Polym. Bull. (2012) 69:1093–1101
DOI 10.1007/s00289-012-0813-z

ORIGINAL PAPER

Temperature-induced thickening of sodium carboxymethylcellulose and poly(*N*-isopropylacrylamide) physical blends in aqueous solution

Bruna V. de Lima · Rosangela R. L. Vidal · Nívia do N. Marques · Ana M. S. Maia · Rosangela de C. Balaban

Received: 19 March 2012 / Revised: 4 July 2012 / Accepted: 10 July 2012 /

Abstract This study describes the synthesis of poly(*N*-isopropylacrylamide) (PNIPAM) via free radical polymerization, the preparation of physical blends containing sodium carboxymethylcellulose (CMC) and PNIPAM in aqueous solution, at total polymer concentrations of 2 and 6 g/L in different compositions, and applies rheology to investigate interactions between PNIPAM and CMC compared to pure polymers, in aqueous solution. Rheological measurements indicated thermothickening behavior for the 50 % PNIPAM–50 % CMC physical blend in aqueous solution, at 6 g/L, as viscosity rose when temperature was increased to a range of 25–40 °C. Similar thermothickening behavior was observed for the 25 % CMC–75 % PNIPAM physical blend in solution, at a total polymer concentration of 2 g/L. These results provide new information for preparing physical blends in aqueous solutions exhibiting thermothickening behavior, indicating that this behavior depends on total polymer concentration and composition of the mixture.

Keywords Sodium carboxymethylcellulose · Poly(*N*-isopropylacrylamide) · Rheology · Thermothickening

---

B. V. de Lima · N. do N. Marques · A. M. S. Maia · R. de C. Balaban (✉)
LAPET—Laboratory of Petroleum Research, Institute of Chemistry, Federal University of Rio Grande do Norte, P.O. Box 1662, Natal, RN 59078-970, Brazil
e-mail: balaban@supercabo.com.br

B. V. de Lima
e-mail: brunavlima@yahoo.com.br

R. R. L. Vidal
Institute of Chemistry, Federal University of Bahia, Campus de Ondina, Salvador, BA, Brazil

Introduction

Intelligent or smart polymers have been the focus of research in recent years. These polymers rapidly undergo ample and reversible structural changes in response to external stimuli, such as alterations in temperature, pH, ionic strength, among others [1–3].

One of the properties of interest for using intelligent polymers is temperature sensitivity. Thermosensitive polymers exhibit modifications in their structure and properties in response to an external stimulus, in particular, a change in temperature system [4–7]. Therefore, for this study it was selected a thermosensitive polymer called poly(*N*-isopropylacrylamide) (PNIPAM), known for having a lower critical solution temperature (LCST) of around 32 °C when in water. When PNIPAM is heated above its LCST, the polymer chains precipitate. PNIPAM contains hydrophilic (C=O and NH) and hydrophobic (isopropyl) groups within the same chain, which are responsible for the balance between hydrophilic and hydrophobic interactions that may have a decisive role in the thermosensitivity of the macromolecule [8, 9].

The other polymer selected for this study was sodium carboxymethylcellulose (CMC). CMC is a low-cost semisynthetic polysaccharide that is anionic, water soluble, nontoxic, biodegradable, and has a rigid chain. As such, it is used in various applications in the cosmetics, food and pharmaceutical industries, and as a thickening agent [10–13].

Vasile et al. [2] performed a comparative study of the behavior of CMC and PNIPAM under graft copolymers form and physical blends, at a total polymer concentration of 2 g/L, in solution and in solid state, using different techniques. They concluded that the thermothickening property is typical only for graft copolymers (CMC-*g*-PNIPAM27, a graft copolymer containing 73 mol% CMC and 27 mol% PNIPAM), while the corresponding blends (CMC/PNIPAM27) in aqueous solution present the Arrhenius thermothinning behavior, i.e., the viscosity decreases as temperature increases [2]. However, a better understanding of the properties of physical blends in aqueous solution can be obtained through their rheological characterization under different conditions such as total polymer concentrations, molar masses, and compositions of the physical blends and temperatures.

In this article, we present a more detailed rheological study on CMC and PNIPAM physical blends in aqueous solution, at different compositions and total polymer concentrations. A clear thermothickening behavior was observed for specific compositions at different total polymer concentrations.

