Thermoresponsive Super Water Absorbent Hydrogels Prepared by Frontal Polymerization of *N*-Isopropyl Acrylamide and 3-Sulfopropyl Acrylate Potassium Salt

SERGIO SCOGNAMILLO,[1] VALERIA ALZARI,[1] DANIELE NUVOLI,[1] JAVIER ILLESCAS,[2] SALVATORE MARCEDDU,[3] ALBERTO MARIANI[1]

[1]Dipartimento di Chimica, Università degli Studi di Sassari, and local INSTM Unit, Via Vienna 2, 07100 Sassari, Italy

[2]Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, C.P. 04510, México D.F.

[3]Istituto di Scienze delle Produzioni Alimentari – Consiglio Nazionale delle Ricerche (ISPA-CNR), Li Punti – Reg. Baldinca, Traversa La Crucca, Sassari 07100, Italy

Received 5 November 2010; accepted 4 December 2010
DOI: 10.1002/pola.24542
Published online 10 January 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Super water absorbent polymer hydrogels were synthesized by frontal polymerization. These materials were obtained by copolymerizing *N*-isopropyl acrylamide (NIPAAm) and 3-sulfopropyl acrylate potassium salt (SPAK) in the presence of *N,N*-methylene-bis-acrylamide as a crosslinker. It was found that their swelling behavior in water can be easily tuned by using either the appropriate monomer ratio or the amount of the crosslinker used. Namely, the swelling ratio was found to range from about 1000% for the NIPAAm homopolymer in the presence of 5.0 mol % of crosslinker, up to 35,000% for the sample containing 87.5 mol % of SPAK and 1.0 mol % of crosslinker. The affinity toward water was also confirmed by contact angle analysis. Moreover, the obtained hydrogels exhibit a thermoresponsive behavior, with a lower critical solution temperature of about 28–30 °C. This value is close to that of poly(NIPAAm) but with a swelling capability that dramatically increases as the amount of SPAK increases. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1228–1234, 2011

KEYWORDS: frontal polymerization; hydrogels; radical polymerization; swelling; thermoresponsive super water absorbent hydrogels

INTRODUCTION Polymer hydrogels are three-dimensional flexible networks[1–3] able to absorb and retain aqueous solutions without dissolving.[3] Some hydrogels can change their own volume in response to external stimuli[4–17] such as solvents,[7] temperature,[8–11] pH,[9,12,13] ionic concentration,[14] electric field,[15,16] light irradiation,[17] and salt concentration.[8]

Because of their high-water content, most hydrogels are very useful for the preparation of biomaterials in contact with biological fluids,[18,19] and for several applications in both pharmaceutical and biomedical fields.[20,21] Hydrogels can also find large applications where mechanical properties are not decisive, such as soft contact lenses,[22,23] electrophoresis,[24] drug delivery,[8,12,25–27] and tissue engineering.[15,28]

Numerous investigations have been reported on thermoresponsive hydrogels,[29] especially those based on poly(*N*-isopropylacrylamide),[30] which show a lower critical solution temperature (LCST) that is close to the physiological temperature (i.e., 31–32 °C).

Hydrogels with the ability to absorb water up to a few hundred times of their own weight are often referred as super water absorbent polymers.[31] They are characterized by a highly hydrophilic network,[32–34] able to maintain high-water amounts inside the structure.[31,35,36] This kind of hydrogels has found wide application in a variety of fields such as sanitary napkins, communication technology, building industry, chromatography, water purification, and agriculture.[37–41]

In 2001, Washington and Steinbock[42] obtained poly(NIPAAm) gels by frontal polymerization (FP),[43] a technique of macromolecular synthesis that allows the fast conversion of a monomer into a polymer by means of the heat released during the polymerization reaction itself. The reaction starts by igniting it in a localized zone and results in the formation of a polymerization front able to self-sustain and propagate along the whole reactor.

A large number of systems have been investigated, namely: acrylates,[44–49] glycidyl ethers,[50,51] polyurethanes,[52–54] oxetanes and oxiranes,[55–57] microencapsulated initiators,[58,59] epoxy-amine systems,[60–65] epoxy resin/polyurethane networks,[66] polyvinyl pyrrolidinone,[67,68] acrylamides,[69,70] epoxy resins in the presence of BX_3-amine complex as curing

Correspondence to: A. Mariani (E-mail: mariani@uniss.it)

