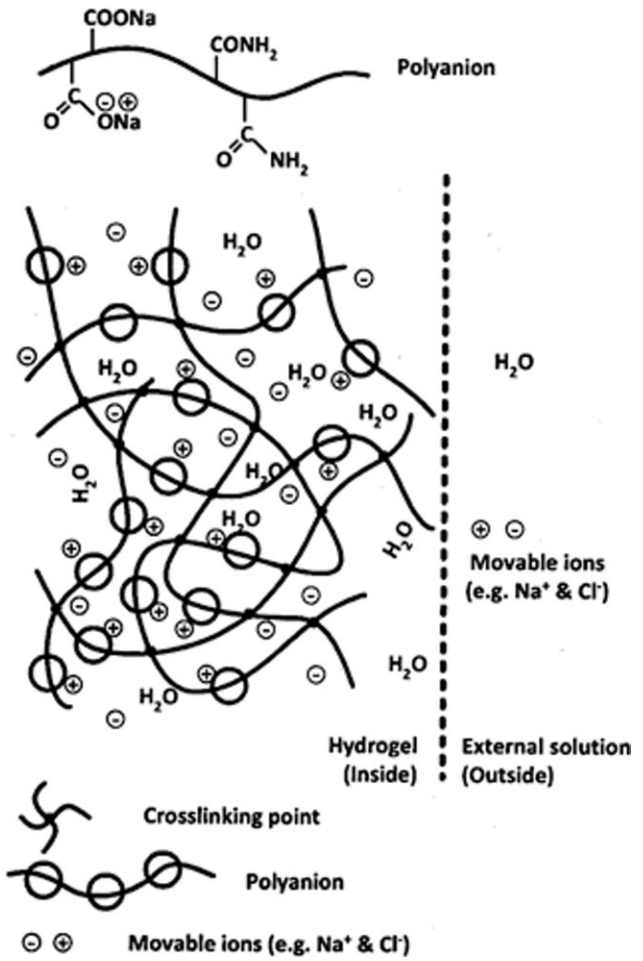

Scheme 4. Representation of swollen anionic superabsorbent hydrogel in equilibrium with electrolyte solution.

formation of hydrogen bonds. The swelling is driven by the repulsion of ionic and hydrophilic groups inside the network and osmotic pressure difference between the hydrogel and the external solution. It can be seen from Figure 3(a) that the hydrogel absorbs 59.81 g/g gel water quickly even within 30 min. Therefore, at this point (30 min), the hydrogel absorbs water with a rate of about 1.99 g/g min^{-1}. However, the swelling ability of the anionic hydrogel in different salt (NaCl, $CaCl_2$, and $AlCl_3$) solutions, having same concentration (0.15*M*), as well as in SU is found to be decreased dramatically at all different timings in comparison with the values measured in low-conductivity water [cf. Figure 3(b–e)]. This well-known undesired swelling loss, which is commonly being observed in the swelling of ionic hydrogels,[34] is attributed to a "charge-screening" effect of the additional counter ions (cations) causing a nonperfect anion–anion electrostatic repulsion.[37] The water-absorption properties are thought to result from osmotic pressure and interaction through hydrogen bonding of the carboxylate and carboxamide groups of the polymeric network with water molecules. When low-conductivity water is used as swelling agent, the absorption capacity is found to be higher. At the swelling equilibrium, the chemical potential of water in the polymer network will be equal to that of the water surrounding it. However, when a certain amount of salt (NaCl or $CaCl_2$ or $AlCl_3$ or SU, as in the present study) in low-conductivity water is used as a swelling agent then the attraction of the strong electrostatic forces exists between the fixed anionic sites or the negatively charged carboxylate groups on the polymer chain and the cations (counter ions) of the salt, as a result of which these cations, by screening the fixed charges on the polymer chain, reduce the electrostatic repulsion tremendously as compared with what it would be in their absence [cf. Figure 3(b–e)]. Thus, because of the strong electrostatic forces the concentration of the cations (e.g., Na^+ or Ca^{+2} or Al^{+3}) will be higher inside the hydrogel than outside (Scheme 4) as a result of which the osmotic pressure outside the hydrogel will decrease drastically and consequently the absorbency amounts will be diminished [cf. Figure 3(b–e)].

