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Stimuli Responsive Hydrogels Prepared by Frontal Polymerization

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Frontal polymerization was used as an alternative method for the easy and fast preparation of polymer hydrogels prepared from *N*-isopropylacrylamide (NIPAAm) and *N*-vinylcaprolactam (VCL), the latter being less toxic and less expensive than NIPAAm. All samples were characterized in terms of their swelling behavior, and their thermal properties were investigated by DSC. It was found that VCL influences both pore size and shape distribution. Moreover, also the swelling ratio of the materials is dependent on the monomer ratio. Eventually, by a comparison with analogous samples prepared by the classical polymerization technique, it was found that the two methods give rise to hydrogels characterized by very diverse swelling capability; furthermore, swelling reversibility was also found to be different when temperature is allowed to cyclically vary between values that are below and above the lower critical solution temperature. In particular, samples prepared by frontal polymerization are characterized by lower swelling ratio and larger swelling recovery capability.

Introduction

Hydrogels are a class of polymeric materials, generally cross-linked, that swell in water or in biological fluids without dissolving.[1] They are organized as three-dimensional networks of polymeric chains, physically and chemically bounded, and partially solvated by water molecules. This structure allows hydrogels to swell but not dissolve in the surrounding fluid. These materials have great interest in particular in biomedical applications, thanks to their three-dimensional structure, high water content, good biocompatibility, and mechanical properties. Common biomedical uses of hydrogels include soft contact lenses made of silicone or polyacrylamide and medical electrodes made of polyethylene oxide.[2]

Some hydrogels belong to the class of "smart materials", which are able to change their size and shape in response to environmental stimuli, such as temperature, pH, electric or magnetic field, ionic force, pressure, light, and so on.[3]

Thermally responsive polymers and their use in biomedical applications are widely investigated nowadays. They exhibit a critical solution temperature at which they show a variation of shape, rigidity, water content, or hydrophobicity. In particular, they may exhibit a lower critical solution temperature (LCST, below which the hydrogel swells) and a higher critical solution temperature (HCST, above which the hydrogel swells).[4]

Poly(*N*-isopropylacrylamide) (PNIPAAm) is the most extensively studied thermoresponsive polymer.[5] Its LCST located at 32−33 °C makes PNIPAAm a very interesting material, in particular, for controlled release applications. PNIPAAm LCST is independent of molecular weight and concentration[6] but can be changed upon shifting the hydrophilic/hydrophobic balance, as a result of proper copolymerization.[7]

However, biocompatibility of PNIPAAm and other acrylamide related polymers may be a problem. For this reason, several attempts of replacing NIPAAM in stimuli-responsive polymer materials having biological interest have been performed. On this respect, various copolymers were synthesized; among them, we remind here those with ethylene glycol,[8] 2-alkyl-2-oxazoline and 2-hydroxyethyl methacrylate,[9] propylacrylic acid,[10] ethylene imine,[11,12] lysine and glutamic acid,[13] and 2-carboxyisopropylacrylamide.[14]

Poly(*N*-vinylcaprolactam) (PVCL) belongs to the same family of polyvinylpyrrolidone (PVP), a polymer widely used in pharmaceutical[15−18] and cosmetic applications.[19]

However, recent findings have indicated PVP as causing time- and dose-dependent toxicity thus suggesting the investigation of other materials.[20]

PVCL is not only nonionic, water-soluble, and thermally sensitive, but also biocompatible. It contains hydrophilic carboxylic and amide groups that are directly connected to the hydrophobic carbon−carbon backbone chain so that its hydrolysis will not produce small amide compounds that are often bad for biomedical applications.[21]

Thermal response of PVCL is similar to that of PNIPAAm; namely, PVCL also collapses when the temperature is about 32 °C,[22] but its phase transition is not sharp and occurs in the temperature range from about 30 to 45 °C, depending on its molecular weight.[22] However, the use of VCL can be considered particularly advantageous in that it is cheaper and less cytotoxic than NIPAAm.[23]

In 2001, Washington and Steinbock[24] prepared PNIPAAm gels by frontal polymerization (FP), a technique that allows the conversion of a monomer into a polymer by formation and consequent propagation of a reaction front. This is a localized zone able to self-sustain and propagate through the monomeric mixture. To create the front, an external energy source is applied only in the first instant. After, it is no longer needed in that the

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exothermicity of the polymerization reaction is sufficient for the front to self-sustain.

