Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(20):339-343
(http://derpharmachemica.com/archive.html)

Hydrogel of poly (SSNa-cross-TeEGDMA): Preparation, characterization, and Swelling behavior

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ABSTRACT

Series of novel hydrogels based on sodium styrene sulfonate(SSNa) and tetraethylene glycol dimethacrylate (TeEGDMA) copolymers, were prepared by free radical cross-linking copolymerization and were characterized using Spectra of Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC).The swelling properties of these hydrogels were achieved in distilled water at different pH at 25°C, the results showed that the swelling ratio are proportional to the sodium styrene sulfonate(SSNa) percent molar composition of 40, 50 and 80 incorporated in each hydrogel, The values swelling ratio of the basic medium are higher than those observed in acidic and neutral medium.

Keywords: Hydrogel network, Swelling properties, sodium styrene sulfonate, *FTIR, DSC*

INTRODUCTION

Hydrogels are three-dimensional networks, can be obtained by copolymerization of monomers having different functional groups, or by post-modification of formed products in polymerization reactions[1,2], functionalized hydrophilic crosslinked materials capable of absorbing large amounts of water and containing functional groups (carboxylic acids, amines, hydroxyls, etc.) [3, 4]

Hydrogels are insoluble, because of its poor solubility in aqueous solutions[5], They can be classified according to the type of cross-linking as: chemical hydrogels, which consist of polymer chains cross-linked by covalent bonds, and physical hydrogels, which rely on electrostatic forces, hydrogen bonding and Van der Waals forces to form the network [6] physically crosslinked hydrogels, will eventually degrade in solvent resulting from the swelling stress whereas chemically crosslinked hydrogels stay intact unless covalent bonds are broken with certain treatments [7,8].

In addition, the formation of a porous structure provides a certain way to improve the absorption rate by increasing diffusion of water into the glassy matrix of dried hydrogel [9]. Therefore, porous hydrogels are structurally crosslinked hydrophilic polymers and by using their porous structure can absorb considerable amounts of water in relatively short periods of time [10], hydrogels are those capable of undergoing selective swelling in response to different stimuli, including pH, temperature or ionic strength [11, 12], it is possible to generate physical as well as chemical hydrogels that are sensitive to external stimuli such as pH. In acidic medium, the protonated amino groups repel one another, thereby promoting swelling [13]

Hydrogel was then characterized by swelling kinetics, mechanical stability, differential scanning calorimetry(DSC), Fourier transform infrared spectra (FTIR).

The application of hydrogels dates back to 1960. When Wichterle and Lim introduced the use of hydrophilic networks of cross-linked poly (2-hydroxyethyl methacrylate) as soft contact lens material Hydrogels are extremely

suitable for a variety of applications in the pharmaceutical and medical industry. Because they are capable of retaining large amounts of water and because of their soft and rubbery consistence, they closely resemble living, tissues. More-over, their high water content also contributes to their excellent bio-compatibility [14]

MATERIALS AND METHODS

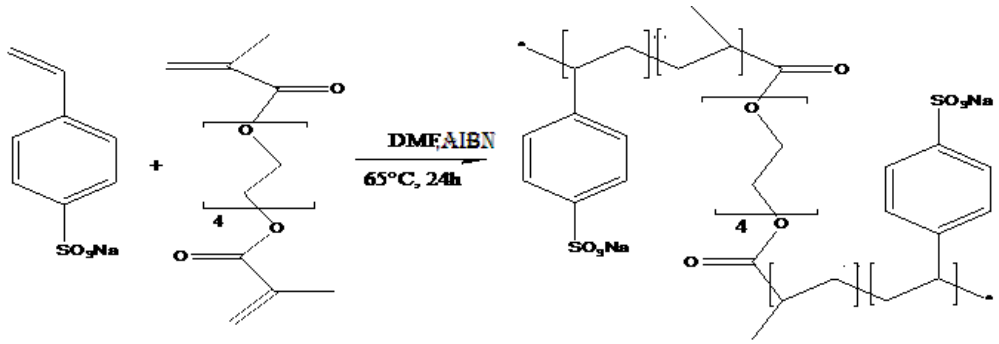
Materials

Sodium styrene sulfonate(SSNa) (Sigma–Aldrich, USA), initiator azobisisobutyronitrile (AIBN) (Sigma–Aldrich, USA),and tetraethylene glycol dimethacrylate (TeEGDMA), solvent dimethylformamide(DMF) (Shanghai Chemical Group, China)