The effect of different cations with a common anion (Cl^-) on the absorbency of the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, can also be explained from the results of Figure 3(b–d). It can be seen from this figure that the absorption capacity of the hydrogel decreases with an increase in the charge of the metal cation ($Al^{+3} < Ca^{+2} < Na^+$) in the solutions having the same concentration (0.15*M*).

This can be attributed to the complexing ability arising from the coordination of the multivalent cations with carboxylate groups of the hydrogel to induce the formation of intramolecular and intermolecular complexes. This leads to an increase in the crosslinking density, which makes the network shrink.[38] This behavior is also in agreement with the results reported by Gugliemelli et al.[39] on the viscosity of hydrolyzed starch PAN dispersions in various saline solutions. They showed that the viscosity of the dispersion decreased with an increase of the counter ion valency. Thus, in the case of $AlCl_3$, because of the high complexing ability of the Al^{+3} ions with the carboxylate groups of the hydrogel, the crosslink density of the network ultimately increases but it may hinder the approach of the water molecules leading to the lowering of the water uptake compared to that of NaCl [cf. Figure 3(b)]. This "ionic crosslinking" phenomenon mainly occurs at the surface of the particles and as a result, in the present case, the hydrogels are found to be rubbery and very hard to the touch when they swell in Ca^{+2} or Al^{+3} solutions, so that it cannot swell well. In contrast to this, the hydrogel particles are found to be swollen in NaCl and water, exhibiting lower gel strength to the touch. Similar results are also reported in the literature.[7,12,14,38,40] However, an attempt has been made to compare the swelling capacities with those of other subperabsorbents[7,9,10,12,17,35,41,42] synthesized by saponification of the polysaccharide-based graft copolymers containing PAN. Zohuriaan-Mehr and Pourjavadi[7] have synthesized superabsorbent hydrogels from starch-*g*-PAN samples using granular corn starch and gelatinized corn starch and measured their equilibrium swelling values in different swelling media. They have observed the absorbency values of the two hydrogel samples that are synthesized from granular corn starch-*g*-PAN to be 36 g/g and 99 g/g in deionized water. On the other hand, they have also observed the absorbency values of the two other hydrogel samples that are synthesized from gelatinized corn starch-*g*-PAN to be 358 g/g and 415 g/g in deionized water. The swelling capacity of these hydrogels in