This technique has led to the formation of polymers having properties that are similar, or even better, than those obtained by the classical polymerization routes. Moreover, FP has some additional advantages: (1) Short reaction times: a typical FP run takes only a few minutes, while classical polymerizations techniques often need hours or days. (2) Low energy consumption: it is a consequence of the fact that the external energy source is applied only in the first instant, while in classical polymerization techniques it is necessary for all the experiment duration. (3) Easy protocols (see Experimental Section).

Since the first pioneering work performed by Chechilo and Enikolopyan[25] an even increasing number of monomers have been polymerized by this technique. In detail, Pojman et al. polymerized epoxy resins,[26] ionic liquid,[27] and acrylic monomers;[28−31] the design and synthesis of glycidyl ethers that undergo frontal polymerization[32,33] were studied by Crivello et al.; Chen et al. frontally polymerized 2-hydroxyethyl acrylate[34] and *N*-methylolacrylamide;[35] moreover, they studied the obtainment of epoxy resin/polyurethane networks,[36] polyurethane−nanosilica hybrid nanocomposites,[37] and PVP.[38] Our group obtained poly(dicyclopentadiene),[39] polyurethanes,[40,41] interpenetrating polymer networks,[42] unsaturated polyester/styrene resins,[43] and poly(diurethane diacrylates).[44] We also applied FP to the consolidation of porous materials;[45,46] moreover, we prepared polymer-based nanocomposites with montmorillonite[47] and polyhedral oligomeric silsesquioxanes,[48] and we have synthesized a new class of ionic liquid based initiators to be used in both classic and frontal radical polymerization.[49] Recently, we have proposed FP as a new method for developing drug controlled release systems based on polyacrylamide[50] and for the preparation of poly(*N*,*N*-dimethylacrylamide) hydrogels.[51]

The present work aimed at the preparation of new thermosensitive polymer materials having potential biological interest and exhibiting an LCST close to that of PNIPAAm; the reduction of the amount of NIPAAm in these materials to decrease their toxicity and cost; the use of FP to obtain stimuli-responsive hydrogels in times that are shorter, and by using protocols that are easier than those typically used and reported so far. Namely, NIPAAm homopolymer and NIPAAm/VCL copolymer hydrogels were frontally obtained, characterized and compared in terms of their swelling behavior, thermal properties, and morphology.

Experimental Section

N-Isopropylacrylamide (FW = 113.16, mp = 60−63 °C), *N*-vinylcaprolactam (FW = 139.19, mp = 35−38 °C), triethylenglycoldimethacrylate (TGDMA, FW = 286.32), and dimethylsulfoxide (DMSO, FW = 78.13, bp = 189 °C, d = 1.101 g/mL) were purchased by Sigma Aldrich and used as received. Aliquat persulphate (APS) was synthesized by us according to the method reported in the literature.[52]

Characterization. Thermal characterization of all samples was performed by DSC by using a Q100 Waters TA Instruments calorimeter, with a TA Universal Analysis 2000 software. Two heating ramps, from −100 to 250 °C, with a heating rate of 10 °C/min, were carried out on dry samples: the first scan was performed to eliminate possible residual solvent; the second was done to determine glass transition temperatures (T_g).

After freeze-drying, hydrogel morphology was studied by scanning electron microscopy (FESEM, Supra 25 Zeiss). Prior to examination, all samples were fractured in liquid nitrogen, and the fractured surface was coated with gold.

Table 1. Characteristics of A Series (TGDMA: 2.5 mol %; APS: 0.5 mol %)

sample code	NIPAAm molar fraction	T_g (°C)
F1	1	142
C1		142
F2	0.75	146
C2		146
F3	0.5	153
C3		150
F4	0.25	163
C4		159

To determine their swelling ratio (SR%) in water, hydrogels were heated from 17 to 38 °C, in an ISCO GTR 90 thermostatic bath, by increasing temperature at a rate of 1 °C/day.