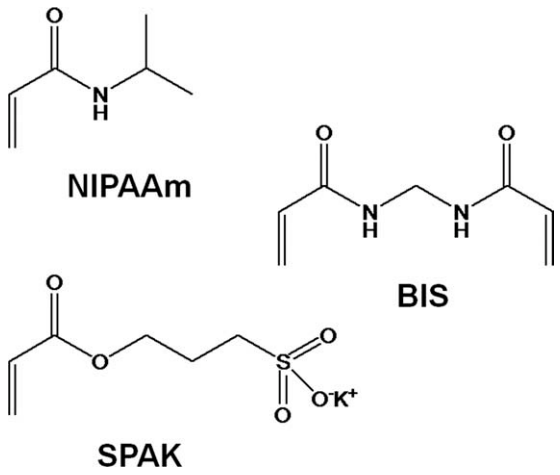

FIGURE 1 Starting materials used for the synthesis of copolymer hydrogels via FP.

agents,[71,72] and phosphonium-based ionic liquids as radical initiators for FP were developed.[73] FP was also applied to the stone consolidation,[74] and to obtain interpenetrating polymer networks,[75] controlled drug release systems,[76] hybrid organic–inorganic epoxy resins,[77] and thermoresponsive hydrogels.[67,78–81]

In a recent article, starting from some reported studies on the large swelling capability of AAm/3-sulfopropyl acrylate potassium salt (SPAK) hydrogel systems,[82–85] we reported the synthesis of super water AAm/SPAK absorbent hydrogels via FP.[81]

In this article, we describe the use of FP for the synthesis of super water absorbent hydrogels made of NIPAAm and SPAK in the presence of *N*,*N*′-methylene-bis-acrylamide (BIS) as crosslinker (Fig. 1).

The influences of the ratio among all components on the front velocity (V_f), on its maximum temperature (T_{max}), and on the network structure of the obtained materials are discussed.

RESULTS AND DISCUSSION

To determine the monomer ratios giving rise to a copolymer able to exhibit the largest swelling, preliminary investigations were carried out on hydrogels containing NIPAAm/SPAK ranging from 0 to 100 mol % and in the presence of 1.0, 2.5, 5.0, and 10.0 mol % of BIS. It was observed that the highest swelling was obtained in the presence of 1.0 or 5.0 mol % of BIS. Thus, as listed in Table 1, the research was focused on the two sets of copolymer hydrogels made of NIPAAm and SPAK using these two BIS concentrations.

In the first series (samples FP1-3, containing 1.0 mol % of BIS), the molar fraction of NIPAAm was allowed to range from 12.5 to 37.5 mol %, which are the compositions allowing for the largest swelling ratio (SR %, see "Experimental" section). In the second series (samples FP4-10, containing 5.0 mol % of BIS), NIPAAm was varied from 0 to 100 mol % (Table 1).

While for the samples containing 1.0 mol % BIS (FP1-3), V_f ranged from 0.5 to 1.0 cm min^{-1}, for those samples containing 5.0 mol % BIS, V_f ranged from 0.38 to 2.0 cm min^{-1} (FP4-10).

The hydrogels containing 12.5, 25.0, and 37.5 mol % NIPAAm and 1.0 mol % BIS (FP1-3) exhibited a V_f that is higher than that of the corresponding samples containing 5.0 mol % BIS (FP5-7). Accordingly, also T_{max} increases as the amount of NIPAAm increases (Table 1). However, the amount of crosslinker does not significantly influence this parameter; indeed, T_{max} of samples FP1-3 goes from 116 to 130 °C, and that of samples FP5-7 from 107 to 137 °C. At variance, when the amount of crosslinker is equal to 5.0 mol %, T_{max} goes from 98 °C (for the copolymer containing 0 mol % NIPAAm: sample FP4), to 179 °C (for the NIPAAm homopolymer: sample FP10).

To investigate the SR % of all hydrogels, they were swollen and equilibrated in water at various temperatures from 10 to 40 °C, and the swelling results are plotted in Figure 2.

TABLE 1 Experimental Data Concerning the NIPAAm/SPAK Hydrogels Prepared in this Work

Sample Codes	NIPAAm (mol %)	BIS (mol %)	T_{max} (°C)	V_f (cm min^{-1})	T_g (°C)		Conversion (%)
FP1	12.5	1.0	116	0.5	168		98
FP2	25.0	1.0	122	0.9	180		99
FP3	37.5	1.0	130	1.0	69	187	98
FP4	0	5.0	98	0.38	70	198	98
FP5	12.5	5.0	116	0.42	69	199	99
FP6	25.0	5.0	107	0.56	61	198	98
FP7	37.5	5.0	137	0.66	55	192	99
FP8	50.0	5.0	135	0.65	51	188	99
FP9	75.0	5.0	152	0.8	50	170	98
FP10	100	5.0	179	2.0	59	158	99