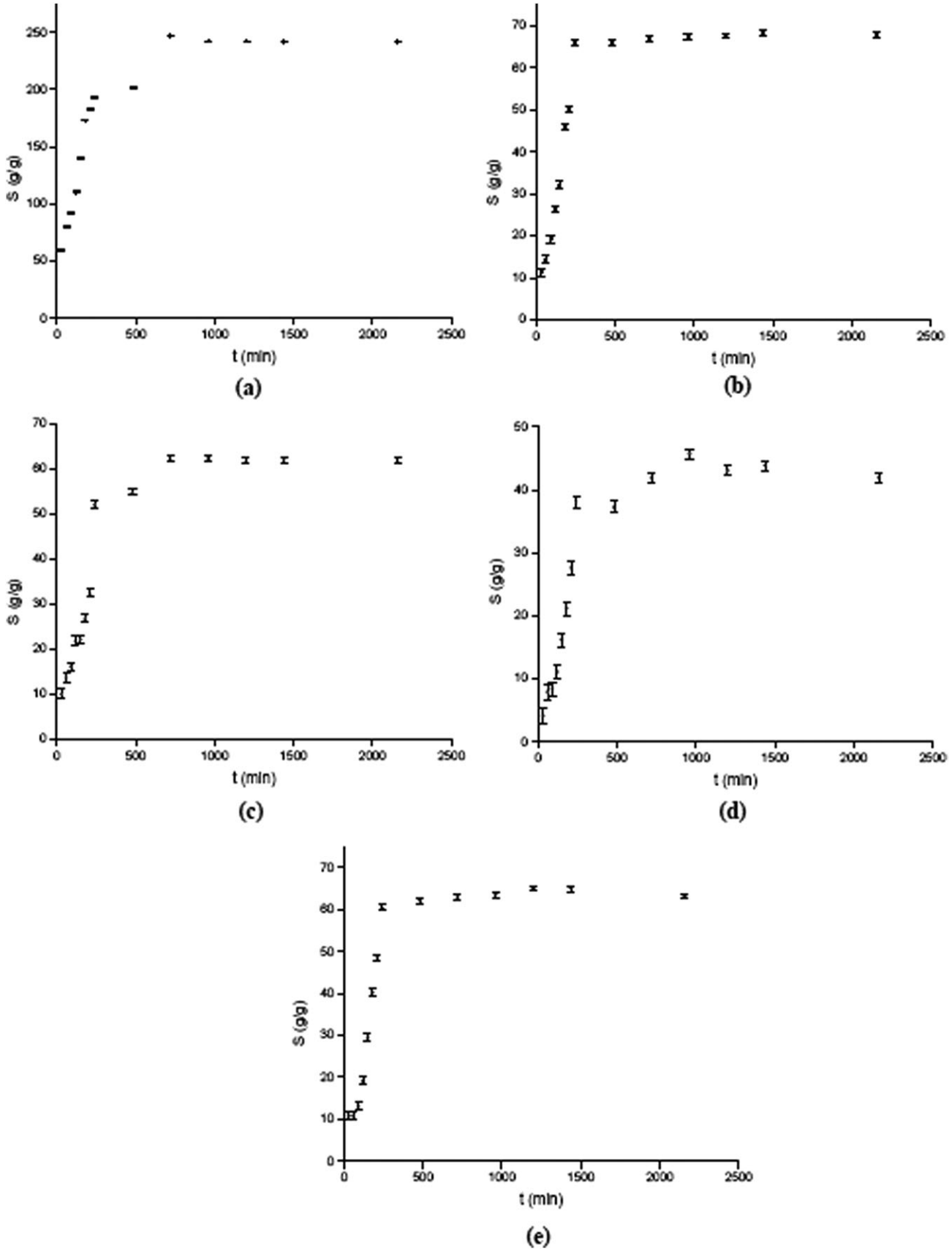

Figure 3. Kinetic swelling curves of the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, in (a) low-conductivity water (●), (b) 0.15*M* NaCl (■), (c) 0.15*M* $CaCl_2$ (▲), (d) 0.15*M* $AlCl_3$ (▼), and (e) 0.15*M* simulated urine (SU) (◆) solutions.

Table I. Dependency of the Dimensionless Salt Sensitivity (f) of the Superabsorbent Hydrogel, H-Na-PCMTKP-*g*-PAN, to the Type of Swelling Media at Different Timings

Time (h)	f_{NaCl}	f_{CaCl_2}	f_{AlCl_3}	f_{SU}	Average salt sensitivity[a]
0.5	0.811	0.832	0.931	0.816	
1.0	0.821	0.828	0.901	0.864	
1.5	0.792	0.825	0.910	0.858	
2.0	0.760	0.801	0.899	0.826	$f_{NaCl} = 0.659$
2.5	0.771	0.841	0.885	0.790	
3.0	0.734	0.845	0.878	0.768	f_{CaCl_2}=0.747
3.5	0.725	0.823	0.849	0.734	
4.0	0.659	0.729	0.802	0.687	$f_{AlCl_3} = 0.659$
8.0	0.672	0.728	0.815	0.691	
12.0	0.729	0.747	0.830	0.745	f_{SU}=0.738
16.0	0.721	0.742	0.811	0.738	
20.0	0.720	0.744	0.822	0.731	
24.0	0.718	0.743	0.819	0.731	
36.0	0.719	0.743	0.827	0.739	