SR% was calculated by applying the following equation:

$$SR\% = \frac{M_s - M_d}{M_d} \times 100 \quad (1)$$

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

To study the swelling reversibility, samples were heated and cooled from 25 to 37 °C and vice versa, four times, to compare the SR% after each of the swelling/deswelling cycles (each one was 12 h long).

Reported swelling data are the average of three single measurements. Reproducibility was always within 10%.

Hydrogel Synthesis. A common glass test tube (i.d. = 1.5 cm, length = 16 cm) was filled with a NIPAAm/DMSO mixture (Table 1) and sonicated in an ultrasound bath at 40 °C for several minutes; the appropriated amount of VCL was added and the mixture was sonicated again. Finally, the cross-linker and the initiator were added. After complete homogenization, the mixture was divided in two parts: one was polymerized by classical polymerization (CP) in an oil bath at 80 °C for 1 h; the other was frontally polymerized. In all cases, yields were quantitative.

After polymerization, all samples were washed in water for several days to remove the residual unreacted monomer and DMSO and allowed them to swell.

Two hydrogel series were prepared: the A series was obtained by varying the molar fraction of the two monomers, from NIPAAm homopolymer to a copolymer containing 75 mol % of VCL (Table 1), keeping constant the total molar amounts of the two monomers (7.2×10^{-2} mol), the amounts of cross-linker (2.5 mol % referred to the total amount of monomers), initiator (0.5 mol % referred to the total amount of monomers), and DMSO (2.5 mL).

The B series collects all samples obtained by polymerizing equal molar amounts of the two monomers (total monomer amount was 7.2×10^{-2} mol) and in which the cross-linker was allowed to vary from 2.5 to 10 mol %. DMSO was always equal to 2.5 mL.

Frontal Polymerization Runs. Test tubes were kept open during polymerization occurrence. 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.

For all samples, front temperature (T_{max}, ±10 °C) and front velocity (V_f, ±0.1 cm/min) were measured. Front temperature measurements were performed by using a K-type thermocouple connected to a digital thermometer (Delta Ohm 9416, ±1.0 °C, Figure 1) used for temperature reading and recording (sampling rate: 1 Hz).

Results and Discussion

T_{max} and V_f, the main parameters generally taken into account in FP studies, were monitored. Figure 1 shows a typical

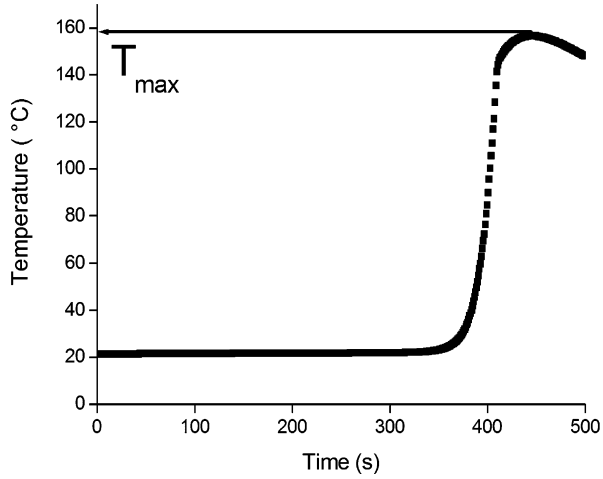

Figure 1. Temperature profile of a typical FP experiment (sample F1).

