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Cross-Linking Structural Effect of Hydrogel Based on 2-Hydroxyethyl Methacrylate

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ABSTRACT: The study presents the possibility to prepare copolymers based on 2-hydroxyethyl methacrylate using two variants of comonomers: ethylene glycol dimethacrylate (**1**) and 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]-undecane (**2**) that act as cross-linkers for the methacrylate networks generation. The chemical structure of the copolymers—synthesized through redox polymerization process using ammonium persulfate and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine as initiator pair was confirmed by FT-IR spectroscopy. The transparent gel structures were prepared in ethylene glycol. The influence of the comonomers type upon gel copolymers formation was put into evidence by the swelling behavior of the polymeric structure. The morphological information concerning the studied polymeric compounds by SEM evidenced the differences between the hydrogels with respect to cross-linker type and its amount in the monomer feed. Also the thermal stability is a function of the type and amount of the cross-linker.

1. INTRODUCTION

Hydrogels are hydrophilic homopolymers or copolymers with three-dimensional network structures that undergo reversible swelling in water and are dependent on the environmental conditions and the hydrophilicity of the polymers in their structure. They have a wide variety of applications in medical, pharmaceutical, and related fields, for use in artificial organs, contact lenses, wound dressings, and drug delivery systems.[1−3] Because of the swelling capacity, their structure is similar to natural tissue.[4,5] Also the hydrogels found an extremely favorable field of applications in agriculture, food industry, photographic technology, and others.

The hydrogels do not dissolve in water at physiological temperature and pH, but they swell considerably in an aqueous medium[6] and demonstrate extraordinary capacity (>20%) for imbibing water into the network structure. The gels exhibiting a phase transition in response to change in external conditions such as pH, ionic strength, temperature, and electric currents are known as "stimuli-responsive" or "smart" gels.[7] Being insoluble, these three-dimensional hydrophilic networks can retain a large amount of water that not only contributes to their good blood compatibility but also maintains a certain degree of structural integrity and elasticity.[8] Thus, the cross-linked polymer networks formed by free radical polymerization of ethylene glycol methacrylates and dimethacrylates have been found attractive as hydrogel matrices, since they swell in aqueous media to a certain extent, depending on the cross-linking density, but do not dissolve.

2-Hydroxyethyl methacrylate (HEMA)-based hydrogels that are well-known and frequently studied are inert to normal biological processes, show resistance to degradation, are not absorbed by the body, and can be prepared in a variety of shapes and forms. They were first described by Wichterle et al[9]. as being obtained by HEMA polymerization in the presence of a suitable cross-linker (such as ethylene glycol dimethacrylate). The cross-linked 2-hydroxyethyl methacrylate hydrogels because of their hydrophilic character and potential biocompatibility have been of great interest to biomaterial scientists for many years.[10−14]

The presence of hydroxyl and carboxyl groups makes this polymer compatible with water, whereas the hydrophobic methyl groups and backbone impart hydrolytic stability and supports the mechanical strength of the polymer matrix. HEMA copolymers have also been investigated as carriers for enzyme and protein immobilization, as absorbents for chromatographic applications, and as scavengers for removing metal ions from solution.[15−18] HEMA can be polymerized and cross-linked easily and the properties of proper hydrogels are dependent upon their method of preparation, polymer volume fraction, degree of cross-linking, temperature, and swelling agent.

With the purpose of drug delivery, the permanent cross-linking is not a desirable property. The decomposition under specific conditions would lead to a faster drug release and an easier clearance of the polymer. The reaction is obtained by using acid-cleavable groups such as acetals, orthoesters, or anhydrides.

Poly(orthoesters) have attracted considerable interest for the controlled delivery of therapeutic agents within biodegradable matrices since they are stable at higher pH conditions, but degrade in an acidic environment. Poly(orthoesters) are susceptible to acid catalyzed hydrolysis *via* the protonation of an alkoxy oxygen followed by bond cleavage, with pentaerythritol, aliphatic acid, and the diol or mixture of diols as degradation products. As the hydrolysis of poly(orthoesters) requires an initial protonation, these polymers may be considered pH sensitive, being stable in basic conditions.[19]

As previously mentioned, cross-links are necessarily present in a hydrogel to prevent the dissolution of the hydrophilic

