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Research Article

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Thermal stability, Synthesis and characterization of a high capacity anionic hydrogel adsorbent aqueous solution

Bradai Masika[a], Sebti Houari[a] , Ould Kada Seghier[a], Sebba Fatima Zohra[a] and Bounaceur Bomediene [a]

[a] *Laboratoire de Chimie Physique Macromoléculaire, Faculté des Sciences Exactes et Appliquées, Université d'Oran1 Ahmed Benbella, Oran, Algeria*

ABSTRACT

Synthesis and characterization of a novel anionic hydrogels , were characterized using Fourier transform infrared spectroscopy (FTIR), their random copolymers have been investigated by thermogravimetric analysis (TGA),the Poly (SSNa sodium styrene sulfonate-cross-TeEGDMA tetraethylene glycol dimethacrylate shows a three-step process of degradation, and differential scanning calorimetry (DSC) show that the melting temperature values are proportional to the rate mole of sodium styrene sulfonate SSNa. 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, 50,60,70, 80 and 90 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, TGA

INTRODUCTION

The synthesis of copolymer gels whose swelling behaviour responds to different external stimuli provide an unique opportunity to tailoring multifunctional materials for specific applications. The polymer network may be collapsed, i.e. a dramatic diminution of the network volume [1,2] can be induced by changing stimuli such as temperature, solvent composition, pH, ionic strength and surfactants [3,4,5].

Hydrogels are essentially hydrophilic polymers capable of taking up a significant amount of water without themselves dissolving gels [6,7], initially swollen at low pH, were shown to swell extensively in a neutral pH medium. These gels contain ionizable carboxylic side chains which are responsible for the extent of swelling. A typical gel sample with 30% of methacrylic acid and 0.5% of crosslinker can absorb up to 84% of water [8]. These ionizing gels often swell To whom correspondence should be very slowly, and the mechanism is yet to be elucidated [9]. For gels, it was suggested that the rate of swelling is controlled by the rate of ion exchange as well as the boundary layer [8].

A physically cross-linked gel, which is often called a pseudo gel, has a continuous, disordered, three-dimensional network formed by associative forces capable of forming non-covalent cross-links [10]. The physically cross-linked gels are not truly homogeneous because the cluster of molecular entanglements, or hydrophobically- or ionically domains, can create heterogenicity [11]. The interactions would bring the polymer chains together, and formation of a stable structure by forming a junction zone would occur. These junction zones maintain the ordered structure

inside the gels[12]. A change in temperature, pH, or the addition of salts, etc. [13], would form, modify, or break the junction zones [14].

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

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 sulfonate and 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, different copolymers were obtained with SSNa percent molar composition of 40, 50,60, 70,80 and 90

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	65	24
	50	50	2	8		
	60	40	2	8		
	70	30	2	8		
	80	20	2	8		
	90	10	2	8		

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

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) , were performed using a LabSys evo Setaram with the heating rate of 10°C/min

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

Swelling Ratio $SR = Q = \frac{W_{hs,exp}}{W_{hd}}$ (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 hydrogels at different SSNa percent molar composition of 40% and 90%, the FTIR spectrum of poly(SSNa-cross-TeEGDMA) crosslinker exhibited the characteristic bands, Two characteristic bands of the ester TeEGDMA (C=O) and C=C aromatic 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, there is no variation in the characteristic signals but the intensity is different, the signal of (C=C) aromatic 90% SSNa is more intense than 40%SSNa, and the signal of (C=O) in 90%SSNa is less intense than the 40%SSNa