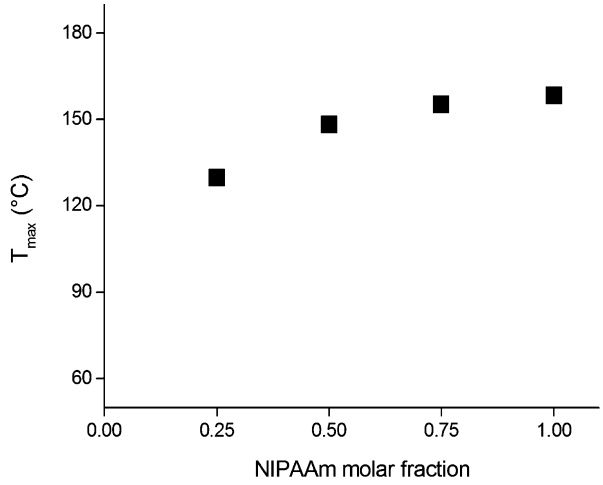

Figure 2. T_{max} as a function of the molar fraction of NIPAAm for A series.

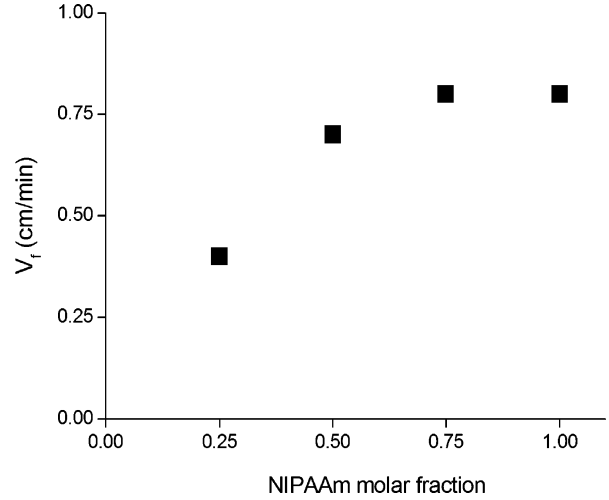

Figure 3. V_f as a function of the molar fraction of NIPAAm for A series.

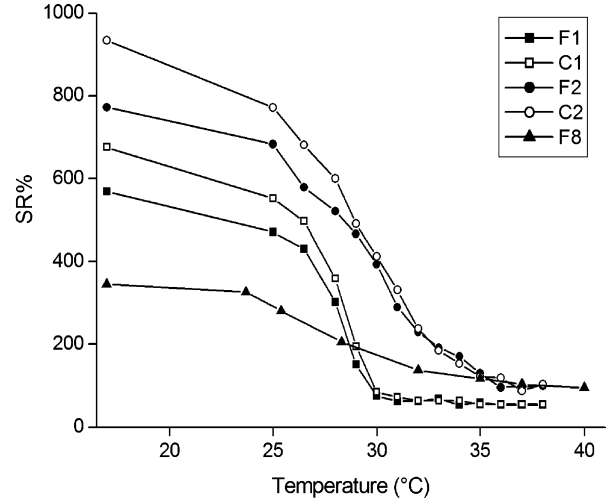

Figure 4. SR% as a function of temperature for some selected samples of the A series. PVCL SR% trend is also reported (sample F8).

temperature profile of an FP experiment, with the indication of T_{max}. As can be seen, the temperature value recorded by the thermocouple remains constant until front crosses its junction: this indicates that *pure* FP is occurring, that is, no other polymerization modes are happening simultaneously. All FP runs here discussed were characterized by this behavior.

Two sets of experiments were carried out. In the A series, the ratio between NIPAAm and VCL was allowed to vary by keeping constant all the other parameters, including total monomer concentration, amount of initiator, cross-linker, and DMSO. This latter solvent was necessary to dissolve NIPAAm. It was found that no FP was observed when 100 mol % VCL was used. However, it should be underlined that PVCL homopolymer was frontally obtained if DMSO was not present; therefore, it cannot be comprised in this series.

Figures 2 and 3, respectively, show the T_{max} and V_f values recorded during FP experiments in the A series. By considering these figures, it comes out that both parameters increase as NIPAAm concentration raises. Indeed, T_{max} goes from 130 °C for copolymer containing 25% NIPAAm to 160 °C for PNIPAAm homopolymer, while V_f goes from 0.4 to 0.8 cm/min.