Experimental

Materials

Sodium CMC, *N*-isopropylacrylamide (NIPAM), and *N*,*N*,*N*′,*N*′-tetramethylenediamine 99 % (TEMED) were purchased from Sigma-Aldrich. Potassium persulfate

(KPS) and NaCl were supplied by VETEC Química Fina Ltda. Hexane (95 %) was acquired from CRQ. NIPAM was purified twice by recrystallization in hexane. The other chemicals were used as received.

Synthesis of PNIPAM

The PNIPAM used in this study was synthesized via free radical polymerization method as described in literature [14], but with some modifications. The system was composed by a 250 mL four-necked flask coupled to a condenser, a thermometer, and a $N_{2(g)}$ inlet and outlet. NIPAM (200 mmol/L) was added to 100 mL of distilled water under magnetic stirring. The system was bubbled through the continuous passage of $N_{2(g)}$ for 30 min at constant temperature (25 °C), maintained by a water bath. Polymerization was initiated by a KPS/TEMED redox pair (10 and 2.5 mmol/L). The reaction was carried out at 25 °C, with water bath, at constant magnetic stirring, for 3 h. The system was heated to 60 °C for precipitation of the PNIPAM formed, which was then filtered. To remove the remaining monomer, initiator, and catalyst, the product was washed several times with hot water. Afterward, the obtained product was dried in a vacuum oven at 40 °C for 24 h and then macerated. The PNIPAM obtained was stored in a desiccator [15].

Viscometry

Viscosity measurements of the CMC and the PNIPAM aqueous solutions were performed in an Ubbelohde capillary viscometer ($\Phi = 0.46$ mm) from Schott, using manual dilution. The temperature was maintained at 25 (±0.05) °C with a thermostatic bath. The stock solution of CMC was prepared in a polymer concentration of 3 g/L, using 0.2 M NaCl aqueous solution as a solvent. The PNIPAM stock solution was prepared at a polymer concentration of 10 g/L, with distilled water as a solvent. Solvents and solutions used in this study were previously filtered through cellulose acetate membranes, with a pore size of 0.45 mm from Millipore. Intrinsic viscosity values $[\eta]$ were determined from the extrapolation of the reduced viscosity curve at zero concentration using the Flory–Huggins equation as shown below [16]:

$$\eta_{sp}/C = [\eta]_h + k_h [\eta]_h^2 C, \tag{1}$$

where η_{sp}/C is the reduced viscosity, $[\eta]_h$ is the intrinsic viscosity determined by Huggins equation, k_h is the Huggins constant, and C is the polymer concentration. Intrinsic viscosity values obtained for the CMC and PNIPAM were 523.9 and 147.9 mL/g, respectively. Once the intrinsic viscosities were determined, the average viscosimetric molecular weights, $\overline{M}_v$, of the polymers could be calculated by using the Mark–Houwink–Sakurada equations $[\eta] = 43 \times 10^{-3}\ M_v^{0.74}$ [6] and $[\eta] = 2.26 \times 10^{-4}\ M_v^{0.97}$ [17]. The viscosity molecular weights of the CMC and PNIPAM were 3.3×10^5 and 9.9×10^5 g/mol, respectively.

Table 1 Compositions of CMC–PNIPAM physical blends in aqueous solution

Total concentration of 2 g/L		Total concentration of 6 g/L		Composition (%)
CMC (g/L)	PNIPAM (g/L)	CMC (g/L)	PNIPAM (g/L)	
0.00	2.00	0.00	6.00	0 % CMC–100 % PNIPAM
0.50	1.50	1.50	4.50	25 % CMC–75 % PNIPAM
1.00	1.00	3.00	3.00	50 % CMC–50 % PNIPAM
1.50	0.50	4.50	1.50	75 % CMC–25 % PNIPAM
2.00	0.00	6.00	0.00	100 % CMC–0 % PNIPAM

Rheological characterization

Preparation of polymers solutions

CMC and PNIPAM solutions were prepared separately, each one at a polymer concentration of 6 g/L, using distilled water as solvent. Polymer solutions were kept under constant stirring, at room temperature, during ~24 h. After that, those solutions were diluted in distilled water to obtain additional polymer concentrations (4.5, 3.0, 2.0, 1.5, 1.0, and 0.5 g/L).

Physical blends in aqueous solution were prepared by mixing appropriate volumes of CMC and PNIPAM solutions, to achieve total polymer concentrations of 2 and 6 g/L, as described in Table 1. Before analysis, each mixture was kept under constant stirring, at room temperature, during 30 min.