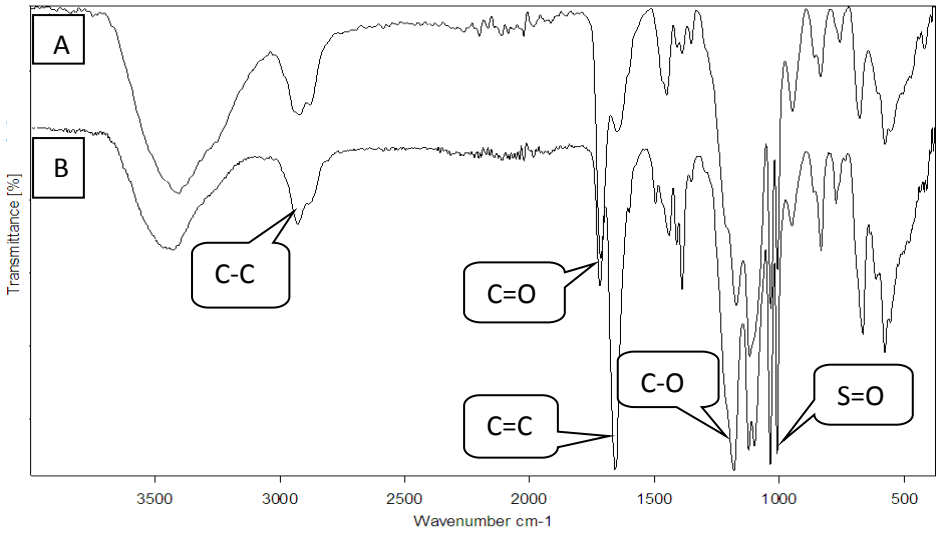


Fig.1 FTIR spectra: (A) - poly (SSNa-cross-TeEGDMA) 40 % SSNa, (B) - poly (SSNa- cross-TeEGDMA) 90 % SSNa

Fig.2 shows 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 (90%SSNa-cross-TeEGDMA) is (145°C), so T_m (90%SSNa) is higher than the T_m (40%SSNa) , Confirming that the melting temperature (Tm) SSNa is higher than the melting temperature(Tm) TeEGDMA

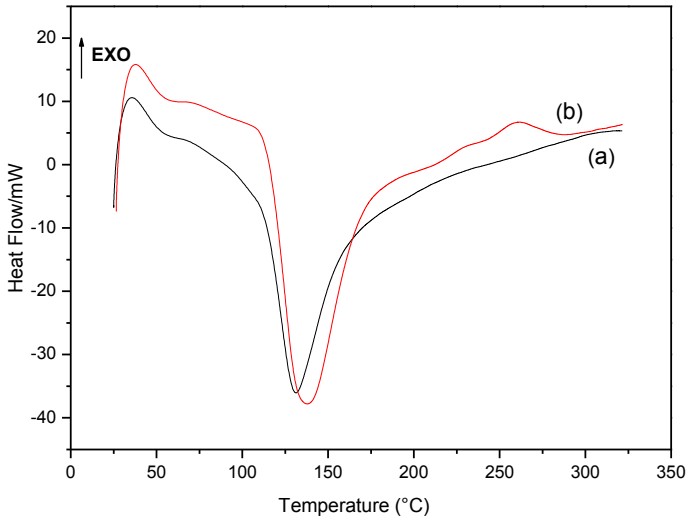


Fig.2 DSC thermograms of poly (SSNa-cross-TeEGDMA) hydrogels: (a) 40 % SSNa, (b) 90 % SSNa

Fig.3 shows three degradations, a decomposition ta 58,6 °C attributed to water, the first decomposition occurs at 320°C-380°C which is attributed to the sulfonic acid salt of sodium styrene sufonate, with the last decomposition at 450°C -490°C, the masse decrease up to 15% decomposed in sufure and carbone dioxide

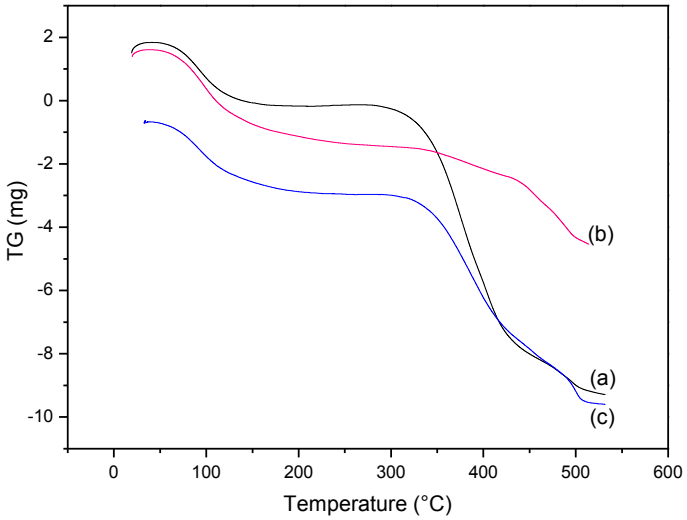
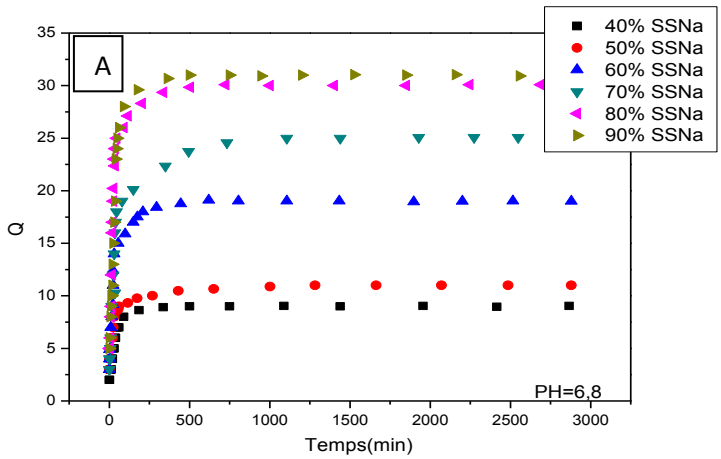