[a]Calculated as per Eq.(3), on the basis of the experimental equilibrium swelling ratio (g/g gel) values (Table II) for different swelling media.

saline solutions was found to be appreciably decreased compared to the values measured in deionized water. Sinha et al.[9] and Shah et al.[10] have also synthesized superabsorbent hydrogels by carrying out saponification of graft copolymers of sodium salt of partially carboxymethylated starch (Na-PCMS) and sodium salt of partially carboxymethylated amylose (Na-PCMA) samples having different degrees of substitution. It has been observed that the hydrogel synthesized from Na-PCMS ($\overline{DS}$ = 0.677) containing PAN (Na-PCMS-*g*-PAN, % G = 230.55) showed the maximum water retention value (WRV) to be 522.90% while the hydrogel synthesized from Na-PCMSA ($\overline{DS}$ = 0.493) containing PAN (Na-PCMA-*g*-PAN, %G = 177.80) showed the maximum WRV to be 284.30% indicating that WRV is not only entirely dependent on the graft level but also on the accessibility of the substrate to water, which is the function of $\overline{DS}$. Pourjavadi et al.[12] have observed the maximum swelling capacity of the superabsorbent hydrogel H-CMC-*g*-PAN in water to be 512 g/g under the optimum alkaline hydrolysis conditions. They have also observed the decreased swelling capacity of the hydrogel in chloride salt solutions (0.15*M*) with different charges of cations. Mohamadnia Z. et al.[17] have measured the swelling capacity values for the hydrolyzed tragacanth gum-*g*-PAN in distilled water as well as NaCl, $CaCl_2$, and $AlCl_3$ solutions (all 0.15*M*) and are found to be 307.0 g/g, 65.5 g/g, 3.5 g/g, and 2.5g/g, respectively. Mahdavinia et al.[35] have studied the water absorbency dependence of H-chitoPAN hydrogels upon add-on value of the chitosan-*g*-PAN copolymer saponified and found a linear relationship between them. The lowest and highest values of the water absorbency were found to be approximately 210 g/g and 460 g/g, respectively, for the graft copolymer sample having add-on values 56.2% and 84.8%. Farag and Al-Afaleq[41] have measured the absorbency of the saponified delignified cellulose-*g*-PAN having different carboxyl content values in the presence of water, saline water (0.5%), and synthetic urine. In the case of the graft copolymer sample having the lowest carboxyl content (2.5 mmol/100 g sample) the absorbency of the hydrogel has been found to be 13 g/g, 9 g/g, and 11 g/g in water, saline water, and synthetic urine, respectively. Conversely, for the graft copolymer sample having the highest carboxyl content (308 mmol/100 g sample), the hydrogel has been found to exhibit the absorbency value to be 423 g/g, 210 g/g, and 85 g/g in water, saline water, and synthetic urine, respectively. Hashem et al.[42] have prepared hydrogels based on saponified products of PAN–starch composites and measured their WRV in water and synthetic urine. The WRV of the hydrogel samples are found to rely on the variables affecting the magnitudes of both polymerization and saponification. Under the optimum reaction conditions 1 g of the hydrogel sample was found to absorb 920 g distilled water and 38 mL synthetic urine.

Thus, in comparison with the results of the swelling behavior of the different hydrogels as discussed above, encouraging and promising results have been obtained in this work also with regard to the swelling behavior of the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, in different swelling media, that is, absorbency in water, 0.15*M* NaCl, 0.15*M* $CaCl_2$, 0.15*M* $AlCl_3$, and 0. 15*M* SU solutions are found to be 242.05 g/g gel, 65.85 g/g gel, 62.43 g/g gel, 41.88 g/g gel, and 63.51g/g gel, respectively.

