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Synthesis and characterization of biresponsive graft copolymer gels

Dirk Kuckling[1,*], Sebastian Wohlrab

Institute of Macromolecular Chemistry and Textile Chemistry, Dresden University of Technology, D-01062 Dresden, Germany

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Abstract

Graft copolymer gels with different compositions were prepared by the radical polymerization of *N*-isopropylacrylamide (NIPAAm) and poly(2-vinylpyridine) (P2VP) macromonomers in dioxane with 1 mol% *N*,*N*′-methylenebisacrylamide (BIS) as the crosslinking agent. The graft copolymer gels were analyzed at different temperatures and pH values. They demonstrated the typical swelling behavior for poly(*N*-isopropylacrylamide) (PNIPAAm) gels with changing temperature. In addition to the temperature dependent measurements, the graft copolymer with a high P2VP content showed a pronounced swelling transition with changing pH value. By separating the temperature and the pH sensitive component, it was possible to obtain a gel which could be swelled independently in response to temperature and pH.

Keywords: *N*-isopropylacrylamide; 2-Vinylpyridine; Graft copolymer gel

1. Introduction

A common method to vary the degree of swelling and the transition temperature (T_c) of temperature responsive hydrogels, e.g. based on poly(*N*-isopropylacrylamide) (PNIPAAm) (T_c around 33 °C), is the incorporation of a weak acid or base component into the network [1–4]. Using this method, it is possible to obtain gels with temperature as well as pH sensitivity [5–7]. Due to protonation–deprotonation reactions altering the pH value of the swelling medium, the network changes from a non-ionic to an ionic state and vice versa. The critical behavior of these polymers is very sensitive to changes in the hydrophilic/hydrophobic balance of the macromolecules. In the ionic state, the network is much more hydrophilic and the degree of swelling and the transition temperature is increased. With a random distribution of the acidic or basic comonomers, it is not possible to vary the comonomer content in order to modify the degree of swelling below the T_c without also changing the T_c itself [8]. For this purpose, the components have to be separated into blocks [9]. A suitable method to prepare crosslinked polymers with blocked components is the preparation of graft copolymer gels. Those structures were realized in order to enhance the response time of PNIPAAm gels [10–12].

The aim of this work was to develop new types of hydrogels which combine temperature (PNIPAAm) and pH (poly(2-vinylpyridine) (P2VP)) sensitive components. The swelling of one of the two components should be initiated independently from the other component. Therefore, graft copolymer gels with PNIPAAm backbones and P2VP graft arms (from P2VP macromonomers) were prepared and analyzed at different temperatures and pH values. In a previous study, the bisensitive behavior of soluble PNIPAAm/P2VP graft copolymers could be shown by dynamic light scattering [13].

2. Experimental part

2.1. Chemicals

N-Isopropylacrylamide (NIPAAm, Aldrich) was purified by recrystallization from hexane and dried in vacuum. 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Dioxane was distilled over potassium hydroxide. All other reagents were of analytical grade.

2.2. Synthesis of poly(2-vinylpyridine) (P2VP) macromonomers

P2VP macromonomer was prepared according to the literature. The molecular weight was measured by GPC

* Corresponding author. Address: Department of Chemical Engineering, Stanford University, 381 North–South Mall, Stanford, CA 94305-5025, USA. Tel.: +1-650-724-4735; fax: +1-650-723-9780.
E-mail address: kuckling@leland.stanford.edu (D. Kuckling).
[1] Tel.: +49-351-463-33788; fax: +49-351-463-37122.
e-mail: dirk.kuckling@chemie.tu-dresden.de.

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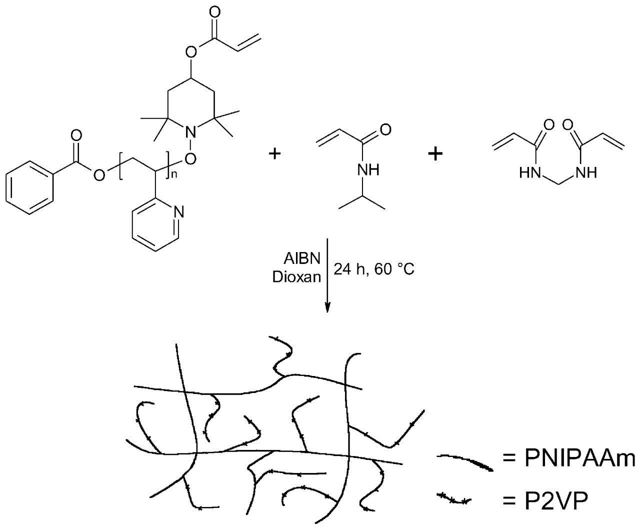


Scheme 1. Synthesis of the graft copolymer gels.

