

Polymer Hydrogels of 2-Hydroxyethyl Acrylate and Acrylic Acid Obtained by Frontal Polymerization

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ABSTRACT: In this work, we report on the synthesis and characterization of homopolymers and copolymers of acrylic acid and 2-hydroxyethyl acrylate prepared by the use of the frontal polymerization (FP) technique. Tetraethyleneglycoldiacrylate was used as a crosslinker and benzoyl peroxide as an initiator. The maximum temperatures reached by the front were in the range between 214 °C and 296 °C. Besides, front velocities ranged between 3.9 and 10.8 cm/min, the latter being one of the highest values reported so far in the FP literature. Differential scanning calorimetry was used to estimate the conversion degree, which was always comprised between 90% and 96%, and to determine the glass transition temperatures, which were found

to be dependent on the composition, with values ranging from 13 °C to 168 °C. Moreover, the obtained materials were allowed to swell in aqueous solutions at various pH. The samples exhibit a moderate increase of the swelling ratio percentage (SR%) at pH \approx 5–6, and a sudden and larger SR% increase at pH \approx 12–13 depending on the composition, thus indicating the obtainment of pH-responsive polymer hydrogels. © 2012 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 1515–1520, 2012

KEYWORDS: acrylic polymers; frontal polymerization; hydrogels; radical polymerization; stimuli-sensitive polymers

INTRODUCTION Hydrogels are three-dimensional macromolecular networks made up of polymers soluble in aqueous solutions, crosslinked to form water insoluble hydrogels, which possess the ability to absorb large amounts of water and swell.

Some of them are stimulus responsive; they undergo relatively large and sharp volume change in response to environmental changes. These polymer systems recognize a stimulus as a signal, value its magnitude, and then change their chain conformation in direct response.¹ Stimuli can be classified as either chemical or physical: the first, such as pH, ionic factors, and chemical agents, change the interactions between polymer chains or between polymer chains and solvents at the molecular level; physical stimuli, such as temperature, electric or magnetic fields, and mechanical stress, affect the level of various energy sources. Because of these characteristics, stimuli-responsive hydrogels have found a number of applications in biomedical and pharmaceutical fields, where they are used for soft contact lens,² artificial tendons and tissues,³ reconstruction of cartilage,^{4,5} controlled drug delivery,^{6–9} and release systems.¹⁰

Particularly, pH-responsive hydrogels are materials that vary their volume with pH changes: they consist of ionizable groups that can accept or donate protons in response to a pH variation.

Polymers with weak ionizable groups show a degree of ionization, which dramatically changes at a specific pH named pK_a . The rapid variation in the net charge on the pendant groups causes an alteration of the hydrodynamic volume of the polymer chains. The transition from collapsed to swollen state is due to the osmotic pressure exerted by mobile counterions, which neutralize the network charges.¹¹

There are two main kinds of pH responsive materials: (i) weak polyacids, which have COOH or SO₃H as acid groups (these materials are generally swollen at high pH and deswell in acid conditions); (ii) the second type, which is characterized by an opposite behavior, are weak polybases bearing basic pendants, like NH₂, and so forth.

The most reported pH-responsive polyacids are poly(acrylic acid)^{12–15} and poly(methacrylic acid),¹⁶ which release protons at neutral and high pH. On the other hand, typical poly-

TABLE 1 Compositions, Conversions, and T_g Values of the Polymer Samples Prepared in This Work

Sample Codes	χ_{AAc}	T_g ($^{\circ}C$)	Conversion (%)
FP1	0	13	96
FP2	0.25	71	92
FP3	0.50	155	90
FP4	0.75	168	96
FP5	1	135	96

bases are poly(4-vinylpyridine),¹⁷ poly(*N,N*-dimethylaminoethylmethacrylate),¹⁸ and poly(*N,N*-diethylaminoethylmethacrylate),^{19,20} which are protonated at high pH and positively ionized at neutral and low pH.

