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Copolymers and Hydrogels Based on Vinylphosphonic Acid

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ABSTRACT: Polyelectrolyte hydrogels have the advantage of a high swelling ratio and to respond to changes in pH and ionic strength which gives them useful characteristics for biomedical applications. To investigate the possibility to synthesize hydrogels from vinylphosphonic acid (VPA), first the free radical copolymerization of VPA and methyl acrylate (MA) was investigated at temperatures between 60 and 80 °C. Second free radical copolymerization of VPA with ethylene glycol diacrylate (EGDA) at 80 °C was studied to obtain a hydrogel. These copolymerizations were successful. For poly(VPA-*co*-MA) the solubility behavior, NMR spectra, and titration curves of the resulting products proved the existence of copolymers, and for poly(VPA−EGDA) gels a high mass swelling ratio in water was observed, showing that they behave as hydrogels. At pH values between 3 and 9 the degree of swelling displayed low dependence on pH, but deswelling upon addition of salt was observed. A total conversion between 15 and 79% was obtained for poly(VPA-*co*-MA) depending on the percentage of VPA in the feed and on the temperature. A higher conversion was achieved when the percentage of VPA in the feed was lower, and the polymerization temperature was higher. A nonideal behavior of the copolymerization in terms of VPA content in the resulting polymers as a function of VPA in the feed was observed. This was attributed to the participation of VPA−anhydride in the copolymerization process as an intermediate giving rise to cyclopolymerization.

Introduction

Hydrogels have attracted much interest due to their widespread applications in personal care products, in medicine, in agriculture as water storage granules and soil conditioners,[1] in chemical separation processes,[2] and in engineering, i.e., to protect communication cables against damaging and corrosive effects of salt water penetration.[3] Various types of gels based on the polymers of *N*-isopropylacrylamide,[2] acrylic acid,[4] vinyl alcohol,[5] ethylene glycol,[6] methacrylic acid,[6] and ethylene oxide[6] have been prepared, and they were analyzed in terms of the properties which change in response to specific environmental stimuli.

Hydrogels based on polymeric networks carrying ionic groups such as carboxylic acid and sulfonic acid moieties are referred to as polyelectrolyte hydrogels. Unlike for neutral hydrogels for which gels prepared from *N*-isopropylacrylamide and ethylene glycol are good examples, the dominant driving force for water uptake by the polyelectrolyte hydrogels is the inherent electrostatic repulsion between charged groups positioned on the polymer segments. The presence of ionizable groups on the polymer chains results in swelling of hydrogels much beyond of what can be achieved by nonionic hydrogels. Ionization equilibrium, buffer composition, and nature of the counterions play a very important role in determining the swelling behavior of polyelectrolyte hydrogels. In other words, swelling and deswelling of such gels can be triggered by changes in pH and ionic strength of the aqueous medium in contact with the gel.[7,8] The swelling behavior of polyelectrolyte networks has been widely studied in the literature.[9] Ionic hydrogels have found applications in biomedicine since they respond to changes in the physiological conditions to which they are exposed.[10] Hydrogels based on poly(acrylic acid) are among the most studied synthetic polyelectrolyte hydrogels.[4,10–15] Although poly(VPA) may be considered as one of the simplest polymer diprotic acids and has already been shown to exhibit properties typical for polyelectrolytes,[16] to the best of our knowledge, there exists only a very limited number of reports on the potential use of this polymer in form of a hydrogel. Copolymerization of acrylamide[17] and *N*-isopropylacrylamide[18] with VPA has been reported in context of the preparation of hydrogels supporting cell adhesion and proliferation which could be used as orthopedic tissue engineering scaffold[17] as well as thermally reversible nonshrinking hydrogels useful for drug delivery and in-situ biocatalyst immobilization.[18] But details of the copolymerization behavior of VPA with other comonomers have not been mentioned in the previous literature.

The aim of this paper is to explore the potential of VPA-based networks for hydrogel applications. We report on the preparation of the vinylphosphonic acid containing hydrogels as well as the swelling behavior of the resulting gels. Moreover, copolymerization of VPA with methyl acrylate was investigated in terms of a model study to prove that true copolymerization with ordinary vinyl monomers is possible.