($M_n = 2700$, PD = 1.39) [13]. The degree of functionalization was 85%.

2.3. Synthesis of the graft copolymer gels

2.3.1. General procedure

A solution consisting of 1.00 g (8.85 mmol) *N*-isopropylacrylamide (PNIPAAm), 101 mg (0.037 mmol) P2VP macromonomer, 14.1 mg (0.091 mmol) *N*,*N*′-methylenebisacrylamide (BIS) and 8.2 mg (0.050 mmol) AIBN was prepared in 3.3 ml of dry dioxane. The mixture was purged with argon for 30 min and then transferred into a glass tube equipped with capillaries. The glass tube was sealed and heated to 60 °C for 24 h. The polymer gel was separated from the capillaries after the reaction by repelling the gels out of the capillaries with a metal stick and washed several times with 0.05N HCl. To measure the degree of swelling, the gels were immersed in different buffer solutions and allowed to equilibrate overnight.

2.4. Characterization

The diameter d of the gels were measured on a computer by magnification of the gels in a thermostated swelling chamber through a microscope (HUND Wetzlar) equipped with a CCD-camera (JVC TK-C1380). As the reference state the gel volume/diameter during preparation was chosen ($d_0 = 775$ μm). The volume degree of swelling V/V_0 was calculated from Eq. (1).

$$\frac{V}{V_0} = \left(\frac{d}{d_0}\right)^3 \tag{1}$$

The gels were kept at a constant temperature until they reached equilibrium, but at least 15 min.

3. Results and discussion

The combination of temperature sensitive PNIPAAm with a pH-sensitive component (poly(2-vinylpyridine) (P2VP)) leads to polymers possessing both of these properties. PNIPAAm aggregates while increasing the temperature to above the phase transition temperature, which lies generally at ca. 33 °C [14]. P2VP is soluble in aqueous media at low pH due to the protonation of the basic aromatic nitrogen and aggregates at higher pH. The critical pH value for the transition from hydrophilic to hydrophobic macromolecule lies at ca. 5.5. It was possible to synthesize P2VP-macromonomers with different chain lengths and relatively small polydispersities by using the controlled radical polymerization method, followed by functionalization to form the macromonomer. The synthesis of the P2VP macromonomer is described elsewhere [13].

Graft copolymer gels with different compositions were prepared by radical polymerization in dioxane from *N*-Isopropylacrylamide (NIPAAm) and poly(2-vinylpyridine) (P2VP) macromonomers with 1 mol% *N*,*N*′-methylenebisacrylamide (BIS) as the crosslinking agent (Scheme 1). The compositions of the gels are listed in Table 1. The polymerization was performed in small capillaries (diameter $d_0 = 775$ μm). After removing the gels from the capillaries and subsequent washing with 0.05N HCl to remove unreacted chemicals, the gels were equilibrated in different buffer solutions. Assuming a full conversion as well as a random distribution of the monomers, an average distance between two P2VP sidechains can be estimated from the NIPAAm/P2VP macromonomer ratio. The

Table 1
Composition of the graft copolymer gels

Gel	Feed composition (g)		Ratio of repeating units in the gel NIPAAm:2VP[a]	Average distance between two P2VP side chains [NIPAAm repeating units][b]
	NIPAAm	P2VP		
1	1.00	–	1:0	–
2	1.00	0.10	10.9:1	280
3	0.41	0.10	4.5:1	116
4	0.23	0.25	1:1	26

[a] Estimated from the feed composition and the degree of functionalization for P2VP macromonomers.
[b] Estimated from the ratio of repeating units and the degree of polymerization for P2VP macromonomers.