METHODS

Synthesis of poly (SSNa-cross-TeEGDMA) copolymers

Poly (SSNa-cross-TeEGDMA) hydrogels were synthesized by free-radical crosslinking copolymerization in solution of Sodium styrene sulfonateand tetraethylene glycol dimethacrylate monomers was dissolved in dimethylformamide(DMF) (8 ml), and nitrogen atmosphere Then the reaction system was kept at 65°C for 24 h, three different copolymers were obtained with SSNa percent molar composition of 40, 50 and 80



Scheme.1 Synthesis of hydrogels poly (SSNa-cross-TeEGDMA)

Table 1 the hydrogels prepared in this paper

Hydrogels	SSNa (mol%)	TeEGDMA (mol%)	AIBN (mol%)	DMF (mL)	T °C	t (h)
Poly(SSNa -cross-TeEGDMA)	40	60	2	8		
	50	50	2	8		
	80	20	2	8	65	24

FTIR analysis

The samples were analyzed using a Fourier transform infrared (FTIR) spectroscope IFS66in the region of 4000–400cm^{-1}. Prior to the measurement, the samples were dried under vacuum until reaching a constant weight. The dried samples were pressed into the powder, mixed with 10 times as much KBr powder, and then compressed to make a pellet for FTIR characterization.

Differential scanning calorimetry

Differential scanning calorimetry (DSC), were performed using a DSC8500 apparatus (Perkin–Elmer). Were carried out in a nitrogen atmosphere

Swelling behaviour of poly (SSNa-cross-TeEGDMA) hydrogels

The swelling ratios of hydrogels in distilled water was determined according to equation (1)
‘‘Swelling Ratio’’ was calculated [15] by

$$\text{Swelling Ratio } SR = Q = \frac{W_{hs,exp}}{W_{hd}} \quad (1)$$

$W_{hs,exp}$: Weight of the hydrogel in the swollen state in distilled water,

W_{hd}: Weight of the hydrogel in the dry state

RESULTS AND DISCUSSION

The structure of poly (SSNa-cross-TeEGDMA) was characterized by FTIR and shown in Fig.1 , compared with poly(SSNa-cross-TeEGDMA) crosslinker and different SSNa percent molar composition of 40and 80 hydrogels, the FT IR spectrum of poly(SSNa-cross-TeEGDMA) crosslinker exhibited the characteristic bands, Two characteristic bands of the ester TeEGDMA (C=O) and C=C groups of SSNa component for the copolymerized hydrogel samples were observed around 1754 cm^{-1} and 1690 cm^{-1}, respectively, bands of the TeEGDMA(C-O) and SSNa (S=O) observed around 1150 cm^{-1} and 1050 cm^{-1}, respectively