Experimental Section

Materials. All chemicals were used as received unless otherwise noted. VPA (Aldrich, 97%; stabilized with 30–50 ppm hydroquinone) was washed with diethyl ether before copolymerization to remove the stabilizer. MA (Fluka, 99.5%) and EGDA (Aldrich, 90%) were distilled under reduced pressure. 2,2′-Azobis(isobutyroic acid amidine) dihydrochloride (AIBA) (Aldrich, 97%) was used as initiator. The synthesis of poly(VPA) has been described elsewhere in detail.[16]

Copolymer Synthesis. The synthesis of copolymers at various monomer feed ratios of VPA and MA was carried out in water or in a mixture of water with methanol at 60, 70, and 80 °C with AIBA as initiator. For instance, a copolymer with a 1:1 molar ratio of the comonomers in the feed was synthesized by dissolving VPA (0.509 g, 4.71 mmol) and MA (0.406 g, 4.71 mmol) in a water–methanol mixture. AIBA (1.26 mg, 0.1 mol % with regard

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Table 1. Experimental Conditions for Copolymerization of VPA with MA

T (°C)	mol % VPA	n_{VPA} (mmol)	mol % MA	n_{MA} (mmol)	n_{AIBA} (μmol)	V_{water} (mL)	V_{methanol} (mL)
60	20	1.93	80	7.72	1.92	0.06	0.045
60	30	2.77	70	6.48	2.77	0.086	0.064
60	40	4.22	60	6.32	4.20	0.130	0.098
60	50	4.71	50	4.71	4.65	0.255	0.189
60	60	13.9	40	9.30	13.9	0.750	0
60	70	16.2	30	6.90	16.2	0.875	0
70	30	2.82	70	6.61	2.81	0.087	0.065
70	70	7.15	30	3.07	7.15	0.385	0
80	30	2.77	70	6.48	2.76	0.086	0.064
80	70	6.48	30	2.78	6.49	0.350	0
80	90	8.34	10	0.93	8.26	0.450	0

to VPA) was added to the solution. The reaction mixture was placed in a NMR tube and was freed from oxygen by purging with argon prior to the polymerization. The reaction mixtures with other monomer feed ratios were prepared in the same way. Further details of the experimental conditions for the copolymerization of VPA with MA are given in Table 1. The reaction time at each temperature was selected such as to allow the same number of half-live times for the decomposition of the initiator in each experiment. More precisely, reaction mixtures were allowed to react for 20, 5.5, and 1.4 h at 60, 70, and 80 °C, respectively. The water-soluble poly(VPA-*co*-MA)s were purified by dialysis with Spectra/Por regenerated cellulose dialysis membrane (1000 g/mol cutoff). The resulting polymers were isolated by freeze-drying.

Synthesis of Poly(MA). Poly(MA) needed for the comparison with the poly(VPA-*co*-MA) was obtained using similar experimental conditions as in the synthesis of the copolymers. MA (0.79 g, 9.25 mmol) and AIBA (2.77×10^{-3} mmol, 0.75 mg) were dissolved in a water/methanol mixture (8.6×10^{-2} mL/1.93×10^{-1} mL) and reacted at 60 °C for 20 h.

Preparation of Hydrogels. The hydrogel was prepared by reacting VPA (0.951 g, 8.33 mmol) and EGDA (0.158 g, 0.93 mmol) in water (0.45 mL) in the presence of 0.1 mol % AIBA with regard to VPA at 80 °C for 1.4 h. The resulting gel was soaked in water to eliminate the unreacted VPA. Purification of the hydrogel was considered as complete when the solution with which the hydrogel was washed attained a constant pH of 7.0.

Gel Swelling. The swelling behavior of the VPA-based hydrogels prepared via free radical polymerization of VPA with EGDA was investigated in aqueous buffer solutions and in pure water. 0.5 M phosphoric acid-based buffer solutions of pH = 3 ($[H_3PO_4] = 0.059$ M, $[KH_2PO_4] = 0.441$ M), pH = 5 ($[H_3PO_4] = 6.65 \times 10^{-4}$ M, $[KH_2PO_4] = 0.499$ M), and pH = 9 ($[KH_2PO_4] = 0.008$ M $[K_2HPO_4] = 0.492$ M) were used. The hydrogels were allowed to equilibrate for 1 h in a buffer solution with a particular pH prior to weighing. At first, the mass of the hydrogel after it had been purified from residual VPA was recorded before it was exposed to any buffer solutions. Afterward, the hydrogel was immersed in 0.5 M phosphoric acid buffer solution of pH = 3 for 1 h and left to equilibrate at 25 °C, before the hydrogels were weighed. Next, the same piece of the hydrogel was allowed to equilibrate with pure water until a constant pH of 7 was attained in the contacting water phase before it was immersed into the next phosphoric acid-based buffer solution at pH of 5. The mass of the hydrogel was recorded before it was immersed into the buffer solution. This procedure was repeated with the buffer solution of pH 9. After the exposure of the sample to the buffer with pH 9, the hydrogel was equilibrated in water for 12 h, and its mass was determined by gravimetry. The mass of the hydrogel in its dry form was determined after storing the hydrogel in a vacuum oven at 20 °C overnight while the mass of the swollen form was determined after blotting off surface attached moisture gently by filter paper. The mass swelling ratio of the gel samples was characterized by the ratio m/m_0, where m is the mass of the gel swollen in aqueous solution and m_0 is the mass of the dry gel.