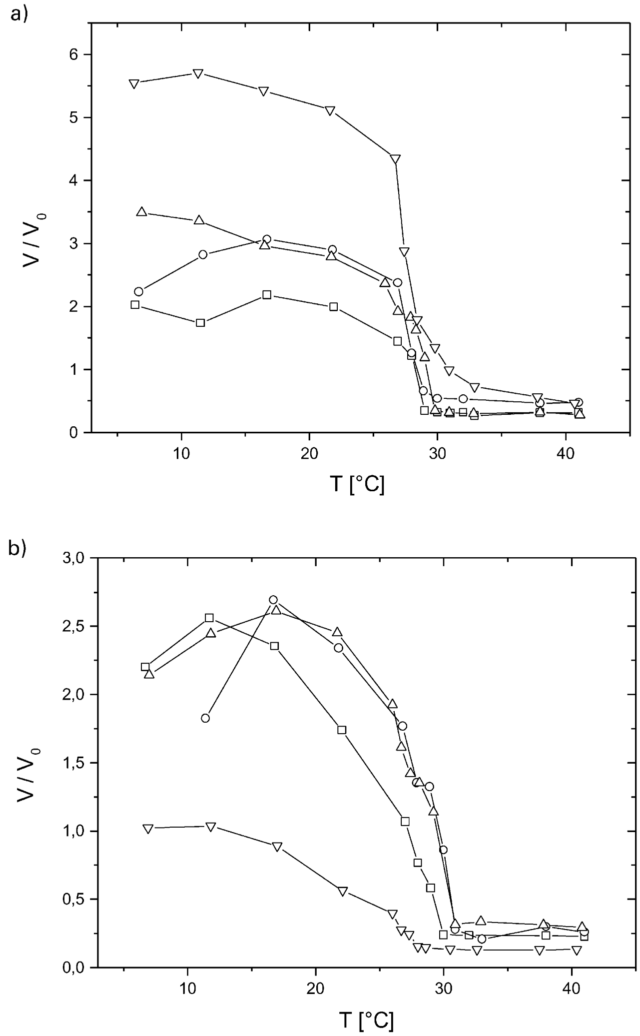


Fig. 1. Volume degree of swelling of graft copolymer gels in response to temperature at constant pH. (a) pH = 3; (b) pH = 7; (□—gel 1; ○—gel 2; △—gel 3; ▽—gel 4).

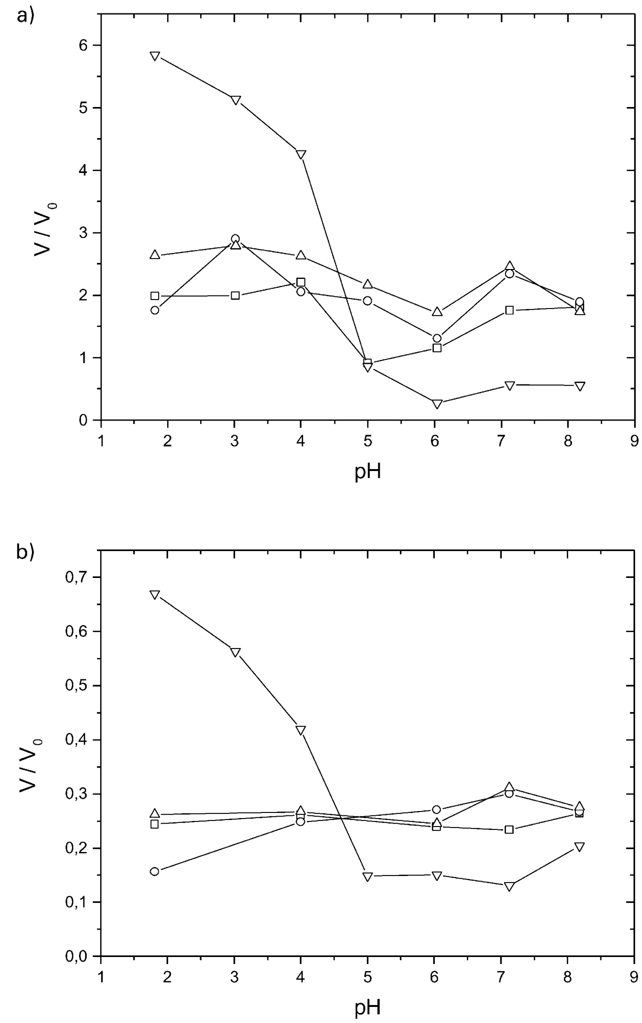


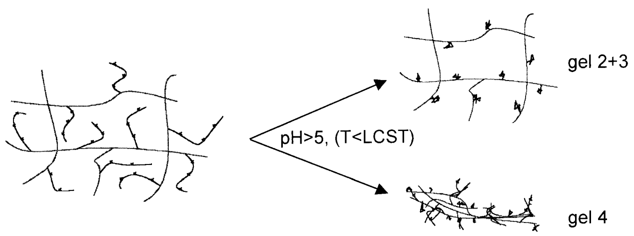
Fig. 2. Volume degree of swelling of graft copolymer gels in response to pH at constant temperature: (a) $T = 22$ °C; (b) $T = 41$ °C; (□—gel 1; ○—gel 2; △—gel 3; ▽—gel 4).

temperature dependent swelling curves of the graft copolymers at different pH values are shown in Fig. 1.