An analogous study was performed for the B series, which, as stated above, collects all copolymers synthesized from equimolar amounts of NIPAAm and VCL. In this series, the amount of cross-linker (TGDMA) was allowed to vary between 2.5 and 10 mol %. In this case, it was found that both V_f and T_{max} remain constant as the amount of cross-linker varied (T_{max} = 147 °C, V_f = 0.7 cm/min).

To study and compare the SR% of all samples, they were swollen and equilibrated in water at various temperatures; the resulting trends for the A series were determined by applying eq 1. For the sake of clarity, only some selected, representative data are reported in Figure 4.

In particular, an SR% as high as 930% was found (sample C2, 17 °C); in addition, PNIPAAM homopolymer shows a sharp transition in the range from 28 to 31 °C, in correspondence of its LCST. By contrast, all copolymers exhibit a much broader transition range and continue to deswell until 38−39 °C, thus clearly indicating that VCL influences the LCST and the swelling behavior of the copolymers.

In general, VCL-containing copolymers swell more than PNIPAAm; in particular, at 17 °C copolymers are characterized by SR% equal to 930 (sample C2) and 670 (sample F3, not displayed), while that of the homopolymer is 570 (sample F1). Moreover, even if PVCL homopolymer (sample F8), which was not obtained in DMSO, exhibits a relatively low SR% (340, at 17 °C), its presence enhances the swelling ratio of the copolymers, especially if its content does not exceed 25 mol %

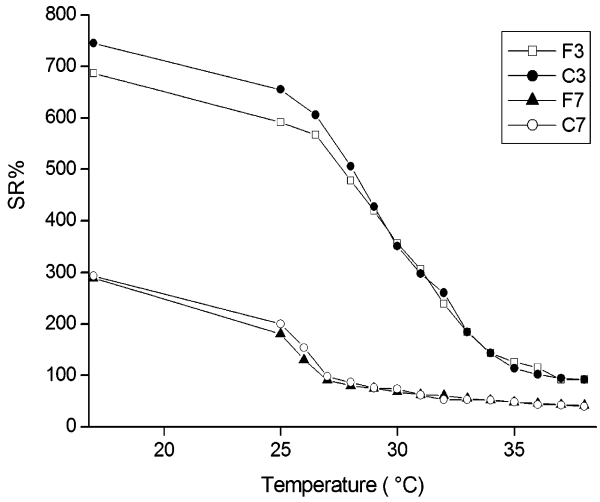

Figure 5. SR% as a function of temperature of samples containing two different amounts of cross-linker (F3, C3 = 2.5 mol % TDGMA; F7, C7 = 10 mol % TGDMA).

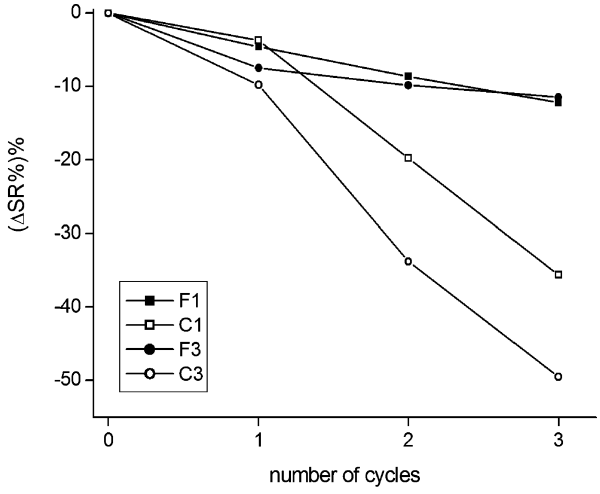

Figure 6. Percentage of SR% loss of some representative hydrogels subjected to cyclic temperature variations from 25 to 37 °C. Displayed data refer to 25 °C.

(sample F2). Indeed, larger amounts of it results in further SR% decrease. Furthermore, it should be noticed that CP samples swell more than the corresponding FP ones.