Lower and Upper Critical Solution Temperature (LCST and UCST) of Poly(VPA). The changes of the physical appearance of the aqueous solutions of poly(VPA) (of concentrations of 21.7, 18.8, 11.0 and 6.5 wt %) was studied as a function of temperature by the naked eye to determine the LCST and UCST of poly(VPA). They were heated from room temperature to 30, 40, 50, 60, 80, and 85 °C and kept at each temperature for at least 30 min. In addition, the physical appearance of the poly(VPA) solutions of 11.0 and 6.5 wt % was followed at 4 °C.

Characterization. ^{1}H NMR spectra were recorded in solution with a Bruker spectrometer operating at 500 MHz. D_2O and $CDCl_3$ were used as solvents unless noted otherwise.

Titrations of the purified copolymer containing 47 mol % of VPA were conducted with a Metrohm Titranda 836 at 25 °C. Solutions of the copolymer (1 g/L) were prepared in aqueous NaCl (0.85 M) and titrated with 0.1 N NaOH.

Results and Discussion

It was the intention to prepare hydrogels of poly(VPA) by free radical copolymerization of VPA and EGDA, the latter working as cross-linker. As data on copolymerization of VPA and acrylic monomers are not only scarce but contradictory, it was decided to first investigate the copolymerization of VPA and MA. This is nontrivial in the light of our findings[13] that homopolymerization of VPA proceeds in reality as a cyclopolymerization of the vinylphosphonic acid anhydride which gives origin to at least two different types of propagating radicals in chain growth and, in consequence, both head−tail and head−head−tail−tail connectivities of the constitutive units of poly(VPA).

Copolymerization of VPA with MA. Free radical copolymerization of VPA with MA was conducted with various feed compositions at 60, 70, and 80 °C (Table 1). The copolymers were obtained from VPA/MA feed molar ratios ranging from 1:4 to 9:1. AIBA was used as a water-compatible initiator because water or water–methanol mixtures were chosen as reaction solvent on account of previous experience in the homopolymerization of VPA.[16] It was necessary to add some methanol to the aqueous reaction mixture containing less than 60 mol % of VPA in the feed when polymerization was carried out at 60 °C to achieve homogeneous solution conditions. Polymerizations carried out at 80 °C needed addition of methanol when the VPA content in the monomer feed was below 30 mol % for the same reason. The reaction time was varied depending on the polymerization temperature such as to allow the same number of half-lives for AIBA decomposition in each experiment.

Conversions to copolymers were determined for all feed compositions and reaction temperatures by taking ^{1}H NMR spectra of the reaction mixtures prior to the purification and comparing the relative intensities of the resonances of the polymer backbone protons with those of vinyl protons left over after the polymerization was stopped. The protons located at the polymer backbone show signals between 1.8 and 3.0 ppm, whereas the resonances due to vinyl protons in VPA appear between 6.0 and 7.0 ppm. Conversions to copolymers were found in the range from 15% to 79% depending on the feed composition as well as on the temperature (Table 2). The conversion was highest (79%) when the copolymerization was carried out at a VPA/MA molar ratio of 30/70 in the feed at 70 °C. The overall conversion was observed to decrease with increasing fraction of VPA in the feed. This observation was valid for all reaction temperatures studied in this work. Since the same concentration of 0.1 mol % of initiator (relative to VPA) was used in all experiments, the decrease of conversion with increasing feed ratio of VPA may be interpreted by suggesting that a fraction of the radicals formed by decomposition of AIBA is quenched in a side reaction with VPA before they can initiate the polymerization.

Table 2. Analytical Composition of the Copolymer and the Conversions of the Copolymerization of VPA with MA

T (°C)	concentration of the initiator (mM)	VPA in feed (%)	total conversion (%)	VPA in the polymer (%)
60	2.0	20	78	13
	2.9	30	56	16
	3.7	40	70	19
	3.8	50	59	22
	3.8	50	72	44
	5.2	60	60	48
	5.2	60	41	59
	5.9	70	49	47
	5.9	70	43	60
	6.9	90	15	80
70	2.9	30	79	13
	5.9	70	45	42
80	2.9	30	78	12
	5.9	70	47	43
	7.0	90	25	68

In the beginning it was not clear whether true copolymers or only a mixture of homopolymers was formed. However, the differences in the solubility between the copolymers and the homopolymers of VPA and MA helped to prove that copolymers of VPA and MA were obtained. The solubility behavior of all resulting polymers is presented in Figure 1, which is divided into three regimes on the basis of the differences in solubility of the resulting copolymers. All (co)polymers were soluble in dimethylformamide which does not dissolve poly(VPA). Polymers obtained from feeds containing 40 to 50 mol % of VPA could be dissolved in methanol, which is a nonsolvent for poly(MA) (regime II in Figure 1). Carrying out the polymerization at a content of 30 mol % of VPA in the feed, or less, at 60 and 70 °C led to products of different solubility. The product obtained at 60 °C was water-soluble, whereas the copolymer prepared at 70 °C was found to be insoluble in water. This indicates that remarkable solubility changes occur on the edges of each regime and that the microstructure of the copolymers may indeed depend to some extent on the temperature of polymerization. Carrying out the copolymerization with more than 70 mol % of VPA in the feed gave water-soluble products only (regime III).