Poly(2-hydroxyethyl acrylate), pHEA, is a common example of polymer whose hydrogels have found a lot of applications in pharmaceutical and biomedical field as hydrophilic sponges,²¹ contact lens,²² and drug delivery systems.²³ It is a biocompatible material and has a high hydrophilicity: its presence assures aqueous compatibility and the ability to form hydrogen bonds with water and with polymers having carboxylic groups.²⁴ Therefore, 2-hydroxyethyl acrylate (HEA) has found application as hydrophilic component in many thermoresponsive copolymers with a number of monomers including butyl acrylate²² and 2-methoxyethyl acrylate.²⁵

In 2007, Chen et al.²⁶ obtained pHEA by frontal polymerization (FP). In most cases, FP is ignited by locally heating the upper layer of a monomer mixture until the polymerization starts. If the reaction is exothermal enough, the result is the formation of a self-propagating and self-sustaining polymerization front due to the fast conversion of monomer into polymer.

FP was initially proposed by Chechilo et al.²⁷ and then thoroughly studied by Pojman et al.^{28–34} and Chen et al.^{35–38}

Our group used FP to prepare polyurethanes,^{39,40} interpenetrating polymer networks,⁴¹ unsaturated polyester/styrene resins,⁴² poly(diurethane diacrylates),⁴³ epoxy-amine systems,^{44–47} poly(ethylene glycol) diacrylate copolymers containing azobenzene groups,⁴⁸ epoxy resins in the presence of BX_3 -amine complex as curing agents,⁴⁹ hybrid organic–inorganic epoxy resins,⁵⁰ and synthesized phosphonium-based ionic liquids as radical initiators for FP.⁵¹ Moreover, we also applied FP to stone consolidation,^{52,53} to prepare photoactive poly(2-phenoxyethyl acrylate) copolymers containing azobenzene units,⁵⁴ and to the obtainment of stimuli responsive hydrogels,^{55–58} controlled drug release systems,⁵⁹ and polymer nanocomposites.^{60–63}

In this work, we report the obtainment of homopolymer and copolymer hydrogels of acrylic acid (AAc) and HEA synthesized by FP, in the presence of tetraethyleneglycoldiacrylate (TEGDA) as crosslinker and benzoyl peroxide (BPO) as initiator. The effects exerted by all the components on the front temperature and its velocity as well as on the thermal characteristics of the obtained materials are reported. Moreover,

the swelling behavior of the corresponding hydrogels was studied as a function of pH.

RESULTS AND DISCUSSION

To investigate the influences exerted by all the components on the synthetic and morphological characteristics, we have varied the ratio between AAc and HEA, keeping constant all the other parameters such as the total molar amount of the two monomers, the amounts of initiator and of crosslinker. All samples were obtained with high conversion, always included between 90% and 96% (Table 1).

In Figure 1, we report the values of the front temperatures (T_{max}) and velocities (V_f) as functions of the molar fraction of acrylic acid (χ_{AAc}). It can be noticed that the front temperatures exhibit a trend characterized by a maximum: they range from 278 $^{\circ}C$ for the homopolymer of HEA (FP1) to 214 $^{\circ}C$ for the pAAc (FP5), with a maximum value of 296 $^{\circ}C$ corresponding to the copolymer having $\chi_{AAc} = 0.50$. As far as the front velocities are concerned, they increase from 4.0 to 10.8 cm/min for the samples having a molar fraction of AAc included between 0 and 0.75 (FP1–4), whereas pAAc (FP5) shows a front velocity of 3.9 cm/min. Moreover, all the samples show high front velocities with the maximum value (10.8 cm/min) recorded for the sample having $\chi_{AAc} = 0.75$ (FP4). It should be also highlighted that 10.8 cm/min is one of the highest V_f values reported so far in the FP literature.^{58,64}

As reported in the “Experimental” section, the swelling studies on the copolymer hydrogels at different pH were done by immersing any sample into buffer solutions at various pH (1–13), until they achieved the equilibrium.

As can be seen in Figure 2, the swelling ratio (SR%) of all the samples remains almost constant along all the pH range included between 1 and 5 (SR% always around 100–200%). Instead, due to the deprotonation reaction and the subsequent electrostatic repulsion among COO^- groups, from pH 6