BIS: 1.0 or 5.0 mol %; AmPS: 1 mol %, DMSO

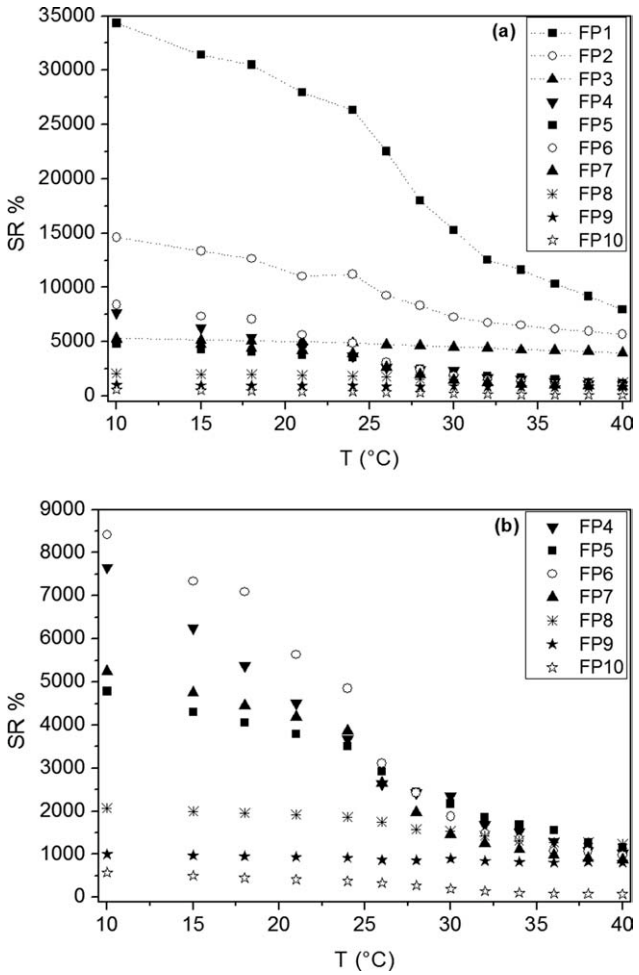

FIGURE 2 SR % as a function of temperature for samples characterized by various monomer ratios and containing: (a) 1.0 and 5.0 mol % BIS; (b) 5.0 mol % BIS.

As said above, some preliminary investigations were carried out in the range from 50 to 100 mol % NIPAAm and in the presence of 5.0 mol % BIS (Fig. 2, samples FP8-10), which confirmed what already observed by us in the AAm/SPAK system:[81] when the amount of NIPAAm is relatively large, only minor swelling variations are observed along all the temperature range investigated. At variance, polymers with a content of 12.5–37.5 mol % NIPAAm and 1.0 mol % BIS [Fig. 2(a), samples FP1-3] or 5.0 mol % BIS [Fig. 2(b), samples FP5-7] exhibited an SR % that is dependent on the amount of both SPAK and BIS.

It should be highlighted that the presence of SPAK influences dramatically the swelling ratio. In particular, samples containing larger amounts of this component are characterized by larger SR %. This finding is in agreement with what expected on the basis of the chemical nature of such a compound, which contains a highly polar group that may partially dissociate in water.

However, for the series of samples containing 5.0 mol % of BIS, this trend is characterized by several exceptions [Fig. 2(b), samples FP4-10].

The hydrogels containing up to 37.5 mol % NIPAAm and 5.0 mol % BIS (FP4-7) exhibited a swelling ratio ranging from 8000 (at 0 °C) down to 1000% (at 40 °C); moreover, for temperatures higher than 26 °C, the SR % trends are almost superimposed. Differently, the samples with NIPAAm comprised between 12.5 and 37.5 mol %, and 1.0 mol % BIS (FP1-3) showed a very different swelling behavior. In this set of polymers, SR % increases as the NIPAAm amount decreases. Indeed, the hydrogel containing 12.5 mol % NIPAAm (FP1) is able to swell from 8000 (at 40 °C) up to 35,000% (at 10 °C), while the hydrogel containing 37.5 mol % NIPAAm (FP3) exhibits an approximately constant SR %, around 5000%, along all the temperature range investigated [Fig. 2(a)]. It is noteworthy that, apart from the sample FP4, which does not contain NIPAAm, all the others exhibit a LCST, and a consequent thermoresponsive behavior, at about 28–30 °C, which was easily determined by the trends reported in Figure 2(a,b).

Namely, it is known that thermoresponsive hydrogels such as those derived from NIPAAm undergo a sharp coil–globule transition in water, thus, changing their state from hydrophilic (below this temperature) to hydrophobic (above it). The thermoresponsive behavior is due to the entropic gain as water molecules associated with the side-chain isopropyl moieties are released into the aqueous solution as the temperature passes LCST, corresponding to the point at which the entropic gain of the system becomes larger than the enthalpic contribution of those water molecules that are hydrogen-bonded to the polymer chain, and, thus, it is largely dependent on the hydrogen-bonding capabilities of the constituent monomer units.[21]

In the present case, such effect is not only due to NIPAAm units but also to the contribution of the SPAK ones, which are characterized by an ionizable, polar group.