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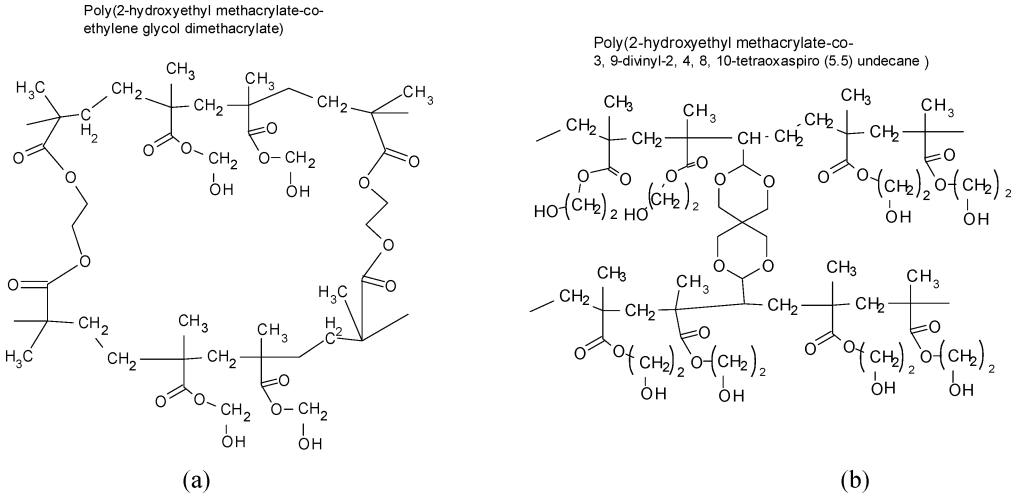
Scheme 1. Idealized Structure of the Copolymers Based on HEMA and EGDMA (a) or U (b)



polymer chains in the aqueous environment. The hydrogel characteristics can be modulated by the amount and type of cross-linker. In this study, the application results of an orthoester type named 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]-undecane) as compared to the usual classical cross-linking agent ethylene glycol dimethacrylate on the structure, water absorption, morphology of the network, and thermal stability of the HEMA-based hydrogels were investigated. These hydrogels may be used as matrices for bioactive compounds entrapment in drug delivery systems or for sensor applications.

2. EXPERIMENTAL SECTION

Materials. 2-Hydroxyethyl methacrylate (HEMA) from Aldrich (purity 97%) was purified by passing it through an inhibitor removal column (for removing hydroquinone and hydroquinone monomethyl ether). 3,9-Divinyl-2,4,8,10-tetraoxaspiro[5.5]-undecane (U) (purity 98%) and ethylene glycol dimethacrylate (EGDMA) (purity 99%) as cross-linking comonomers were purchased from Aldrich and were used without further purification.

Ammonium peroxodisulfate (APS, Merck) and *N,N,N′,N′*-tetramethylethylenediamine (TEMED, Sigma Aldrich) was used as the redox initiator pair. Ethylene glycol was used as reaction medium. Initiator and buffer solutions were freshly prepared before use, using doubly distilled water.

Hydrogel Preparation. The hydrogels based on hydroxyethyl methacrylate were prepared by simultaneous redox polymerization and cross-linking in solution of ethylene glycol. The monomers HEMA, EGDMA, or U concentration in ethylene glycol as reaction medium is 8 wt %. EGDMA or U as cross-linking agent was used at two concentrations 1 and 5 wt % with respect to HEMA content. APS and TEMED were used as initiators in 1:1 wt ratio, at concentrations of 0.6 wt %, each of them with respect to the total amount of monomers.

A typical procedure for the copolymerization can be described as follows: HEMA 1 mL and EGDMA (0.02 mL) or U (0.02 g) were dissolved in 22 mL of ethylene glycol, then APS (1.2 mL water solution of 1%) and TEMED (0.016 mL) were added into the monomer solution mixture, respectively. The solution was gently stirred for 90 s until thoroughly mixed. A 2 mL portion of each of the samples was polymerized in stationary 5 mL glass tubes (7 mm i.d.), as the polymerization reactors, for 24 h at room temperature to ensure complete polymerization.

The hydrogels obtained in the form of long cylinders were removed from the tubes and placed in 60 mL glass sample bottles filled with deionized water. Then they were washed with distilled water at room temperature for 24 h to remove any unreacted monomers and physically entrapped reaction components. The purity was verified by UV spectroscopy of the washing waters.

The prepared hydrogels were purified by dialysis and lyophilization at −50 °C and 0.040 mbar in an Alpha 2-4 LD Plus system. The dried samples were stored in a desiccator at room temperature until tested by swelling, spectroscopy, SEM, and thermal stability analyses.

Fourier Transform Infrared Spectroscopy. FTIR spectra were recorded on a Vertex Bruker spectrometer in the absorption mode ranging from 400 to 4000 cm^{-1}, at 4 cm^{-1} resolution, as an average of 64 scans, on BrK pellets.