Fig.3 Thermogravimetric analysis of poly (SSNa-cross-TeEGDMA) hydrogels: (a) 40%SSNa, (c) 70%SSNa, (b) 90%SSNa

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 2,03; 6.8; 10 in distilled water, at 25° C according to Fig.4 We 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.



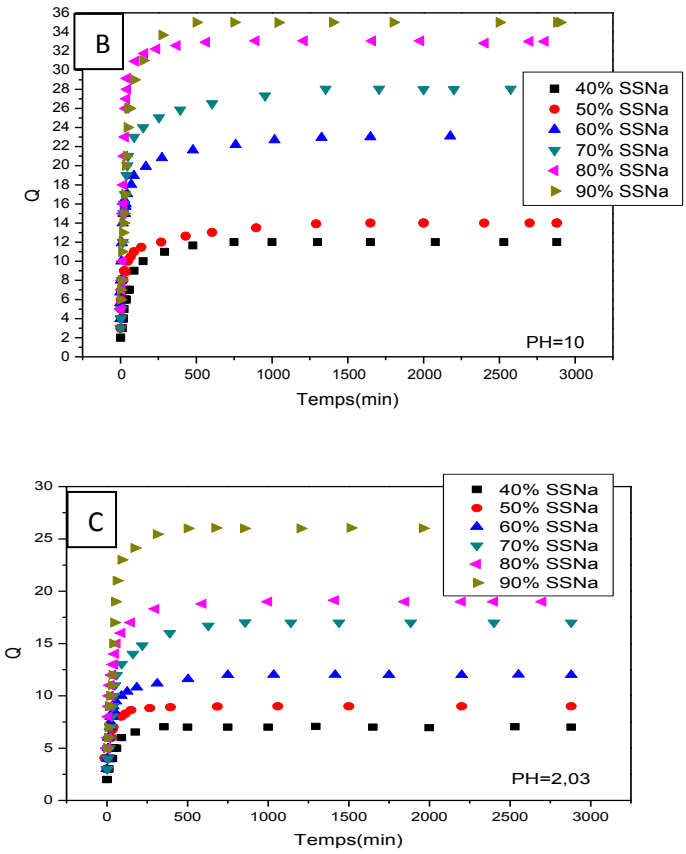


Fig.4 : Swelling ratio, as a function of time for cross-linked poly (SSNa-cross-TeEGDMA) at different pH at 25 °C: (A) pH=6,8 (B) pH=10, (C) pH=2,03

Fig.5 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.

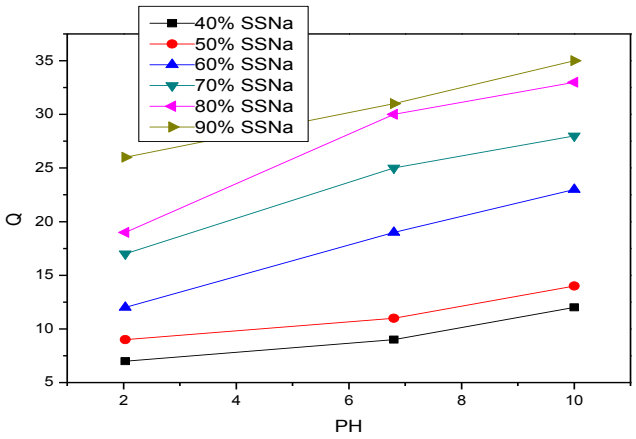


Fig.5: swelling ratios values of the poly (SSNa-cross-TeEGDMA) hydrogels as a function of pH at 25°C

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 ,60,70,80 and 90, 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 (90%SSNa-cross-TeEGDMA) is (145°C), confirming that T_m (SSNa) is higher than that of the T_m (TeEGDMA).

TGA indicate three degradations, 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

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