Because of the presence of such LCST, which is close to the physiological temperature, these systems might be potentially useful in biological applications.

It is also worth mentioning that the sample containing 12.5 mol % NIPAAm and 1.0 mol % BIS (FP1) showed an SR % always comprised between 10,000 and 35,000%, making it a thermoresponsive super water absorbent hydrogel. Moreover, the above results suggest that the NIPAAm/SPAK copolymers are more advantageous than the AAm/SPAK ones[81] in that, even if they exhibit a similar LCST (~30 °C), the present system has the advantage of being characterized by a tunable swelling that can range from 35,000% to 5000% when temperature raises from 10 to 40 °C; by contrast, in the AAm/SPAK the highest SR % was found to be equal to 15,000% only.

The morphological structure of the hydrogels was investigated by environmental SEM analysis (ESEM). As an example, Figure 3 shows ESEM micrographs of samples FP1 and FP5 containing 12.5 mol % NIPAAm, and 1.0 and 5.0 mol % of BIS, respectively. As can be seen, the samples turned out to be characterized by a sponge-like structure. Pore dimensions were found to be dependent on the amount of

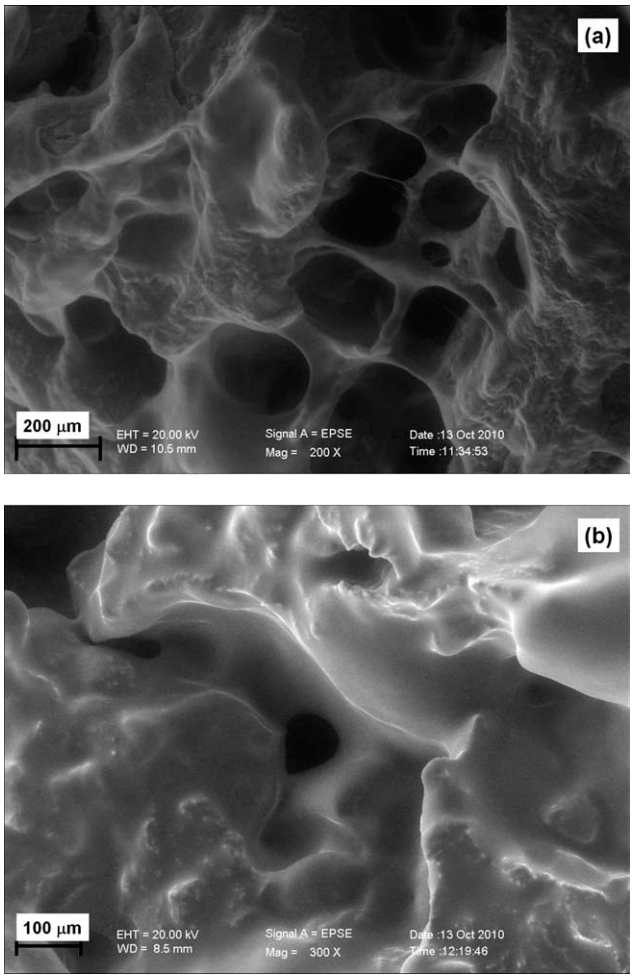

FIGURE 3 ESEM micrographs of sample (a) FP1 and (b) FP5 (containing 12.5 mol % NIPAAm and 1.0 or 5.0 mol % BIS, respectively).

crosslinker. Namely, sample FP1 (1.0 mol % BIS) is characterized by pore diameters between 150 and 200 μm [Fig. 3(a)], whereas sample FP5 (5.0 mol % BIS) has pores comprised between 50 and 100 μm [Fig. 3(b)]. However, also by taking into account some previous findings,[38,78,79,81] it is hardly to establish a reliable relationship among pore dimension and structure, and reaction parameters such as composition, monomer ratio, amount of crosslinker, type of solvent, and temperature.

The crosslinked structure has been confirmed by FTIR spectra. For the sake of simplicity, Figure 4 shows the IR spectrum of sample FP1 compared with those of the monomers and the crosslinker. In particular, the peak at about 1680 cm^{-1} regarding the stretching of the conjugated carbonyl, which is visible in the NIPAAm and BIS spectra, disappeared in that of sample FP1, thus indicating that the double bond has reacted.

Recently, Chen et al.[80] and our group[81] proposed the use of water contact angle analysis (WCA) for the characterization of frontally polymerized hydrogels. By this technique, in the present system, an increase of temperature resulted in an increase of WCA because of the corresponding decrease of water affinity. Moreover, for the same reason, at a given temperature the larger the amount of SPAK is, the lower the contact angle is. For instance, WCA goes from 37, 42, and 56° (at 10 °C) to 47, 65, and 74° (at 35 °C), respectively, for samples FP1, FP2, and FP3. The explanation for such a behavior is in agreement with that already given for the SR % trends. Indeed, as the content of SPAK, which contains an ionic group, increases, the whole affinity of the copolymers toward water increases, thus resulting in a decrease of the contact angle measured.