Rheological measurements

Rheological measurements of the solutions were carried out in a Haake Mars Controller Rheometer, using coaxial cylinder geometry (DG41 Ti). The measurements were obtained at a constant shear rate (7.3 s^{-1}), in a temperature range of 25–40 °C, kept constant through a thermostatic bath coupled to the equipment.

Results and discussion

Rheological characterization of pure CMC and PNIPAM in aqueous solution

Rheological behavior of the systems was investigated with respect to polymer concentration, composition, and temperature in distilled water, as it is described in "Rheological characterization" section. Figure 1a shows that ln η of CMC aqueous solutions, in the concentration range of 0.5–6.0 g/L, increases with the inverse of temperature, that is, viscosity of CMC solutions decreases as the temperature is increased. This is in accordance with standard behavior described by the Arrhenius equation, typical for hydrophilic polymeric chains, though not for thermosensitive ones [10]. Moreover, in distilled water, increasing polymer concentration resulted in

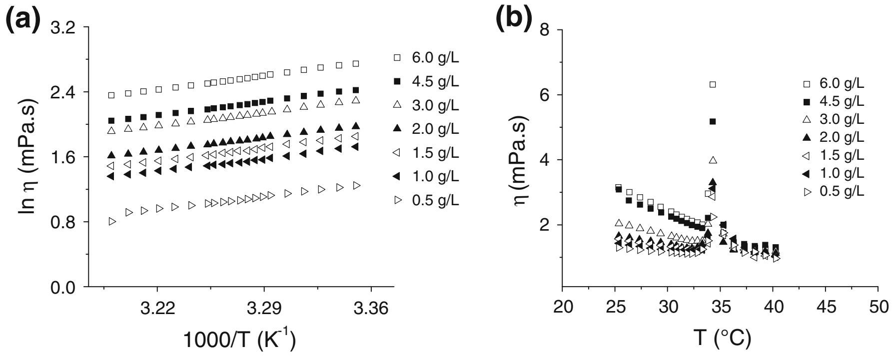

Fig. 1 Apparent viscosity as a function of temperature of aqueous solutions of **a** CMC and **b** PNIPAM, at polymer concentrations between 0.5 and 6.0 g/L, at a shear rate of 7.3 s^{-1}

a rise in apparent viscosity. This could be attributed to the larger amount of macromolecules in the medium [18].

On the other hand, the apparent viscosity curves of PNIPAM aqueous solutions exhibited three different behaviors (Fig. 1b), as it was described by Tam et al. [19]. The first may also reflect typical Arrhenius behavior where apparent viscosity of PNIPAM aqueous solutions declined as temperature rose, until reaching the association temperature (T_{ass}) of 33.85 °C, defined as the starting point for increasing viscosity [20]. Below the T_{ass}, this behavior can be attributed to the intermolecular hydrogen interactions between hydrophilic groups (NH, C=O) of PNIPAM chains and the water which favor the solubility of PNIPAM in aqueous medium. However, the second behavior occurs between T_{ass} and lower critical solution temperature (LCST) at 34.3 °C, indicated by an intense peak, and is related to two factors: (i) intermolecular hydrogen bonding between PNIPAM and water, leading to enhanced dissolution in water and (ii) hydrophobic interactions between PNIPAM isopropyl groups, that increase as temperature rises, promoting intermolecular aggregation of PNIPAM chains. Formation of these aggregations leads to physical networks, resulting in high viscosity and in the thermothickening behavior.

Finally, above the LCST, viscosity declined rapidly, owing to the increase in both intramolecular hydrogen interactions of PNIPAM chains and hydrophobic interactions. This leads to the collapse of physical networks and precipitation of PNIPAM chains in the medium, resulting in the decrease of viscosity of polymer solutions. Moreover, the apparent viscosity was enhanced as the polymer concentration increased due to the increase of macromolecules in the medium [8, 10, 21–23].