Equilibrium Swelling Experiments. The equilibrium swelling degree Q_{eq} of the hydrogels was determined by the gravimetric method, in the buffer solutions: Na_2HPO_4/CH_3COOH for pH 5.5 and 7.4, at 22 and 37 °C, by applying the eq 1:

$$Q_{eq}\ (\%) = \frac{W_{eq} - W_o}{W_o} 100 \quad (1)$$

where W_{eq} is the weight of the swollen gel when thermodynamic equilibrium was reached and W_o is the weight of the dried gel at time 0.

The kinetic of solvent diffusion (swelling) into the polymeric matrices was determined by applying the eq 2:

$$F_t = \frac{W_t}{W_{eq}} = k_{sw} t^{n_{sw}} \quad (2)$$

where F_t is the fractional uptake at time t; k_{sw} is the swelling constant characteristic of the system; W_t, W_{eq} denote the amount of buffer solution absorbed by polymeric network at the predetermined t time and at equilibrium; n_{sw} is the power law diffusion exponent, which takes into account the swelling mechanism. This equation is applied to initial states of swelling (swelling degree <60%), when linearity is observed in log F_t vs log t plot.

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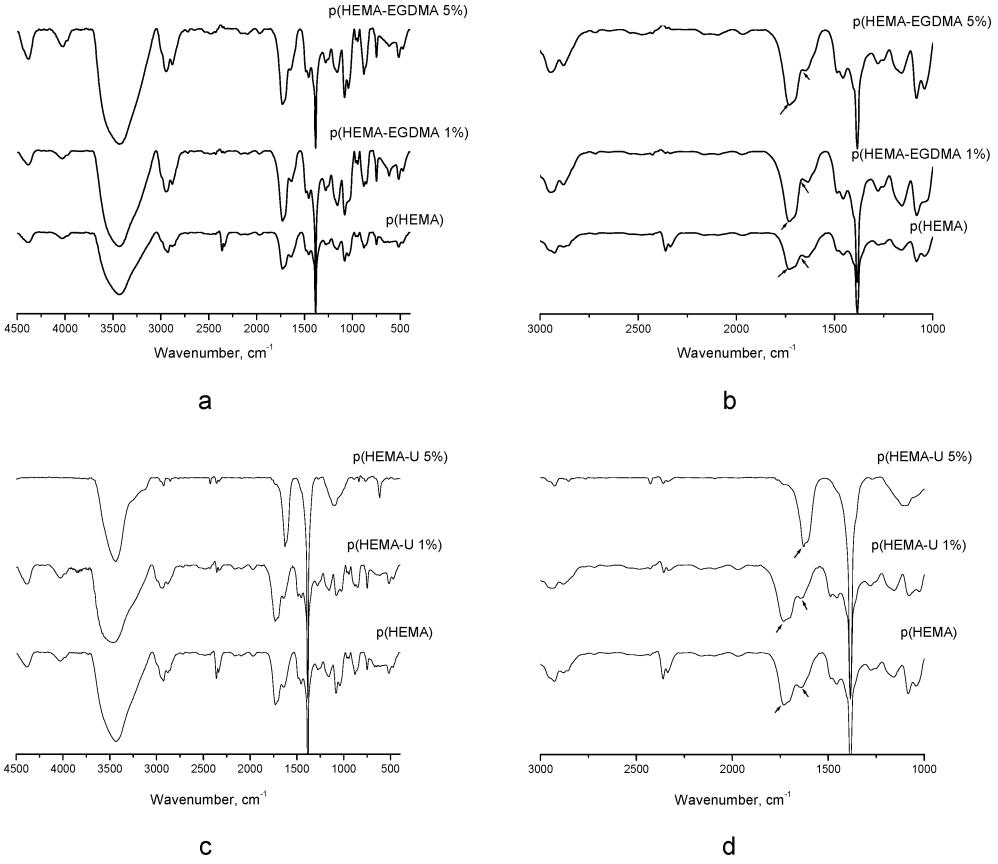

Figure 1. FTIR spectra for the hydrogel samples based on HEMA cross-linked with EGDMA ranging from 4500 to 500 cm^{-1} (a) and 3000 to 1000 cm^{-1} (b). Cross-linked with U ranging from 4500 to 500 cm^{-1} (c) and 3000 to 1000 cm^{-1} (d).

The obtained swelling (diffusion) data were extrapolated by using the Korsmeyer–Peppas mathematical model[20] through eq 3 to know the mechanism of the buffer diffusion and implicit for drug release from these formulations:

$$\frac{M_t}{M_\infty} = kt^n \tag{3}$$

where M_t/M_∞ represents the fractional uptake at time t, k is a constant incorporating characteristic of the macromolecular network system and the solvent, and n is the diffusion exponent, used to characterize the transport mechanism. Also, eq 3 is valid for the first 60% of the fractional uptake.