Differential scanning calorimetry (DSC) investigations were carried out on the dry polymers. By the comparison between the first and the second scans, it was found that conversions were always almost quantitative (no residual polymerization heat was recorded). Table 1 lists the values of T_g found for all the samples synthesized in the present work.

First of all, it can be seen that both crosslinked homopolymers are characterized by two T_g values: the first at 70 and 59 °C (for samples FP4 and FP10, respectively) and the second at 198 (FP4) and 158 °C (FP10).

Two transition temperatures have been found also in all the copolymers: the first one at about 50–70 °C, without any apparent relationship with the actual sample composition. The second value is comprised between 158 and 199 °C. In detail, as expected the samples containing 1.0 mol % BIS are characterized by T_g values that are lower than those containing 5.0 mol % of crosslinker. This finding is probably due to the reduced mobility of the chains caused by the increased amount of BIS. As far as the trends along the series is concerned, the samples containing 1.0 mol % BIS (samples FP1-3) are characterized by values of glass transition temperature that increase as the amount of SPAK decreases, going from 168 to 187 °C. At variance, for those samples containing 5.0 mol % of BIS (samples FP4-10), T_g decreases

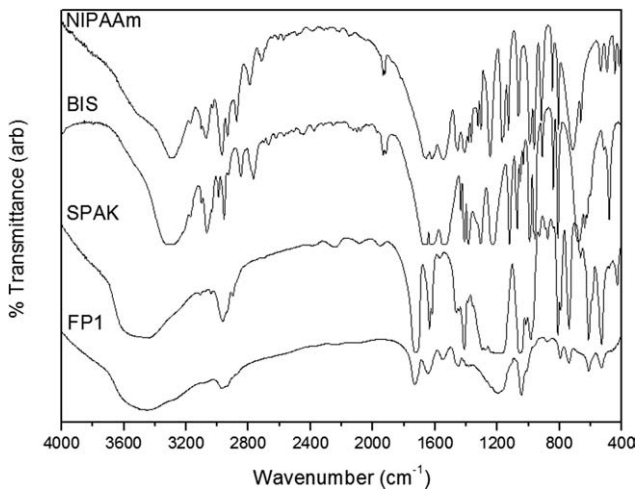

FIGURE 4 FTIR spectrum of sample FP1, containing 12.5 mol % NIPAAm and 1.0 mol % BIS, compared with the spectra of unreacted NIPAAm, BIS, and SPAK.

as SPAK decreases. Although the second series behavior can be reasonable explained by taking into account the polarity of the SPAK monomer, which results in a reduced chain mobility and a subsequent increase of T_g, an analogous explanation for the first series cannot be done, this trend being probably more complicated and probably dependent on various complex interactions between BIS, SPAK, and NIPAAm units.

EXPERIMENTAL

Materials

N-isopropyl acrylamide (NIPAAm, 97 %, FW = 113.16, mp = 60–63 °C), SPAK (FW = 232.3, mp = 302 °C), ammonium persulfate (AmPS, FW = 228.20), dimethyl sulfoxide (DMSO, FW = 78.13, bp = 189 °C, d = 1.101 g mL^{-1}), and BIS (FW = 154.17, mp = 300 °C) were purchased from Sigma-Aldrich and used as received (Fig. 1). At 25 °C, all the monomer mixtures discussed below were stable for several days, that is, without undergoing spontaneous polymerization.

Characterization

DSC characterization was performed by means of a Q100 Waters TA Instruments calorimeter, with a TA Universal Analysis 2000 software. Two heating ramps, from −80 to 250 °C, with a heating rate of 10 °C min^{-1}, were carried out on dry samples: the first scan was performed to remove eventual residual solvent and to establish monomer conversion. WCAs of dried samples were determined by a Dataphysics OCA 5, 10 instrument.

A Fourier transform infrared spectroscope (JASCO FT 480 spectrometer) was used for recording the FTIR spectra of the samples. The powders were ground into a dry KBr disk and 32 scans at a resolution of 4 cm^{-1} were used to record the spectra.

The morphological features of the hydrogels were investigated by an ESEM analysis using a Zeiss EVO LS10.

To determine their swelling ratio (SR %) in water, hydrogels were heated from 10 to 40 °C in a thermostatic bath by increasing temperature at a rate of 2 °C/day. The SR % was calculated by applying the following equation:

$$\mathrm{SR}\,\% = (M_s - M_d)/M_d \times 100 \qquad (1)$$

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

For each sample, three SR % measurements were carried out, and the average values have been reported: reproducibility was always within 5–7%.