Rheological characterization of CMC–PNIPAM physical blends in aqueous solution

In Fig. 2a, the apparent viscosities of CMC–PNIPAM physical blends in aqueous solution at different compositions are plotted as a function of temperature, at a shear rate of 7.3 s^{-1} and at a total polymer concentration of 6 g/L. The physical blend of

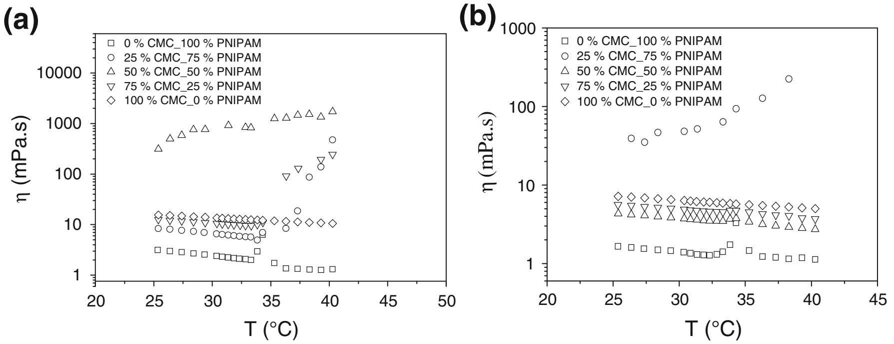

Fig. 2 Apparent viscosity as a function of temperature of physical blends of CMC and PNIPAM in aqueous solution of **a** 6 g/L and **b** 2 g/L, in different compositions, at a shear rate of 7.3 s^{-1}

50 % CMC–50 % PNIPAM in aqueous solution showed thermothickening behavior, as viscosity rose when temperature increased to a range of 25–40 °C. This behavior is synergistic when compared to pure polymers in distilled water, which showed a decrease in viscosity with the increase of temperature, in accordance with the Arrhenius equation. At temperatures below the LCST of PNIPAM, the behavior of this physical blend was synergistic at total polymer concentration of 6 g/L and average molecular weights for CMC and PNIPAM of 3.3×10^5 and 9.9×10^5 g/mol, respectively. This is likely due to the combination of two factors: (i) the presence of intermolecular hydrogen interactions and (ii) the presence of carboxylate groups (COO^-) along the CMC backbone. It was also observed that at temperatures above the LCST, apparent viscosity of the physical blends in aqueous solution increased with rising temperatures given the hydrophobic contribution of the PNIPAM chains [8, 18].

In contrast, the apparent viscosity of physical blends (25 % CMC–75 % PNIPAM and 75 % CMC–25 % PNIPAM) in aqueous solution fell when temperature rose from 25 to 33 °C, and increased above the LCST of PNIPAM (thermothickening behavior).

Below the LCST of PNIPAM, the physical blend 75 % CMC–25 % PNIPAM in aqueous solution showed a slight increase in viscosity values compared to the 25 % CMC–75 % PNIPAM, where CMC concentrations are equal to 4.5 and 1.5 g/L, respectively. This result indicates that the greater CMC concentration contributes to higher viscosity values. Above the LCST of PNIPAM, viscosity gain observed for these solutions is probably mostly related to a delicate balance between hydrophilic and hydrophobic interactions. This is because higher temperatures cause partial displacement of water from polymers coils, weakening hydrogen bonds, and increasing hydrophobic interactions between hydrophobic groups of PNIPAM macromolecules [21].

Furthermore, these solutions clouded, but they did not precipitate. On a macroscopic scale, this behavior was reversible and the original properties of the solutions were recovered when the stimulus was removed, in particular a temperature variation. This behavior is mostly attributed to intermolecular hydrogen interactions between hydrophilic groups (NH, C=O) of PNIPAM chains and OH groups along the charged CMC chains in aqueous medium. These interactions contributed to stabilization of the physical blends, as the hydrophilic CMC backbone prevents the full collapse of PNIPAM chains, thereby inhibiting macroscopic phase separation of the PNIPAM chains. In this case, turbidity of the physical blends was significantly lower than that of PNIPAM solutions under the same conditions, promoting the formation of less or smaller PNIPAM aggregates under these conditions [10].

This study found that varying at least one of the experimental condition parameters, such as total polymer concentration of the physical blends in aqueous solution, resulted in different rheological properties at 6 and 2 g/L. According to Fig. 2b, apparent viscosity of the physical blends (75 % CMC–25 % PNIPAM and 50 % CMC–50 % PNIPAM) in aqueous solution, at a total concentration of 2 g/L, decreased with the increase of temperature and no thermothickening behavior was exhibited. Moreover, their viscosity values were intermediate to those of pure polymers (0 % CMC–100 % PNIPAM and 100 % CMC–0 % PNIPAM).