Figure 5 shows SR% as a function of temperature for some representative samples the B series, thus evidencing the influence of the cross-linker amount on the swelling properties. In samples containing a large amount of TGDMA (10 mol %, samples F7 and C7), swelling is severely limited: for example, at 17 °C, SR% is about 200. At variance, when TGDMA is 2.5 mol % (sample F3 and C3), SR% is about 900.

To evaluate the swelling/deswelling recovery capability, several cooling/heating cycles between 25 and 37 °C, that is, below and above LCST, were carried out. Figure 6 shows the percentage of SR% loss for two representative FP-obtained samples compared with that of the two corresponding materials synthesized by the classical method. After three cooling cycles, the maximum swelling capability of all CP samples was only about 50−60% of the initial value. At variance, it is noteworthy that, after the same number of cycles, FP samples lost only about 10% of their starting SR%, thus demonstrating once more that this technique allows the obtainment of materials characterized by unique features.

However, it should be highlighted that as in all previous works on frontal polymerization, also in the present case, the actual

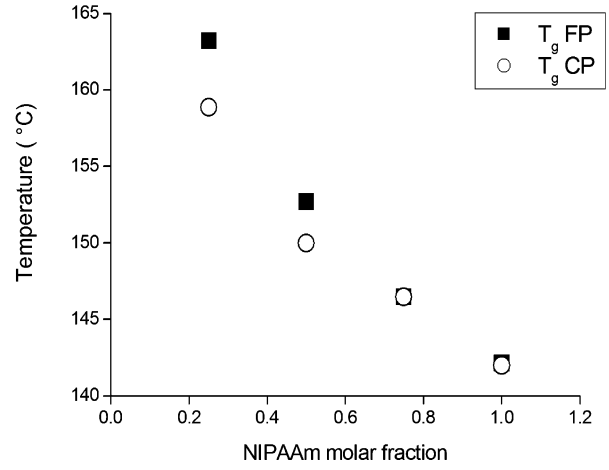

Figure 7. T_g values of A series (FP and CP samples).

Table 2. Characteristics of B Series ([NIPAAm]/[VCL] = 1/1; APS 0.5 mol %)

sample code	TGDMA (mol %)	T_g (°C)
F3	2.5	153
C3		150
F5	5.0	153
C5		153
F6	7.5	159
C6		152
F7	10	154
C7		155

reason for the FP peculiar behavior, if compared with the traditional synthetic routes, is not really understood. Namely, even if this technique is characterized by factors like higher reaction temperature, with probable increased importance of kinetics factors and thermal shock due to the sudden increase of temperature as front reaches a given monomer portion, no real evidence of significant differences at molecular scale have been found so far. For such a reason, an explanation of the above findings cannot be given; on the other hand, this fact justifies any further research effort on this technique.

DSC Analysis. As described in the experimental, T_g was obtained by analyzing the second DSC scan (Table 1).

Even if PNIPAAm and PVCL homopolymers have almost the same T_g (144 and 147 °C, respectively[53,54]), their copolymers are characterized by glass transition temperatures that monotonically increase up to 163 and 159 °C for the FP and CP samples containing 25% of NIPAAm, respectively.

Moreover, Figure 7 clearly shows that FP samples exhibit a T_g that is never below that of the corresponding classical materials.

As displayed in Table 2, all samples belonging to the B series exhibit a T_g in the range between 150 and 159 °C. No characteristic trend was found as the amount of TGDMA increases. Moreover, at variance to what found in the previous series, there is an apparent correlation with the polymerization mode.

SEM Analysis. To investigate their morphology, pore structure, and distribution, the synthesized samples were examined in detail by SEM.

Figure 8 shows SEM micrographs of the PNIPAAm homopolymer (Figure 8A) and of the copolymer containing 75% of VCL (Figure 8B), prepared by frontal polymerization. Although both of the above samples show a typical hydrogel sponge structure, some differences can be noticed. Indeed, while the homopolymer is characterized by a homogeneous porous

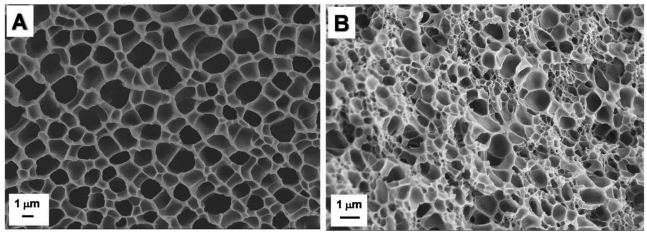

Figure 8. SEM micrographs of (A) PNIPAAm homopolymer (F1); (B) copolymer containing 75% of VCL (F4).