Hydrogel Synthesis

A common glass test tube (i.d. = 1.5 cm, length = 16 cm) was filled with the appropriate amounts of NIPAAm, SPAK, BIS, AmPS, and DMSO (Table 1). In all runs, the total molar amount of the two comonomers (5.0 × 10^{-2} mol), initiator (AmPS, 1.0 mol % referred to the total amount of double bonds), and DMSO (3.0 mL) were kept constant. This solvent was added to obtain homogeneous solutions.

The mixtures were sonicated in an ultrasound bath at 30 °C for 30 s to remove the gas bubbles present in it.

A thermocouple junction was located at about 1 cm from the bottom of the tube and connected to a digital temperature recorder (Delta Ohm 9416). 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. Front velocities were determined by measuring the front position (easily visible through the glass wall of test tubes) as a function of time. Front temperature measurements were performed by using a K-type thermocouple connected to the above digital thermometer used for temperature reading and recording (sampling rate: 1 Hz). For all samples, T_{max} (±10 °C) and V_f (±0.05 cm min^{-1}) were measured. Conversions, determined by DSC, were always almost quantitative (Table 1).[64]

After polymerization, all samples were washed in water for several days to remove DMSO and allow them to swell.

CONCLUSIONS

In this work, a series of thermoresponsive super water absorbent copolymer hydrogels composed of NIPAAm and SPAK was successfully prepared by FP. The LCST was found to be independent of the copolymer composition and equal to about 30 °C. At variance, the swelling ratio was found to be largely affected by the ratio between NIPAAm and SPAK. In particular, it was larger for relatively large amounts of the latter. Namely, for the sample containing 12.5 mol % NIPAAm, an SR % value as high as about 35,000% was found, which is much larger that the value of 7500% exhibited by the NIPAAm homopolymer. This represents a great advantage, because it allows one to tune this property by simply varying the monomer ratio. Moreover, SPAK is much cheaper than NIPAAm, and the possibility of replacing this latter with the former may result in a significant economical advantage.

S. Scognamillo is grateful to “Regione Autonoma della Sardegna” for the financial support (“Master and Back” program). The authors are in debt with Porto Conte Ricerche (Tramariglio, Sassari, Italy) for the water contact angle measurements.

REFERENCES AND NOTES

1 Carretti, E.; Dei, L.; Weiss, R. G. Soft Matter 2005, 1, 17–22.

2 Kopeček, J.; Yang, J. Polym Int 2007, 56, 1078–1098.

3 Kashyap, N.; Kumar, M. N. V. Crit Rev Ther Drug Carrier Syst 2005, 22, 107–150.

4 Ozmen, M. M.; Okay, O. J Macromol Sci Part A: Pure Appl Chem 2006, 43, 1215–1225.

5 Zhang, X. Z.; Wang, F. J.; Chu, C. C. J Mater Sci Mater Med 2003, 14, 451–455.

6 Yamashita, K.; Hashimoto, O.; Nishimura, T.; Nango, M. React Funct Polym 2002, 51, 61–68.

7 Hirokawa, E., Tanaka, T. J Chem Phys 1984, 81, 6379–6380.

8 Jeonga, B.; Kimb, S. W.; Baeb, Y. H. Adv Drug Deliv Rev 2002, 54, 37–51.

9 Zhao, C.; Zhuang, X.; He, P.; Xiao, C.; He, C.; Sun, J.; Chen, X.; Jing, X. Polymer 2009, 50, 4308–4316.

10 Okano, T.; Yui, N.; Yokoyama, M.; Yoshida, R. In Japanese Technology Reviews Section E; Ikoma, T., Ed.; Gordon Science: Yverdon, Switzerland, 1993; Vol. 4, pp 67–105.

11 Hoffman, A. S. J Controlled Release 1987, 6, 297–305.

12 Schmaljohann, D. Adv Drug Deliv Rev 2006, 58, 1655–1670.

13 Ying, Z.; Haijia, S.; Li, F.; Tianwei, T. Polymer 2005, 46, 5368–5376.

14 Afrassiabi, A.; Dong, L. C. J Controlled Release 1986, 4, 213–222.

15 Park, K. In Controlled Release: Challenges and Strategies; Park, K. (Purdue University), Ed.; American Chemical Society: Washington, DC, 1997; p 629.

16 Gil, E. S.; Hudson, S. M. Prog Polym Sci 2004, 29, 1173–1222.

17 Suzuki, A.; Tanaka, T. Nature (London) 1990, 346, 345–347.

18 Huang, X.; Lowe, T. L. Biomacromolecules 2005, 6, 2131–2139.

19 Chen, S. C.; Wu, Y. C.; Mi, F. L.; Lin, Y. H.; Yu, L. C.; Sung, H. S. J Controlled Release 2004, 96, 285–300.

20 Kopeček, J. Biomaterials 2007, 28, 5185–5192.

21 de las Heras Alarcón, C.; Pennadam, S.; Alexander, C. Chem Soc Rev 2005, 34, 276–285.