According to equations 2 and 3, Case I (Fickian diffusion) and Case II transport are defined by $n_{sw}(n)$ values of 0.5 and 1, respectively. Fickian diffusional release occurs by the usual molecular diffusion of the drug due to a chemical potential gradient. Case II relaxational release is the drug transport mechanism associated with stresses and state-transition in hydrophilic glassy polymers which swell in water or biological fluids. Anomalous transport behavior (nonFickian diffusion) is intermediate between Fickian and Case II, which is reflected on a value $0.5 < n_{sw}(n) < 1$. Also, $n > 1$ indicates a special Case II transport mechanism.[21−25]

Scanning Electron Microscopy. SEM microphotographs were obtained by using Quanta 200 with EDAX elemental analysis system. The samples were cross-sectioned, and the morphological structure was investigated in an accelerating voltage of 10.60 kV and high vacuum.

Thermal Analysis. The thermal behavior of the samples was evidenced by using a STA 449F1 Jupiter model (Netzsch-Germany) system at a heating rate of 10 °C/min. The experiments under nonisothermal conditions were followed in nitrogen atmosphere with a 50 mL/min flow rate. Samples of 7.5−8 mg of polymeric mass were heated from 30 to 580 °C.

3. RESULTS AND DISCUSSION

The polymerization techniques based on addition, such as free radical chain growth cross-linking copolymerization of HEMA and EGDMA or U as it is illustrated in Scheme 1, are usually used for the preparation of polymers, which are subsequently converted into hydrogels, by moderate cross-linking of the polymeric chains in fairly concentrated solutions.

It was evidenced in the literature that the incorporation of spiroacetal groups in the polymer structures improves the solubility and the adhesive properties.[26] More than that, the polymers which include these moieties are stable in the basic pH domain, hydrolyze at very slow rates at the physiological pH of 7.4, and become progressively more labile as the pH is lowered in the acidic range. Also, these kinds of comonomers induce good oxidative and thermal stability, are good fiber formers, and the prepared films present good flexibility and tensile strength.[27] These characteristics are attributed to the properties inherent into the spiroacetal ring: stiffness, which is higher than cycloaliphatic rings but lower than aromatic rings; interactions on ether oxygen such as hydrogen bonds or coordinate bonds with other functional groups; and bulkiness. Different researchers described the developments in the synthesis of alternating poly(ester ether)s from spiro-orthoesters, which were also considered biodegradable and useful for biomedical applications.[28,29]

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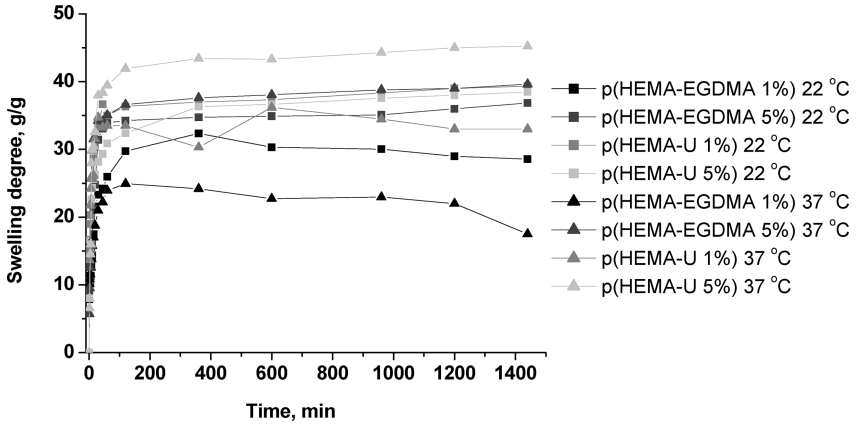

Figure 2. Swelling behavior of the network structures HEMA-EGDMA (U) in buffer solution pH 5.5.