The physical blend 75 % CMC–25 % PNIPAM in aqueous solution showed similar behavior to that verified by Vasile et al. [2] for the CMC/PNIPAM27 blend (66.7 % CMC–33.3 % PNIPAM). This was expected, given that both blends have the same total polymer concentration (2 g/L) and a similar composition, although molecular weights of polymers are different.

On the other hand, thermothickening behavior was observed for the physical blend 25 % CMC–75 % PNIPAM in aqueous solution, at a total polymer concentration of 2 g/L. This confirms that below the LCST, increased viscosity of the physical blend can be attributed to the presence of intermolecular hydrogen interactions and the expansion of CMC chains, which is favored by electrostatic repulsions between the carboxylate groups. However, above the LCST, the physical blend exhibited higher viscosity values as temperature increased, due to the tendency of the PNIPAM hydrophobic groups to form intermolecular aggregates in aqueous solution, in addition to the fact that the physical blend did not undergo phase separation [23].

In the case of physical blends in aqueous solution at 6 g/L of total polymer concentrations (Fig. 2a), a thermothickening behavior was detected for all compositions above the PNIPAM LCST, and no phase separation was observed for any blend. For the physical blend 50 % CMC–50 % PNIPAM, the highest viscosities were obtained, indicating a synergistic effect due to specific interactions between the polymers.

Conclusions

This study revealed that the rheological properties of CMC–PNIPAM physical blends in aqueous solution depend on the total polymer concentration and their corresponding compositions. These solutions can lead to thermothickening or the typical Arrhenius behaviors.

Rheological data showed that some physical blends of CMC–PNIPAM in aqueous solution may also display thermothickening behavior, indicating that this behavior is not only typical of graft copolymers of PNIPAM and CMC, as described by Vasile et al. This result can be particularly useful in applications under severe temperature conditions, such as enhanced oil recovery, given the ability of physical blends to produce highly viscous aqueous solutions under heating.

Increased viscosity of the physical blends in aqueous solution was probably caused by hydrophilic and hydrophobic interactions between CMC and/or PNIPAM chains. However, further examination of their interactions in different solvents at temperature range of 25–85 °C, below and above the PNIPAM LCST, is necessary and will be undertaken in a forthcoming study.

Acknowledgments The authors thank the PRH30/ANP/MCT, PETROBRAS and CAPES—an entity of the Brazilian Government directed toward the training of human resources—for their financial support.

References

1. Shi HY, Zhang LM, Ma YQ, Yi JZ (2007) Synthesis and characterization of water-soluble cellulose derivatives with thermo- and pH-sensitive functional groups. J Macromol Sci Part A 44:1109–1113. doi:10.1080/10601320701524179
2. Vasile C, Bumbu GG, Dumitriu RP, Staikos G (2004) Comparative study of the behavior of carboxymethyl cellulose-*g*-poly(*N*-isopropylacrylamide) copolymers and their equivalent physical blends. Eur Polym J 40:1209–1215. doi:10.1016/j.eurpolymj.2003.12.023
3. Chee CK, Rimmer S, Soutar I, Swanson L (2001) Fluorescence investigations of the thermally induced conformational transition of poly(*N*-isopropylacrylamide). Polymer 42:5079–5087. doi:10.1016/S0032-3861(00)00821-1
4. Gao C, Möhwald H, Shen J (2005) Thermosensitive poly(allylamine)-*g*-poly(*N*-isopropylacrylamide): synthesis, phase separation and particle formation. Polymer 46:4088–4097. doi:10.1016/j.polymer.2005.02.115
5. Schmaljohann D (2006) Thermo- and pH-responsive polymers in drug delivery. Adv Drug Deliv Rev 58:1655–1670. doi:10.1016/j.addr.2006.09.020
6. Dimitrov I, Trzebicka B, Müller AHE, Dworak A, Tsvetanov CB (2007) Thermosensitive water-soluble copolymers with doubly responsive reversibly interacting entities. Prog Polym Sci 32:1275–1343. doi:10.1016/j.progpolymsci.2007.07.001
7. O'Shea J-P, Tallon C (2011) Yield stress behaviour of concentrated silica suspensions with temperature-responsive polymers. Colloids Surf A 385:40–46. doi:10.1016/j.colsurfa.2011.05.042
8. Lin SY, Chen KS, Liang RS (1999) Thermal micro ATR/FT-IR spectroscopic system for quantitative study of the molecular structure of poly(*N*-isopropylacrylamide) in water. Polymer 40:2619–2624. doi:10.1016/S0032-3861(98)00512-6
9. Burdukova E, Li H, Bradshaw DJ, Franks GV (2010) Poly(*N*-isopropylacrylamide) (PNIPAM) as a flotation collector: effect of temperature and molecular weight. Miner Eng 23:921–927. doi:10.1016/j.mineng.2010.03.003
10. Bokias G, Mylonas Y, Staikos G, Bumbu GG, Vasile C (2001) Synthesis and aqueous solution properties of novel thermoresponsive graft copolymers based on a carboxymethylcellulose backbone. Macromolecules 34:4958–4964. doi:10.1021/ma010154e
11. Charpentier D, Mocanu G, Carpov A, Chapelle S, Merle L, Muller G (1997) New hydrophobically modified carboxymethycellulose derivatives. Carbohydr Polym 33:177–186. doi:10.1016/S0144-8617(97)00031-3
12. Guillot S, Delsanti M, Désert S, Langevin D (2003) Surfactant-induced collapse of polymer chains and monodisperse growth of aggregates near the precipitation boundary in carboxymethylcellulose-DTAB aqueous solutions. Langmuir 19:230–237. doi:10.1021/la0206561