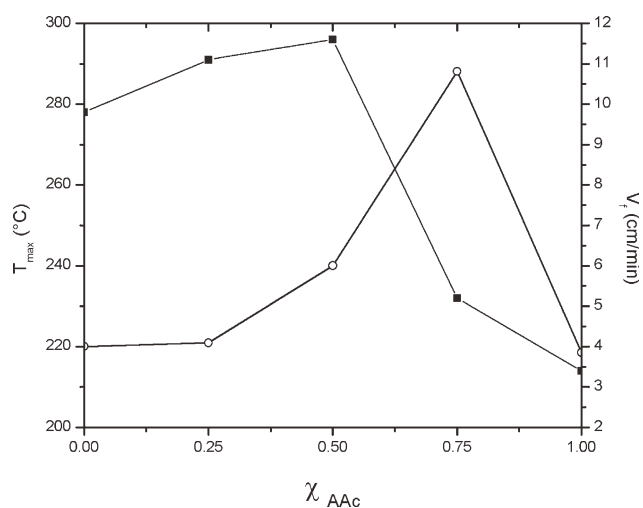


FIGURE 1 T_{max} (■) and V_f (○) as functions of the molar fraction of AAc in the poly(acrylic acid-*co*-2-hydroxyethyl acrylate) copolymers.

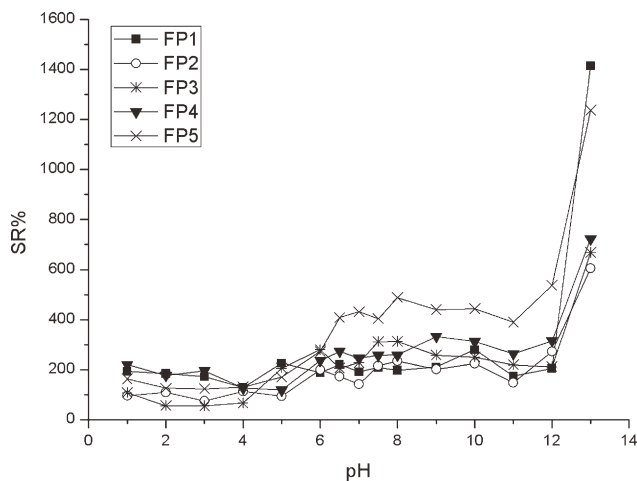


FIGURE 2 SR% as function of pH for samples having a different monomer ratio.

to 8, the swelling ratio of the hydrogels starts to increase up to values that are higher for the hydrogels containing larger amounts of AAc. For instance, at pH 8, the SR% goes from 230%, for the hydrogel with $\chi_{AAc} = 0.25$ (sample FP2), to 260%, for the sample with a molar fraction of AAc equal to 0.75 (FP4).

Moreover, at pH around 12–13, apart from the very large SR% reached by the AAc and HEA homopolymers (1200% and 1400%, respectively), the swelling ratio of the copolymers reached the maximum values of 600–720% due to alkoxylate group formation.

To check whether such a large increase might be due to the occurrence of partial hydrolysis (mainly because of the presence of TEGDA ester groups), all samples allowed to swell at the highest pH values (12–13) were successively equilibrated at pH = 7 (not shown). In all cases, the SR% was almost equal ($\pm 10\%$) to that of the same sample previously swollen at this latter pH, thus indicating that no significant hydrolysis occurred.

The above results suggest classifying these polymer hydrogels among those exhibiting a pH responsive behavior, with two critical pH values: one at about 6 and the second at about 11–13, depending on their composition (Fig. 2).

In Figure 3, the glass transition temperatures of all samples after swelling at pH 2 and pH 12 and successively dried are reported together with those of the samples which did not undergo any swelling treatment.

First of all, it can be seen that the T_g recorded for the non-treated samples tend to increase with the amount of AAc from 13 °C for the homopolymer of HEA up to a maximum at 168 °C for the sample having $\chi_{AAc} = 0.75$, and then to decrease again to 135 °C for the AAc homopolymer. As one may expect, this behavior is qualitatively similar to that of the series comprising the samples, which were swollen at pH 2 before drying. Indeed, because these copolymers are characterized by the presence of acid protons, they were not influenced by the treatment at low pH. However, the T_g val-

ues of these materials are generally lower than those of the non-treated materials probably because of the presence of residual water (around 3%, as determined in thermogravimetric analysis (TGA) experiments, not shown), which might have some plasticizing effect.

By considering the series of samples which were dried after swelling at pH 12, it can be noticed that the glass transition temperature monotonically increases with the molar fraction of AAc from 64 °C to 161 °C, thus clearly confirming that the presence of an increasing amount of carboxylate groups enhance the interactions among the macromolecular chains, thus reducing the general mobility.