The graft copolymer gels show the typical swelling behavior for PNIPAAm gels. Independent from the composition the transition temperature (T_c) is around 28 °C. The shift of T_c towards lower values as compared with the behavior of PNIPAAm gels in water can be explained by the influence of the buffer solution (electrolyte effect). At pH 3 at lower temperatures, an increase of the P2VP content increased the degree of swelling of the gels, due to an increased electrostatic repulsion of the charged P2VP side arms. Interestingly at higher temperatures, all networks collapse to nearly the same degree of swelling. A dependence of the degree of swelling on the P2VP content could not be observed. It seems, that the attractive force of the collapsed network backbone is much stronger than the repulsive force of the charged side arms. At pH 7, the P2VP side arms are in their non-charged, hydrophobic form. A difference in the swelling curve due to additional hydrophobic interactions could only be observed at the highest P2VP content (Fig. 1(b)). There is no pH effect on the swelling behavior of gel 1.

The pH dependent degree of swelling of the graft copolymer gels at temperatures below and above T_c is shown in Fig. 2. In contrast to the temperature dependent measurements, only the graft copolymer with the highest P2VP content showed a pronounced swelling transition on changing pH value. The swelling ratios of the other gels remained nearly constant, approx. 2 at low temperatures (Fig. 2(a)) and approx. 0.2 at high temperatures (Fig. 2(b)). The difference between the swelling rates only corresponds to the transition of the PNIPAAm backbone.

The different behavior of graft copolymer gels with low and high P2VP contents might be explained as followed. In Table 1, the theoretical statistical distance between two P2VP side arms are listed. The different side arms are only able to interact and form additional junction points at the highest graft density. In this case, an additional effect on the degree of swelling was observed (Scheme 2). At lower



Scheme 2. Schematic picture of the deswelling of the graft copolymer gels in response to an increase of pH.

graft densities, the side arms are spacially separated. In the case of a transition of the side arms, they are too far from one another for aggregation. Thus the influence on the degree of swelling is only marginal. The swelling of the gels is dominated by the PNIPAAm backbone.

4. Conclusions

Through the synthesis of graft copolymer gels from NIPAAm and P2VP macromonomers, it is possible to obtain hydrogels with temperature and pH dependent swelling properties. The swelling behavior is mostly dominated by the PNIPPAm backbone. At high P2VP graft densities, a cooperative effect on changing the pH value could be observed. Hence, due to the separation of the temperature and the pH sensitive component it was possible to obtain a gel which could be swelled by either a change in the temperature or the pH.

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References

[1] Hirotsu S. Adv Polym Sci 1993;110:1–26.
[2] Liu Y, Velada JL, Huglin MB. Polymer 1999;40:4299–306.
[3] Champ S, Xue W, Huglin MB. Macromol Chem Phys 2000;201:931–40.
[4] Shibayama M, Fujikawa Y, Nomura S. Macromolecules 1996;29:6535–40.
[5] Feil H, Bae YH, Feijen J, Kim SW. Macromolecules 1992;25:5528–30.
[6] Yu H, Grainger DW. J Appl Polym Sci 1993;49:1553–63.
[7] Brazel CB, Peppas NA. Macromolecules 1995;28:8016–20.
[8] Kuckling D, Adler HJP, Arndt KF, Ling L, Habicher WD. Macromol Chem Phys 2000;201:273–80.
[9] Vakkalanka SK, Peppas NA. Polym Bull 1996;36:221–5.
[10] Chen G, Hoffman AS. Nature 1995;373:49–52.
[11] Yoshida R, Uchida K, Kaneko Y, Sakai K, Kikuchi A, Sakurai Y, Okano T. Nature 1995;374:240–2.
[12] Kaneko Y, Nakamura S, Sakai K, Aoyagi T, Kikuchi A, Sakurai Y, Okano T. Macromolecules 1998;31:6099–105.
[13] Wohlrab S, Kuckling D. J Polym Sci A, Polym Chem 2001;39:3797–804.
[14] Schild HG. Prog Polym Sci 1992;17:163–249.