22 Liu, T. Y.; Hu, S. H.; Liu, D. M.; Chen, S. Y.; Chen, I. W. Nano Today 2009, 4, 52–65.

23 Kopeček, J. J Polym Sci Part A: Polym Chem 2009, 47, 5929–5946.

24 Righetti, P. G.; Gelfi, C. J Chromatogr B Biomed Sci Appl 1997, 699, 63–75.

25 Bajpai, A. K.; Shukla, S. K.; Bhanu, S.; Kankane, S. Prog Polym Sci 2008, 33, 1088–1118.

26 Dai, H.; Chen, Q.; Qin, H.; Guan, Y.; Shen, D.; Hua, Y.; Tang, Y.; Xu, J. Macromolecules 2006, 39, 6584–6589.

27 Reis, A. V.; Guilherme, M. R.; Moia, T. A.; Mattoso, L. H. C.; Muniz, E. C.; Tambourgi, E. B. J Polym Sci Part A: Polym Chem 2008, 46, 2567–2574.

28 Peppas, N. A.; Langer, R. Science 1994, 263, 1715–1720.

29 Zhang, X. Z.; Yang, Y. Y.; Chung, T. S.; Ma, K. X. Langmuir 2001, 17, 6094–6099.

30 Kulawardana, E. U.; Kuruwita-Mudiyanselage, T.; Neckers, D. C. J Polym Sci Part A: Polym Chem 2009, 47, 3318–3325.

31 Karadağ, E.; Üzüm, Ö. B.; Saraydin, D. Eur Polym J 2002, 38, 2133–2141.

32 Bell, C. L.; Peppas, N. A. Biopolym II Adv Polym Sci 1995, 22, 125–175.

33 Gutowska, A.; Bae, Y. H.; Jacobs, H.; Feijen, J.; Kim, S. W. Macromolecules 1994, 27, 4167–4175.

34 Muniz, E. C.; Geuskens, G. Macromolecules 2001, 34, 4480–4484.

35 Chen, J.; Park, H.; Park, K. J Biomed Mater Res 1999, 44, 53–62.

36 Chen, J.; Park, K. J Controlled Release 2000, 65, 73–82.

37 Buchholz, F. L.; Graham, T. Modern Superabsorbent Polymer Technology; Wiley: New York, 1998.

38 Dorkoosh, F. A.; Brussee, J.; Verhoef, J. C.; Borchard, G.; Tehrani, M. R.; Junginger, H. E. Polymer 2000, 41, 8213–8220.

39 Ende, M.; Hariharan, D.; Peppas, N. A. React Polym 1995, 25, 127–137.

40 Raju, K. M.; Raju, M. P.; Mohan, Y. M. Polym Int 2003, 52, 768–772.

41 Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1992, 44, 249–253.

42 Washington, R. P.; Steinbock, O. J Am Chem Soc 2001, 123, 7933–7934.

43 A comprehensive list of frontal polymerization bibliography is reported at http://www.pojman.com/FP_Bibliography.html.