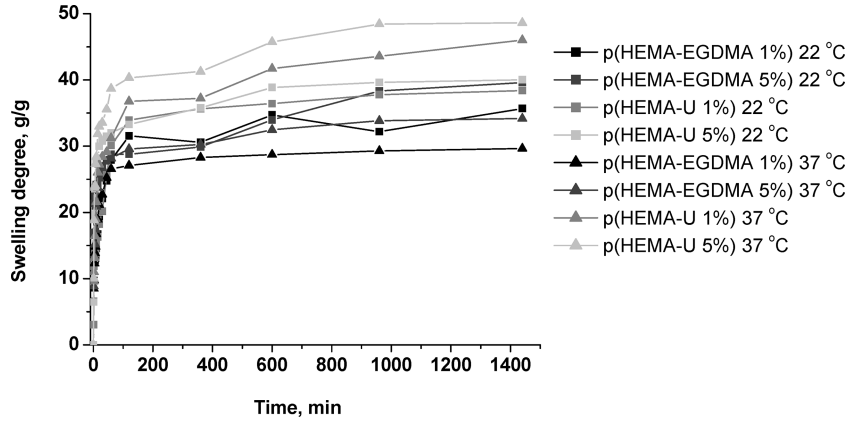

Figure 3. Swelling behavior of the network structures HEMA-EGDMA (U) in buffer solution pH 7.4.

Figure 1 panels a and c present the FTIR spectra ranging from 4500 to 400 cm^{-1}, for the samples of hydrogels based on HEMA cross-linked with EGDMA (1 and 5 wt % in the monomer phase) and U (1 and 5% in the monomer phase). First, from the FTIR spectrum the presence of the main comonomer HEMA in the hydrogel structure is confirmed by the hydroxyl and strong carbonyl bands appearing at 3500 cm^{-1} (O−H stretching) and 1730 cm^{-1} (C═O stretching), respectively. Also, there are evidently bands at 1172 cm^{-1} (O−C−C stretching), 2951 cm^{-1} (asymmetric stretching of methylene group), and 1454 cm^{-1} (O−H bending).

In spectra presented in Figure 1b ranging from 3000 to 1000 cm^{-1}, the peaks assigned to ν(C═C) stretching (near 1635 cm^{-1}) were observed only as very weak shoulders, especially for the sample p(HEMA-EGDMA) (95/5). This may be assumed as a measure for the conversion of vinyl bonds with the consumption during the polymerization. The intensity of the peak at 1730 cm^{-1} assigned to ν(C═O) stretching is much higher than the band ascribed to ν(C═C). It means that most of the double bonds C═C were opened and replaced by single bonds. Thus, double bonds C═O remained not opened and did not participate in network formation while there were appropriate conditions to create the gel.

In spectra ranging from 3000 to 1000 cm^{-1} of p(HEMA-U) networks presented in Figure 1d, the same observations may be underlined, with respect to ν(C═C) and ν(C═O) stretching. The difference is that ν(C═C) stretching near 1635 cm^{-1} for the p(HEMA-U) (95/5) is not visible in this spectrum.

The spiroacetal moieties inclusion is also confirmed by the new strong bands in the region of 1000−1200 cm^{-1} (due to ether C−O−C stretching and C−H in plane bending) and at ∼1715 cm^{-1} (due to C═O stretching of conjugated ether). The supplementary absorption at 2887 cm^{-1} is attributed to the $-CH-CH_2$ symmetric stretching from U. The carbonyl peak of EGDMA appears at 1730 cm^{-1} and the lactone carbonyl at 1764 cm^{-1}.

Second, in a general view, the spectra of HEMA-based gels are almost qualitatively similar, but with the exception of a peak at about 1573 cm^{-1} which can be assigned to the stretching of the COO− group.[30] As it can be seen for both cross-linking comonomer EGDMA and U, the intensity of this peak increases comparative to P(HEMA) as a function of cross-linking density, respectively, the increase of cross-linker concentration from 1 to 5% in the monomer phase. The aspect is more evidenced for the sample hydrogel with EGDMA.

In the chemically cross-linked hydrogel structures the swelling process in a solvent may be controlled and markedly influenced by the introduction of an appropriate amount of a second monomer with hydrophobic character, as cross-linker. In the swelling behavior of the hydrogels, the percentage of swelling increases with time but after a while constant percentage swelling is observed. This value of swelling represents the equilibrium swelling.

Rydzewski[31] mentioned that the equilibrium in the polymer network−solvent system is a result of the interaction between the competing thermodynamic forces which try to establish a

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Table 1. Equilibrium Swelling Degree Q_{eq} for the Network Structures

	1% EGDMA		5% EGDMA		1% U		5% U	
T, °C	pH 7.4	pH 5.5	pH 7.4	pH 5.5	pH 7.4	pH 5.5	pH 7.4	pH 5.5
22	35.68	28.57	39.64	36.40	38.40	39.33	40.02	38
37	29.65	17.53	34.22	39.38	46.01	33.01	47.96	45

balance: osmotic pressure of free ions in the gel, molecular interaction of solvent and polymer molecules that might either work for or against swelling, network elasticity, Debye−Huckel interaction of ions.