The dimensionless salt sensitivity factor (f)[7] was calculated for 0.15*M* salt solutions according to the equation:

$$f = 1 - \left(\frac{S_{salt}}{S_{water}}\right) \quad (3)$$

where S_{salt} and S_{water} are the values of the swelling ratio in a given saline solution and low-conductivity water, respectively. Thus, the values of f calculated for the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, in 0.15*M* different salt solutions and

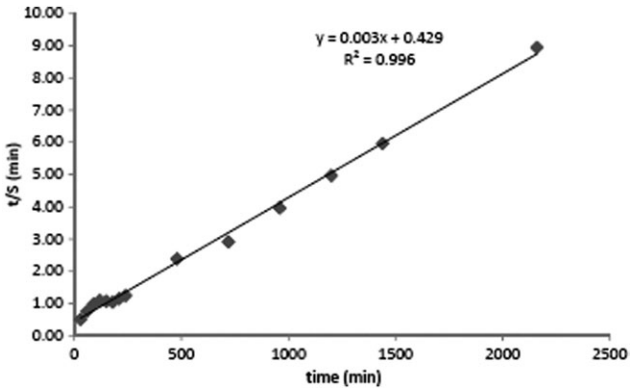

Figure 4. Plot of t/S versus t for the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, in low-conductivity water as swelling medium.

SU at different timings are recorded in Table I. The influence of increasing cation charge on the ultimate absorption for the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, can be evident upon comparing the average salt sensitivity values (Table I). It can be seen from this table that due to ionic crosslinking by multivalent cations (Ca^{+2} and Al^{+3}), the average salt sensitivity values of the superabsorbent hydrogel are found to be higher in 0.15*M* $CaCl_2$ and $AlCl_3$ solutions in comparison with univalent cation Na^+, in 0.15*M* NaCl solution. The average salt sensitivity value for the case of SU solution is also found to be higher compared to 0.15*M* NaCl solution as the solution contains multivalent cations (Mg^{+2} and Ca^{+2}) in addition to univalent cation (Na^+). Thus, the lower the cationic charge, the lower will be the average salt sensitivity. In other words, this low average salt sensitivity value is attributed to the low charge screening effect in the hydrogel when the swelling media is 0.15*M* NaCl solution. Similar results are also reported in literature.[18,35]

Swelling Kinetics. In practical applications, for a hydrogel both a higher swelling rate and a higher swelling capacity are required. Figure 3(ae) represents the kinetic swelling curves of the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, in different swelling media [low-conductivity water, NaCl (0.15*M*), $CaCl_2$ (0.15*M*), $AlCl_3$ (0.15*M*) solutions, and SU (0.15*M*)].

In order to evaluate the mechanism of the swelling process of hydrogels, several kinetic models are used to test the experimental data. However, in the present work, for evaluating the dynamic swelling properties of the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, a simple kinetic analysis based on the second-order kinetics model was adopted and accordingly the second-order equation can be expressed as Eq. (4).[43–45]

$$\frac{dS}{dt} = k_S\,(S_{eq} - S)^2 \tag{4}$$

where S_{eq}, S, and k_S denote the equilibrium swelling (theoretical), swelling at any time, and swelling rate constant, respectively. The integration of Eq. (4) over the limits $S = S_0$ at $t = t_0$ and $S = S$ at $t = t$ gives

$$\frac{t}{S} = A + Bt \tag{5}$$

where $B = 1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A = \left(1/k_S\,S_{eq}^2\right)$ is the reciprocal of the initial swelling rate of the hydrogel (r_i), and k_S is the swelling rate constant.

For analyzing the experimental results of this work in terms of the above kinetic model, the plots of t/S versus t were plotted for the hydrogel, H-Na-PCMTKP-*g*-PAN, in different swelling media. The plots were found to be linear with good linear correlation coefficient (Table II), indicating that the swelling behavior of the hydrogel in the different swelling media follows the pseudo second-order model. Figure 4 represents such type of typical plot of t/S versus t obtained for the H-Na-PCMTKP-*g*-PAN hydrogel in water as swelling media. The values of the initial rate of swelling (r_i), swelling rate constant (k_S), and theoretical equilibrium swelling (S_{eq}) were calculated from the slope and intersection of the lines obtained in the graphs[46,47] for the hydrogel, H-Na-PCMTKP-*g*-PAN, in different swelling media. The results are summarized in Table II. The value of the initial swelling rate (r_i) is found to be higher, that is, 2.33 [(g/g gel) min] when low-conductivity water was used as swelling media in comparison with its values obtained for other swelling media, that is, different salt solutions (0.15*M*) and SU. The value of r_i