The morphological characteristics of the obtained hydrogels were investigated by scanning electron microscopy (SEM) analysis (Fig. 4). By comparing the 1:1 AAc-HEA copolymer with the corresponding homopolymers, all swollen at pH 2 (respectively: b_2 , a_2 and c_2 images in Figure 4), it can be noticed that both the HEA homopolymer and the copolymer are characterized by a hydrogel structure with relatively large pores, whereas the AAc homopolymer has pores having much smaller dimensions. This finding is in agreement with the relatively larger SR% found for this sample at this pH value. Indeed, as we reported in our previous work on thermoresponsive polymer hydrogels, the smaller is the pore dimension, the larger is SR%.⁴²

Quite surprising, the discussed pore structure is not held at pH 12. Namely, in these conditions, all hydrogels exhibit a much denser and more compact aspect. However, again, the lack of relatively large pores results in an increase of the swelling ratio.

EXPERIMENTAL

Materials

HEA (FW = 116.12, $d = 1.011$ g/mL), AAc (FW = 72.06, $d = 1.050$ g/mL), tetraethylenglycoldiacrylate (TEGDA, FW =

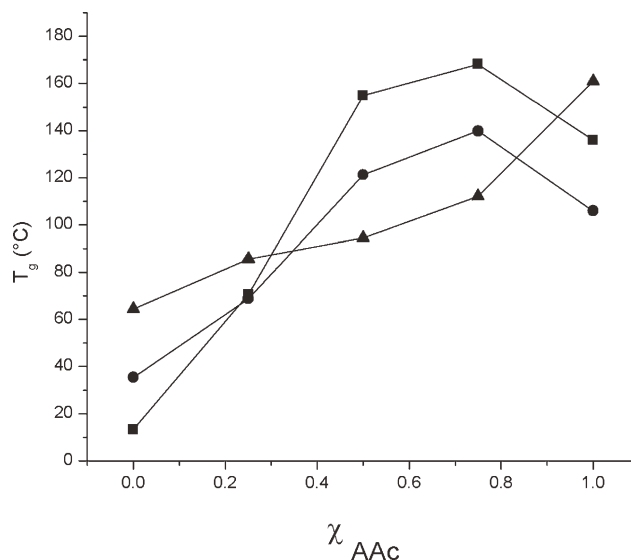


FIGURE 3 T_g of the non-treated samples (■), dried samples after swelling at pH 2 (●), and dried samples after swelling at pH 12 (▲) as functions of the molar fraction of AAc.