This balance is disturbed by temperature modification or by the change in the solution ionic strength. The increase in entropy of the chains when they are able to move apart, having an increased amount of solvent to move in favors the swelling, while the decrease in entropy when the chains becomes more stretched, works against swelling.

The effect of the cross-linker type (EGDMA or U) and degree of cross-linking on the swelling was investigated by varying their concentration in the feed mixture of the polymerization recipe. In this study we have chosen two values for the cross-linker amount: 1 and 5% from the monomer mixture. For all the samples, the impact of polymer network with the buffer solution led to a rapid swelling in the first minutes (Figures 2 and 3) with a maximum swelling achieved after about 360 min.

From the swelling degree−time presentation for the network structures p(HEMA-EGDMA (U)) with 1 and 5% cross-linker (Figures 2 and 3) as a function of temperature (22 and 37 ° C) some remarks are resulted. The hydrogels show similar swelling profiles with approximate linear swelling kinetics during the first 40 min, then nonlinear kinetics were observed during 40−360 min, and finally plateau values were obtained up to 1400 min. P(HEMA-U) hydrogels have slightly increased values in connection with its before-specified sensibility at acidic pH.[19] This behavior manifests at 5.5 pH (Figure 2), at 22 and 37 ° C, when after the first 40 min, the network p(HEMA-U) has a greater swelling degree comparared to that of poly(HEMA-EGDMA). Also, the increase in the amount of cross-linker from 1 to 5% induces a raise in the swelling capacity in the buffer solution.

At pH 7.4 for the both temperatures of testing (Figures 3) the rising of the swelling degree with an increase in the percent of cross-linker U or EGDMA is observed. Also, the network p(HEMA-U) has a greater swelling degree compared to that of poly(HEMA-EGDMA).

Table 1 presents the equilibrium swelling degrees Q_{eq} determined at 22 and 37 °C, for pH 5.5 and 7.4, taking into account the potential applicability for the sensitive materials at the environmental parameters (temperature and pH).

From the data presented in Table 1 it is observed that the equilibrium swelling degree Q_{eq} determined in buffer solution increases as the extent of cross-linking grows, and its values demonstrate the temperature and pH sensitivity of the hydrogel samples. Also, the spiroacetal moieties in U induce higher swelling degree than the hydrogel with 5% EGDMA. Usually the swelling degree is expected to decrease with increasing cross-linking. Surprisingly, in an inherent contradiction the water absorption is more significant for the relatively high degree of cross-linking (with 5% of EGDMA or U) than for the hydrogel with a low degree of cross-linking (with 1% of EDGMA or U). These results reflect the existence of two absorption mechanisms in the HEMA-based hydrogel: absorption within the P(HEMA) walls through interaction with the hydrophilic polymer and absorption within the porous structure through capillary action. The literature[32,33] also describes three different diffusion mechanisms for the transport of water through cross-linked pHEMA gels, which depend on the cross-linker content: a pore flow mechanism for low cross-linking content, a water−matrix interaction mechanism for higher cross-linking content, and an intermediate mechanism at intermediate cross-linker concentration. At the same time, the synthesis of hydrogels that combine the water absorption through hydrophilic interactions and through capillary action can be used to synthesize better water-absorbent materials for different biotechnological applications, such as drug delivery or tissue engineering.

Because of the important applications of hydrogels in biomedicine, pharmaceutical, environmental, and agricultural engineering, the understanding of the water diffusion mechanisms has gained great attention in the study of swellable polymeric systems. At the contact of a hydrogel with water, this diffuses into the hydrogel structure, by migration into the preexisting or dynamically formed spaces between hydrogel chains. Thus, it results in a larger separation distance between the macromolecular chains.

The Korsmeyer and Peppas equation (eq 3)[20] was used to analyze the data from the swelling study: the diffusion exponent (n) in the evaluation of swelling kinetics was obtained by fitting the fractional change mass (M_t/M_∞) and for setting $W_t/W_{eq} \leq 0.6$. The results are recorded in Table 2, where the R^2 is the correlation factor (regression value).

Table 2. The n and k Parameters for the Hydrogel Samples

sample	n	k	R^2
p(HEMA-EGDMA) (99/1)	0.63	0.19	0.99
p(HEMA-EGDMA) (95/5)	0.83	0.18	0.85
p(HEMA-U) (99/1)	0.96	0.37	0.95
p(HEMA-U) (95/5)	0.56	0.44	0.97

For all the hydrogel samples, the diffusion exponent (n) that determines the type of diffusion was found to be over 0.5, as can be seen in Table 2. Hence the diffusion of buffer solutions into the hydrogels is generally non-Fickian in character. For n value up to 0.5 the rate of polymer relaxation and the solvent diffusion are about the same order of magnitude, and as the solvent diffuses into the hydrogel, the rearrangement of the chains does not occur immediately.[34,35]

The correlation coefficient R^2 chosen to define the approximation accuracy of an individual model of diffusion and having higher values (Table 2) shows the diffusion (release) data fit better with the diffusion kinetics established by Korsmeyer and Peppas model.