13. Lin OH, Kumar RN, Rozman HD, Noor MAM (2005) Grafting of sodium carboxymethylcellulose (CMC) with glycidyl methacrylate and development of UV curable coating from CMC-*g*-GMA induced by cationic photoinitiators. Carbohydr Polym 59:57–69. doi:10.1016/j.carbpol.2004.08.027
14. Moura MR, Rubira AF, Muniz EC (2008) Hidrogéis semi-IPN baseados em rede de alginato-Ca^{2+} com PNIPAAm entrelaçado: propriedades hidrofílicas, morfológicas e mecânicas. Polim Cienc Tecnol 18:132–137. doi:10.1590/S0104-14282008000200010
15. Marques NN, Maia AMS, Curti PS, Balaban RC (2010) Efeito da temperatura de síntese sobre a massa molar do polímero termossensível poli(*N*-isopropilacrilamida). Livro eletrônico—Anais/Resumos da 62ª Reunião Anual da SBPC. http://www.sbpcnet.org.br/livro/62ra/resumos/resumos/2891.htm. Accessed 10 Nov 2011
16. Harding SE (1997) The intrinsic viscosity of biological macromolecules. Progress in measurement, interpretation and application to structure in dilute solution. Prog Biophys Mol Biol 68:207–262. doi:10.1016/S0079-6107(97)00027-8
17. Muniz EC, Geuskens G (2001) Compressive elastic modulus of polyacrylamide hydrogels and semi-IPNs with poly(*N*-isopropylacrylamide). Macromolecules 34:4480–4484. doi:10.1021/ma001192l
18. Vidal RRL, Balaban R, Borsali R (2008) Amphiphilic derivatives of carboxymethylcellulose: evidence for intra- and intermolecular hydrophobic associations in aqueous solutions. Polym Eng Sci 48:2011–2026. doi:10.1002/pen.21180
19. Tam KC, Wu XY, Pelton RH (1992) Viscosimetry—a useful tool for studying conformational changes of poly(*N*-isopropylacrylamide) in solutions. Polymer 33:436–438. doi:10.1016/0032-3861(92)91008-P
20. Zhang X, Zhou L, Zhang X, Dai H (2010) Synthesis and solution properties of temperature-sensitive copolymers based on NIPAM. J Appl Pol Sci 116:1099–1105. doi:10.1002/app.31574
21. Bajpai A, Shukla S, Saini R, Tiwari A (2010) Stimuli responsive drug delivery systems: from introduction to application. In: Temperature-sensitive release systems. iSmithers, Shawbury, pp 107–112
22. Aguilar MR, Elvira C, Gallardo A, Vázquez B, Román JS (2007) Smart polymers and their applications as biomaterials, chap 6. In: Ashammakhi N, Reis R, Chiellini E (eds) Topics in tissue engineering, vol 3., pp 1–23
23. Bokias G, Hourdet D, Iliopoulos I, Staikos G, Audebert R (1997) Hydrophobic interactions of poly(*N*-isopropylacrylamide) with hydrophobically modified poly(sodium acrylate) in aqueous solution. Macromolecules 30:8293–8297. doi:10.1021/ma970884f