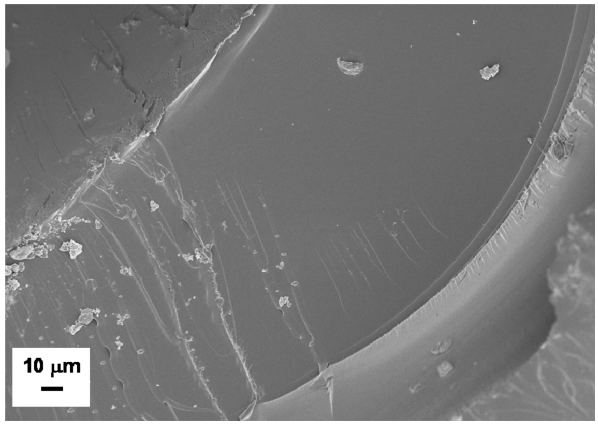

Figure 9. SEM micrographs of an FP sample containing 10 mol % of TGDMA (sample F7).

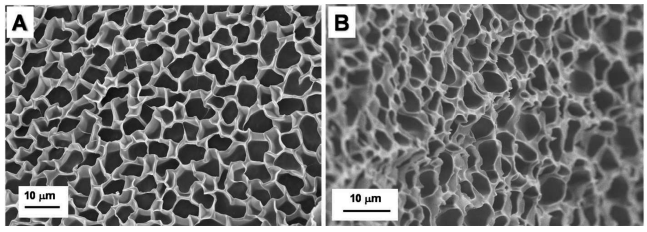

Figure 10. SEM micrographs of FP and batch copolymers prepared from equimolar amounts of VCL and NIPAAm (A: sample F3; B: sample C3).

structure with pore diameter between about 1 and 2 μm, the copolymer shows a broader pore size distribution, having pores from about 0.1 to 1.5 μm. By taking into account SEM observations, it is possible to conclude that polymer morphology influences the material swelling behavior, as the above differences in the porous structure lead to a variation of SR%.

Similar results have been obtained also by analyzing the other synthesized copolymers prepared from different VCL/NIPAAm ratios.

As shown in Figure 9, also cross-linker concentration deeply affects the polymer morphology and its swelling behavior. Indeed, by increasing the amount of TGDMA, the porosity visible by SEM decreases until it completely disappears when the concentration of cross-linker in the reaction mixture reaches 10 mol % (Figure 9); moreover, because TGDMA affects the porosity also at molecular level, SR% becomes smaller as well.

As far as the influence of the polymerization technique on the material features is concerned, Figure 10 compares SEM micrographs of two samples prepared by FP and CP starting from the same reaction composition. Analyzing the above micrographs, it comes out that both polymer surfaces turn out to be characterized by very similar pore distribution, thus demonstrating the small effect of the synthetic approach on the morphology.

Conclusions

In this work, a number of cross-linked polymer hydrogels made from NIPAAm and/or VCL were successfully prepared by both FP and CP.

It should be underlined that, for specific applications in which a sharp transition phase is not required, amounts of VCL can be used instead of NIPAAm. This fact represents a great advantage in terms of biocompatibility, which is now increased because copolymer hydrolysis would produce a smaller amount of toxic low molecular weight amide compounds. Moreover, VCL is less toxic and less expensive than NIPAAm.

About the comparison between materials prepared by FP and CP, the first ones were found to be characterized by a much larger reversibility of SR% if temperature is allowed to cyclically oscillate above and below LCST. Furthermore, materials obtained by FP are prepared in times that are much shorter and with protocols that are much easier than those used for their classically obtained analogues.

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