Figure 4 presents the SEM images of the P(HEMA)-based hydrogel (a), cross-linked with 5% EGDMA (b), and 5% U (c). In detail are the SEM micrographs for hydrogels cross-linked with 1% EGDMA (b) and 1% U (c).

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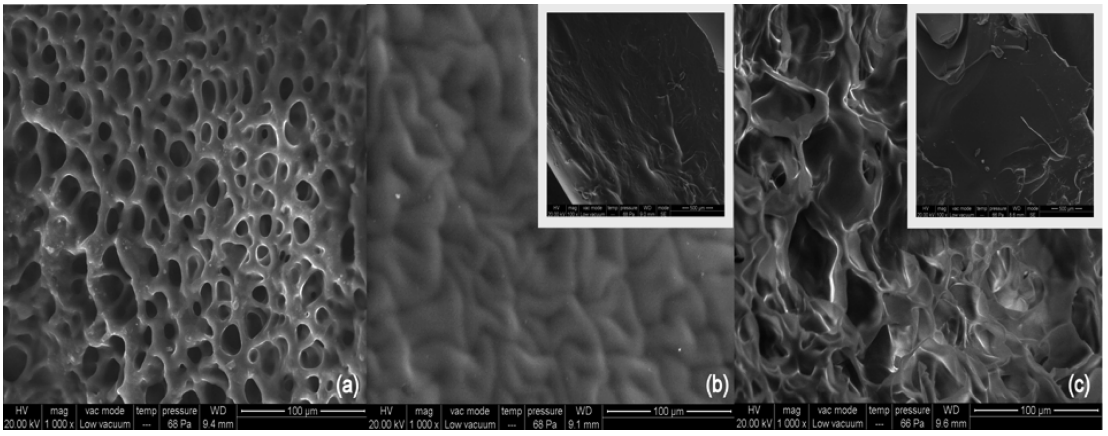

Figure 4. SEM micrographs of the P(HEMA) based hydrogel (a), cross-linked with 5%EGDMA (b), and cross-linked with 5% U (c). In detail are the SEM micrographs for hydrogels cross-linked with 1% EGDMA (b) and 1% U (c). Magnification: 1000×.

As it is observed in the SEM images, the hydrogels porous structure consists of distorted interconnected spherical voids separated by walls. These walls themselves have an unusual nanoscale porous structure with voids from the evacuated droplets of the organic phase (ethylene glycol).

The SEM images reflect two main conclusions: first, the cross-linked hydrogel with 5% EGDMA and 5% U have structures that are reminiscent of a typical P(HEMA) hydrogel. Second, the morphology of the hydrogels with higher degree of cross-linking (samples with 5% of EDGMA or U) is a porous structure completely different to that of the pHEMA hydrogels with EGDMA 1% or U 1%.

These hydrogels are able also to swell with a greater amount of water, as reflected by the Q_{eq} values in the swelling experiment (Table 1). The more porous structures and high surface area enhance capillary action and yield the large amount of water absorbed.

Thermal analysis (TA) is a well-known technique enabling qualitative and quantitative information about the effects of various heat treatments on polymer materials. It provids complementary and supplementary characterization information that can be used to select the materials for certain end-use applications, predict the performance, estimate the lifetime, and improve the quality. Together with biocompatibility and/or biodegradability the thermal properties might allow for the materials' use on several of the proposed biomedical applications, thus avoiding the problem of unexpected and unpredictable physical changes that can happen when they are applied in/on the human body.

Figure 5 panels a and b depict the results for the mass loss and decomposition behavior for the polymeric networks cross-linked with EGDMA and U. Table 3 presents the main characteristic temperatures in the decomposition process of the dried hydrogel samples.

As it can be observed, the thermal decomposition of p(HEMA) hydrogels cross-linked with 1 and 5% EGDMA and with 1% U happens in two stages, while p(HEMA-U 5%) has three stages and pHEMA only one stage of decomposition.