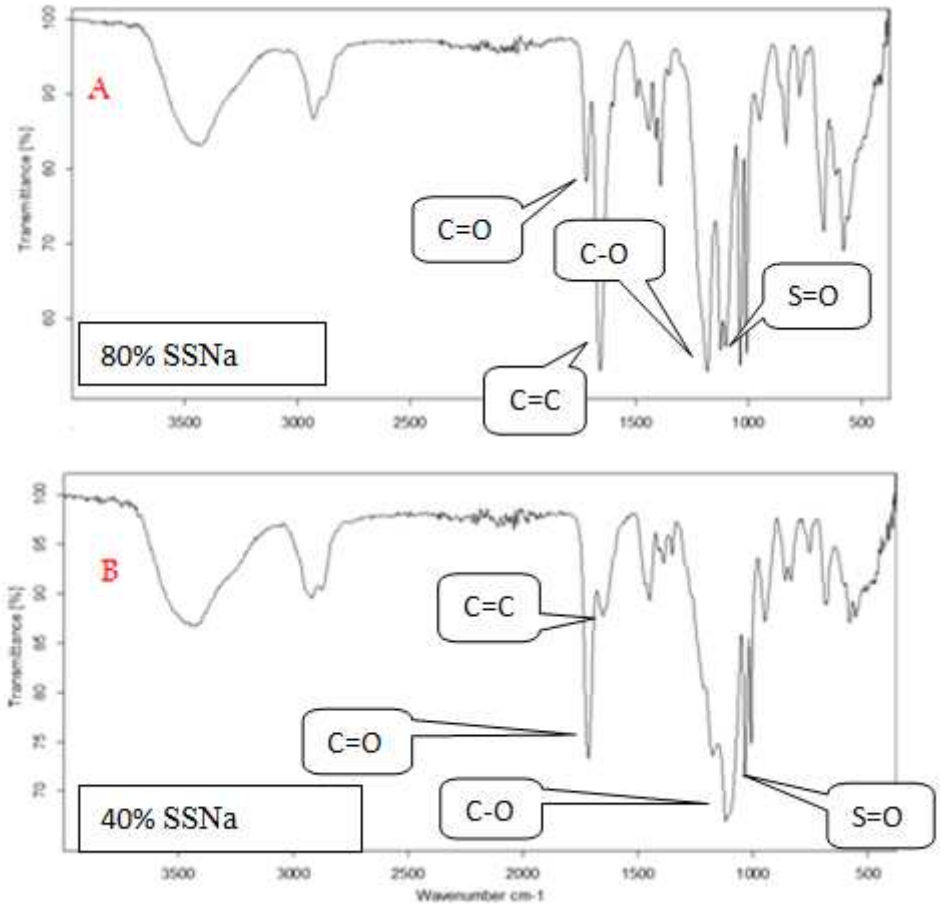


Fig.1 FTIR spectra: A) - poly (SSNa-cross-TeEGDMA) 80 % SSNa, (B) - poly (SSNa-cross-TeEGDMA) 40 % SSNa

Fig.2 show the DSC thermo-grams of hydrogels each thermo-gram has one peak and the melting temperature (T_m) of the poly (40%SSNa-cross-TeEGDMA) is (130°C), (T_m) of the poly (50%SSNa-cross-TeEGDMA) is (131°C), of the poly (80%SSNa-cross-TeEGDMA) is (139°C), confirming that T_m (SSNa) is higher than that of the T_m (TeEGDMA).

The swelling of the poly (SSNa-cross-TeEGDMA) hydrogels were obtained with SSNa percent molar composition of 40, 50 and 80 in the pH range from 2; 6.8; 10 in distilled water, at 25° C according to Fig.3We thus observe that the values of swelling ratios at equilibrium of hydrogels of poly (SSNa-cross-TeEGDMA) in distilled water at 25°C are proportional to the rate of SSNa incorporated in each hydrogel could be explained by the incorporation of more and more of the SSNa which, in this case, probably contributes to the increase of the swelling through hydrogen bond formation between SSNa and water.

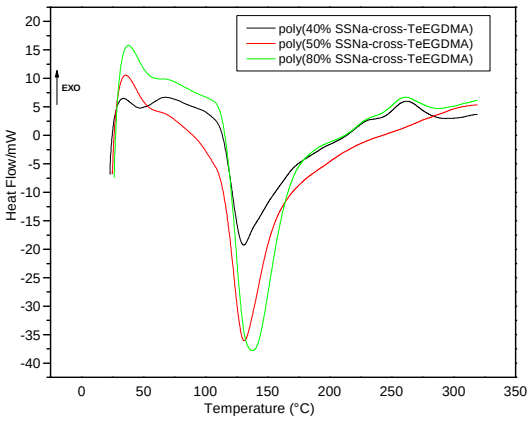


Fig.2 DSC thermograms of hydrogels poly (SSNa-cross-TeEGDMA)