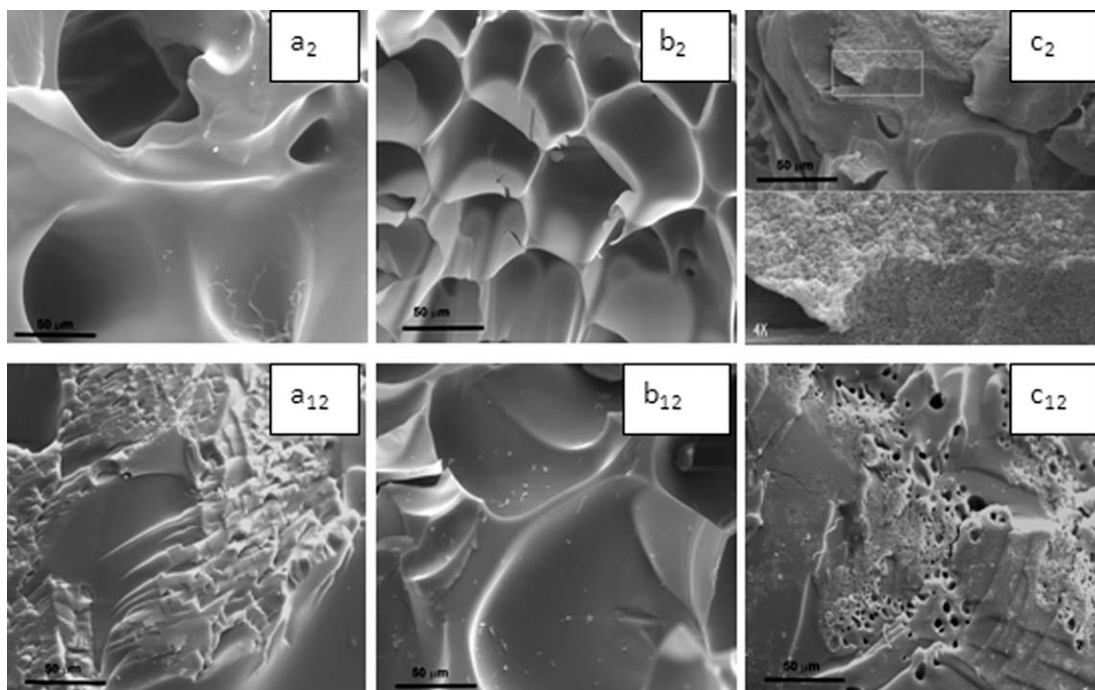


FIGURE 4 SEM micrographs of: (a) pHEA (sample FP1), (b) poly(AAc-co-HEA) (sample FP2), and (c) pAAc (sample FP5), swollen at pH 2 (a_2 , b_2 , c_2) and swollen at pH 12 (a_{12} , b_{12} , c_{12}).

302.33 g/mol, $d = 1.11$ g/mL), BPO (FW = 242.23), potassium hydrogen phthalate (FW = 204.22 g/mol), sodium dihydrogen phosphate (FW = 137.99 g/mol), potassium nitrate (FW = 101.103 g/mol), and sodium tetraborate decahydrate (FW = 381.37 g/mol) were purchased from Sigma Aldrich and used as received without any further purification.

Synthesis of Homopolymers and Copolymers of Acrylic Acid and 2-Hydroxyethyl Acrylate

The polymer samples were synthesized keeping constant the total molar amount of the two monomers (6.96×10^{-2} mol), the amounts of crosslinker and of initiator (5 mol % and 1 mol % referred to the total amount of the two monomers, respectively). HEA and/or AAc were introduced in a common glass tube (i.d. = 1.5 cm, length = 16 cm) and were sonicated in an ultrasonic bath for 1 min. Then, TEGDA and BPO were added, and the solution was again sonicated for other 2 min to have a homogeneous mixture.

A thermocouple junction was located at about 1 cm from the bottom of the tube and connected to a digital temperature recorder. Front started by heating the external wall of the tube in correspondence of the upper surface of the monomer mixture until the formation of the front became evident. The position of the front (easily visible through the glass wall of test tubes) against time was measured. Front temperature measurements were performed by using a K-type thermocouple connected to a digital thermometer (Delta Ohm 9416) used for temperature reading and recording (sampling rate: 1 Hz). For all samples, front temperature (T_{\max} , ± 10 °C) and front velocity (V_f , ± 0.5 cm/min) were measured. Each sample was synthesized in triplicate, and all the experimental data were averaged.

Characterization

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analyses were performed using a DSC Q100 Waters TA Instruments calorimeter, with a TA Universal Analysis 2000 software. Dried samples were subjected to two DSC scans from -80 to 300 °C, with a scan rate of 20 °C/min: the first scan was performed to determine monomer conversion, and the second one was to establish the glass transition temperature (T_g).

SEM Analyses

SEM analyses of the hydrogels were executed using a Zeiss EVO LS10.

Swelling Experiments

To study the swelling behavior at different pH values, the hydrogels were immersed in buffer solutions of the desired pH (1–13) and containing KNO_3 at the constant concentration of 0.1 mol/L, necessary to have a sufficiently high ionic strength. Buffer solutions were prepared by using various combinations of potassium hydrogen phthalate, sodium dihydrogen phosphate, sodium tetraborate decahydrate, NaOH, and HCl.

When the equilibrium was attained, the samples were weighed and their SR% at different pH was calculated applying the following equation:

$$\text{SR}(\%) = \frac{M_s - M_d}{M_d} \times 100$$

where M_s and M_d are the hydrogel masses in the swollen and in the dried state, respectively.

CONCLUSIONS

In this work, homopolymers and copolymers of AAC and HEA were successfully prepared by FP. As expected, it was found that both T_{max} and V_f are dependent on the ratio between the monomers. It is noteworthy that, when the AAC molar fraction was 0.75, V_f reaches 10.8 cm/min, which is one of the highest values reported so far in the FP literature.

The obtained materials were allowed to swell in aqueous solutions at different pH values. The resulting hydrogels were found to exhibit a pH-responsive behavior at two critical values located at $pH \approx 6$ and ≈ 11 –13, respectively, depending on the composition.

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