As expected, the presence of the cross-linking comonomer 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]-undecane (U) in the network structures positively affects the thermal stability because of the spiroacetal ring that controls the thermal properties. Thus, in stage II of decomposition, T_i for p(HEMA-U 5%) registered an increase of 10 °C as compared to that for p(HEMA-EGDMA 5%) and of 6 °C as compared to that for

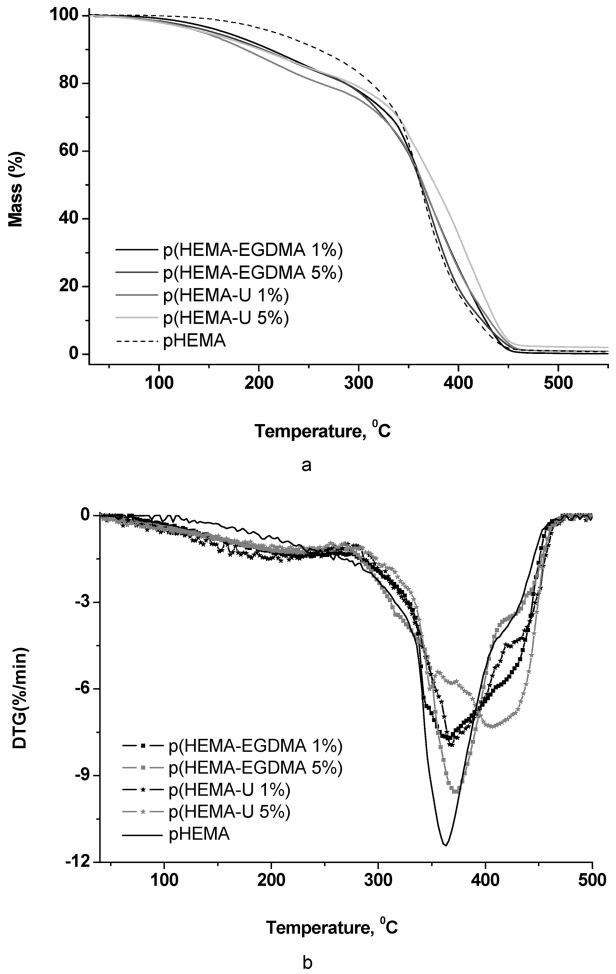

Figure 5. Thermogravimetric analysis of the polymeric networks cross-linked with EGDMA and U: mass loss (a) and DTG data (b).

p(HEMA-U 1%), while T_{50} recorded for 50% of weight losses is 12 °C higher than that of the network cross-linked with EGDMA 5% and 10 °C higher than that of the network cross-linked with U 1%. Also the increase of the cross-linker comonomer content from 1 to 5% caused an increase in the residual mass at the end of the process.

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Table 3. The Main Characteristic Temperatures (T, °C) and the Residual Mass (%) in the Thermal Decomposition Process of the Hydrogel Samples[a]

	stage I			stage II			stage III				
sample	T_i	T_{max}	T_f	T_i	T_{max}	T_f	T_i	T_{max}	T_f	T_{50}	residual mass
pHEMA				190	362	425; 431sh				362	0.5
p(HEMA- EGDMA 1%)	107	228	268	275; 344sh	365	478				365	0.1
p(HEMA- EGDMA 5%)	108	209	269	276	368; 423sh	480				365	0.76
p(HEMA -U 1%)	122	233	260	280	372; 440sh	485				367	0.83
p(HEMA -U 5%)	127	213	262	286	365	366	368	407	483	377	1.94

[a]Abbreviations: T_i, T_{max}, T_f, onset, maximum, and final decomposition temperature; T_{50}, temperature for the decomposition reaction at weight loss of 50%; sh, shoulder.

CONCLUSIONS

The study analyzes the structural effects induced by the cross-linker type in the synthesis of 2-hydroxyethyl methacrylate-based hydrogels by simultaneous redox polymerization and cross-linking with one of the two comonomers: ethylene glycol dimethacrylate and 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]-undecane. The hydrogels were prepared in solution of ethylene glycol, by using ammonium peroxodisulfate, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine as the redox initiator pair.

The influence of the cross-linker type is estimated, and the hydrogels are characterized from the viewpoint of chemical structure, swelling behavior, morphology, and thermal stability, by FTIR spectroscopy, equilibrium swelling degree Q_{eq} determination, SEM, and TGA. The success of synthesis was confirmed in terms of spectroscopic and morphological aspects with observation of porous network formation. Upon the results of swelling testing, the new network macromolecular structures show a dependency on cross-linker type and pH of swelling medium.

The thermal stability results of the samples showed that the presence of comonomer 3,9-divinyl-2,4,8,10-tetraoxaspiro [5.5]-undecane improves the thermal stability of polymeric system.

The study underlines the possibility to optimize the network macromolecular structure using a properly cross-linker choice, taking into account the potential application in biomedical and sensors domain.

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Notes

The authors declare no competing financial interest.

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