44 Hu, T.; Chen, S.; Tian, Y.; Pojman, J. A.; Chen, L. J Poly Sci Part A Polym Chem 2006, 44, 3018–3024.

45 Hu, T.; Chen, S.; Tian, Y.; Chen, L.; Pojman, J. A. J Polym Sci Part A: Polym Chem 2007, 45, 873–881.

46 Pojman, J. A. J Am Chem Soc 1991, 113, 6284–6286.

47 Mariani, A.; Bidali, S.; Fiori, S.; Malucelli, G.; Ricco, L. Macromol Symp 2004, 218, 1–9.

48 Pojman, J. A.; Gunn, G.; Owens, J.; Simmons, C. J Phys Chem Part B 1998, 102, 3927–3929.

49 Nagy, I. P.; Sike, L.; Pojman, J. A. Adv Mater 1995, 7, 1038–1040.

50 Crivello, J. V. J Polym Sci Part A: Polym Chem 2006, 44, 6435–6448.

51 Crivello, J. V. J Polym Sci Part A: Polym Chem 2006, 44, 3036–3052.

52 Chen, S. H.; Sui, J.; Chen, L. Colloid Polym Sci 2005, 283, 932–936.

53 Mariani, A.; Fiori, S.; Bidali, S.; Alzari, V.; Malucelli, G. J Polym Sci Part A: Polym Chem 2008, 46, 3344–3351.

54 Chen, S. U.; Sui, J.; Chen, L.; Pojman, J. A. J Polym Sci Part A: Polym Chem 2005, 43, 1670–1680.

55 Crivello, J. V.; Falk, B.; Zonca, M. R., Jr. J Polym Sci Part A: Polym Chem 2004, 42, 1630–1646.

56 Crivello, J. V.; Bulut, U. Des Monom Polym 2005, 8, 517–531.

57 Crivello, J. V. Polymer 2005, 46, 12109–12117.

58 McFarland, B.; Popwell, S.; Pojman, J. A. Macromolecules 2004, 37, 6670–6672.

59 McFarland, B.; Popwell, S.; Pojman, J. A. Macromolecules 2006, 39, 53–63.

60 Arutiunian, K. A.; Davtyan, S. P.; Rozenberg, B. A.; Enikolopyan, N. S. Dokl Akad Nauk SSSR 1975, 223, 657–660.

61 Surkov, N. F.; Davtyan, S. P.; Rozenberg, B. A.; Enikolopyan, N. S. Dokl Phys Chem 1976, 228, 435–438.

62 Frulloni, E.; Salinas, M. M.; Torre, L.; Mariani, A.; Kenny, J. M. J Appl Polym Sci 2005, 96, 1756–1766.

63 Mariani, A.; Bidali, S.; Caria, G.; Monticelli, O.; Russo, S.; Kenny, J. M. J Polym Sci Part A: Polym Chem 2007, 45, 2204–2211.

64 Mariani, A.; Bidali, S.; Fiori, S.; Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A. J Polym Sci Part A: Polym Chem 2004, 42, 2066–2072.

65 Mariani, A.; Alzari, V.; Monticelli, O.; Pojman, J. A.; Caria, G. J Polym Sci Part A: Polym Chem 2007, 45, 4514–4521.

66 Chen, S.; Tian, Y.; Chen, L.; Hu, T. Chem Mater 2006, 18, 2159–2163.

67 Fang, Y.; Yu, H.; Chen, L.; Chen, S. Chem Mater 2009, 21, 4711–4718.

68 Cai, X.; Chen, S.; Chen, L. J Polym Sci Part A: Polym Chem 2008, 46, 2177–2185.

69 Hu, T.; Fang, Y.; Yu, H.; Chen, L.; Chen, S. Colloid Polym Sci 2007, 285, 891–898.

70 Chen, S.; Hu, T.; Yu, H.; Chen, L.; Pojman, J. A. J Polym Sci Part A: Polym Chem 2007, 45, 4322–4330.

71 Pojman, J. A.; Griffith, J.; Nichols, H. A. e-Polymers 2004, 13, 1–7.

72 Scognamillo, S.; Bounds, C.; Luger, M.; Mariani, A.; Pojman, J. A. J Polym Sci Part A: Polym Chem 2010, 48, 2000–2005.

73 Mariani A, Nuvoli D, Alzari V, Pini, M. Macromolecules 2008, 41, 5191–5196.

74 Brunetti, A.; Princi, E.; Vicini, S.; Pincin, S.; Bidali, S.; Mariani, A. Nucl Instrum Methods Phys Res Sect B-Beam Interactions with Materials and Atoms 2004, 222, 235–241.

75 Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. e-Polymers 2002, 029, 1–10.

76 Gavini, E.; Mariani, A.; Rassu, G.; Bidali, S.; Spada, G.; Bonferoni, M. C.; Giunchedi, P. Eur Polym J 2009, 45, 690–699.

77 Scognamillo, S.; Alzari, V.; Nuvoli, D.; Mariani, A. J Polym Sci Part A: Polym Chem 2010, 48, 4721–4725.

78 Caria, G.; Alzari, V.; Monticelli, O.; Nuvoli, D.; Kenny, J. M.; Mariani, A. J Polym Sci Part A: Polym Chem 2009, 47, 1422–1428.

79 Alzari, V.; Monticelli, O.; Nuvoli, D.; Kenny, J. M.; Mariani, A. Biomacromolecules 2009, 10, 2672–2677.

80 Tu, J.; Fang, Y.; Chen, L.; Wang, C.; Chen, S. J Polym Sci Part A: Polym Chem 2010, 48, 823–831.

81 Scognamillo, S.; Alzari, V.; Nuvoli, D.; Mariani, A. J Polym Sci Part A: Polym Chem 2010, 48, 2486–2490.

82 Tanaka, T. Phys Rev Lett 1978, 40, 820–823.

83 Shibayama, M.; Tanaka, T. Adv Polym Sci 1993, 109, 1–62.

84 Baselga, J.; Llorente, M. A.; Hernandez-Fuendez, I.; Pierolo, I. F. Eur Polym J 1989, 25, 471–475.

85 Funke, W.; Okay, O.; Joos-Muller, B. Adv Polym Sci 1998, 136, 139–234.