Table II. Swelling Characteristics for the Superabsorbent Hydrogel, H-Na-PCMTKP-*g*-PAN, in Different Swelling Media

Swelling media	Experimental equilibrium swelling ratio (g water/g gel)	t_{req}[a] (h)	S_{eq}[b] (g water/g gel)	EWC[c] (%)	r_i[d] [(g water/g gel) min]	Ionic strength[e] (mole-ion dm^{-3})	k_s[f] $\times 10^5$ [(g.gel/g.water)/min]	R^2
Low conductivity water	242.05 ± 0.7	16	333.33	99.59	2.33	-	2.10	0.996
NaCl (0.15*M*)	65.85 ± 1.1	04	76.92	98.50	0.49	0.15	8.28	0.987
$CaCl_2$ (0.15*M*)	62.43 ± 1.3	12	71.43	98.42	0.32	0.45	6.30	0.983
$AlCl_3$ (0.15*M*)	41.88 ± 1.5	12	52.63	97.66	0.19	0.90	6.90	0.963
Simulated urine (SU)	63.51 ± 1.2	16	76.92	98.45	0.37	0.18	6.24	0.970

Values are recorded as mean ± standard deviations.
[a]Time required to achieve Experimental Equilibrium Swelling Ratio value.
[b]Theoretical equilibrium swelling ratio.
[c]Equilibrium water content.
[d]Initial swelling rate.
[e]$\mu = \frac{1}{2}\sum mz_i^2$, where μ, m, and z_i are the ionic strength, the ionic concentration, and charge on each individual ion, respectively.
[f]Swelling rate constant.

is also found to be decreased with increase in the ionic strength (cation charge) of the swelling media as per the order:

$$NaCl > SU > CaCl_2 > AlCl_3$$

This observed decrease in the value of the initial swelling rate (r_i) with an increase in the ionic strength (cation charge) of the salt solution (Table II) is attributed to the decrease in the osmotic pressure difference between the gel network and the corresponding external solution. The values of the experimental equilibrium swelling ratio for different swelling media are reported in Table II along with the corresponding time required to achieve these swelling ratio values. As per Eq. (2), the equilibrium water content (EWC%) values were also calculated for the hydrogel in different swelling media and are included in Table II.

CONCLUSION

A novel superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, has been prepared by grafting of AN onto Na-PCMTP ($\overline{DS} = 0.15$), followed by alkaline hydrolysis of the Na-PCMTKP-*g*-PAN graft copolymer to achieve an in situ crosslinked hydrogel network, H-Na-PCMTKP-*g*-PAN, with high capability of water absorption (absorbency in water, 242.05 g/g gel; absorbency in 0.15*M* NaCl, $CaCl_2$, and $AlCl_3$ solutions to be 65.85 g/g gel, 62.43 g/g gel, and 41.88 g/g gel, respectively). The synthesized hydrogel also exhibited the maximum swelling capacity of the order of 63.51 g/g gel in SU. These promising results make it worth to prepare hydrogel suitable for utilization as diaper as well as adsorbent material. The results regarding the absorbency measurements of the hydrogel in low-conductivity water, 0.15*M* different salt (NaCl, $CaCl_2$, and $AlCl_3$) solutions and SU have been explained successfully on the basis of "charge screening" effect and "ionic crosslinking" phenomenon. The experimental data clearly suggested that the swelling process of the hydrogel obeys second-order kinetics in different swelling media. The swelling characteristics as well as equilibrium water contents have also been investigated for the superabsorbent hydrogel, H-Na-PCMTKP-*g*-PAN, in different swelling media.

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