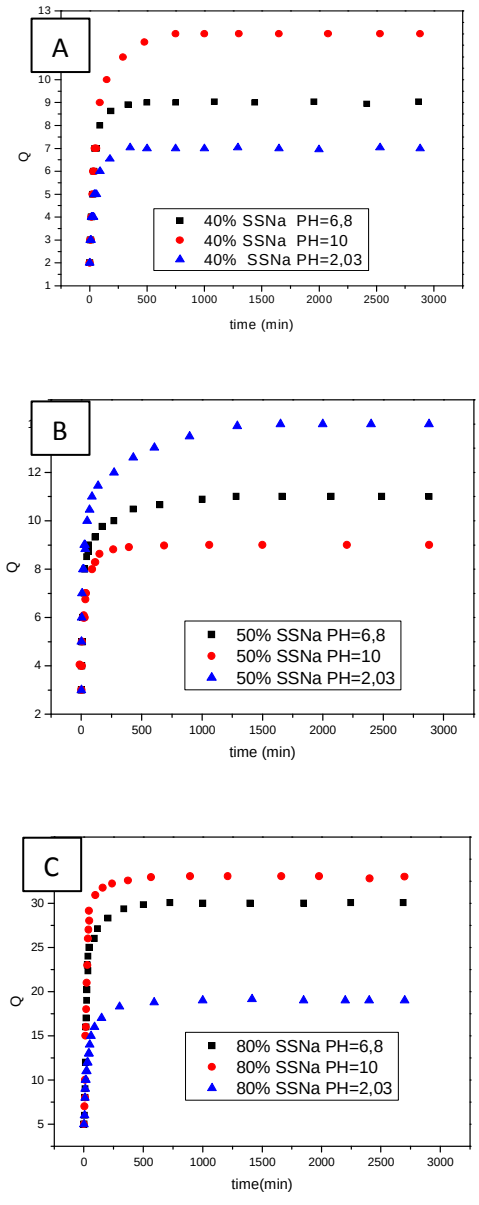


Figure3: Swelling ratio, as a function of time for cross-linked poly (SSNa-cross-TeEGDMA) at different pH at 25 °C: (A) poly (40%SSNa-cross-TeEGDMA) (B) poly (50%SSNa-cross-TeEGDMA)(C) poly(80%SSNa-cross-TeEGDMA)

Fig. 4 indicates pH-dependent swelling ratios of the obtained poly (SSNa-cross-TeEGDMA) hydrogels. Show that the values swelling ratios of the basic medium are higher than those observed in neutral medium and acidic medium, these values of swelling ratio are proportional with SSNA percent molar.

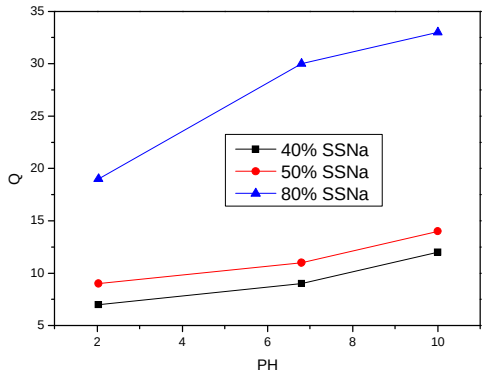


Fig.4: swelling ratios values of the poly (SSNa-cross-TeEGDMA) hydrogels as a function of pH at 25°C

CONCLUSION

Poly (SSNa-cross-TeEGDMA) hydrogels were synthesized by free-radical crosslinking copolymerization in solution of sodium styrene sulfonate (SSNa) and tetraethylene glycol dimethacrylate (TeEGDMA) monomers with SSNa percent molar composition of 40, 50 and 80, DSC thermo-grams of hydrogels each thermo-gram has one peak and the melting temperature (T_m) of the poly (40%SSNa-cross-TeEGDMA) is (130°C), (T_m) of the poly (50%SSNa-cross-TeEGDMA) is (139°C), of the poly (80%SSNa-cross-TeEGDMA) is (141°C), confirming that T_m (SSNa) is higher than that of the T_m (TeEGDMA).the values of swelling ratios by weight in the equilibrium of hydrogels of poly (SSNa-cross-TeEGDMA) in distilled water at 25°C are proportional to the rate of SSNa incorporated in each hydrogel could be explained by the incorporation of more and more of the SSNa

Acknowledgements
I extend my sincere thanks to Tubex, Sarl Company of Oran for the helpin characterization of Differential scanning calorimetry (DSC).

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