^{1}H NMR spectra of the samples revealed the analytical composition of the polymers. The integration of the peak corresponding to the methyl groups in the copolymer gives the proportion of MA reacted with VPA. The fraction of VPA incorporated was calculated by subtracting the intensities of the backbone protons due to the polymerization of MA from the sum of the intensities of backbone protons. Knowing the fraction of each comonomer in feed and in the polymer, a preliminary copolymerization diagram was obtained as shown in Figure 1. We like to call it "preliminary" since for the reasons of solubility of the polymer in the reaction medium the composition of that medium could not be kept constant over the full range of monomer composition ratio. Moreover, as the data in Table 2 indicate, the conversion was in almost all cases above 50%, and in consequence, the composition of the product does not truly reflect the initial composition at small conversions. Nevertheless, the data in Figure 1 indicate that the fraction of VPA incorporated into the polymer is rather independent of the feed composition as long as the concentration of VPA does not exceed 40 mol % in the feed when the polymerization was performed at 60, 70, and 80 °C. Beyond this point, the fraction of VPA in the copolymer increases remarkably with increasing content of VPA in the feed. It displays dependency on the feed composition as well as on the reaction temperature. The maximum amount (80 mol %) of VPA was incorporated when the copolymerization was carried out in the presence of 90 mol % of VPA in the feed at 60 °C (cf. Table 2). The temperature was observed to influence the proportion of each comonomer in the polymer to a greater extent when the feed ratio of VPA was higher than 40 mol %. The copolymerization diagram implies that the copolymerization of VPA with MA follows a nonideal behavior (the solid diagonal in Figure 1 represents the ideal case where monomers have equal reactivity in propagation). The deviation from the ideality becomes more pronounced with increasing reaction temperature and increasing fraction of VPA in the feed. The deviations from the ideality may be a consequence of the nature of the polymerization mechanism of VPA. As was reported earlier,[16] the homopolymerization of VPA was shown to involve cyclopolymerization of VPA anhydride as an intermediate. The extent to which VPA anhydride is formed depends on several parameters such as concentration of VPA solvent composition and temperature. In light of the present results, one is tempted to conclude that the nature of the polymerization mechanism of VPA leads to a competition between the propagation of the chain via different radicals created by cyclopolymerization of the anhydride. This is reflected by the unusual features of the copolymerization diagram and the temperature dependence of the copolymer composition which is outside the expectations for free radical copolymerizations. In particular, the nonsteady behavior of the system around 50% VPA in the feed may indicate that the contribution of the VPA anhydride becomes significant around this concentration.

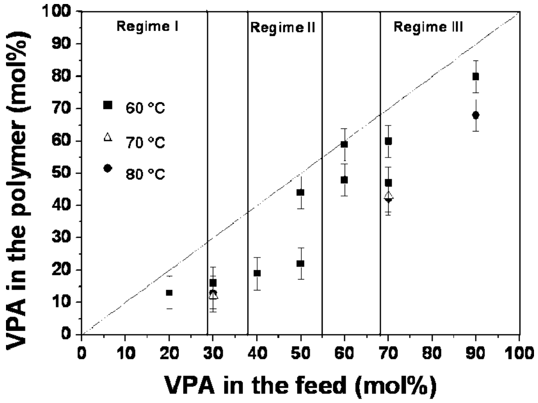


Figure 1. Copolymerization diagram and solubility behavior of the poly(VPA-*co*-MA). Different regimes indicate differences in the solubility of the copolymers. Regime I: water and methanol insoluble, DMF soluble. Regime II: water insoluble, methanol soluble, DMF soluble. Regime III: water and methanol soluble, DMF soluble. The error bars indicate the estimated error in determining composition from the ^{1}H NMR spectra of the products.

Figure 2 shows the ^{1}H NMR spectrum of poly(VPA-*co*-MA) with 47 mol % of VPA incorporated into its structure, and this spectrum is given as an example for the features seen in all the spectra of the obtained copolymers. The ^{1}H NMR spectra of all copolymers were similar but with signal intensities varying according to composition. However, copolymer spectra are significantly different from the spectra of the respective homopolymers, namely poly(VPA)[16] and poly(MA),[19] synthesized under similar experimental conditions. ^{1}H NMR spectra of the homopolymers are presented in Figure 2a,c. The copolymer spectra exhibit signals between 3.0 and 4.0 ppm, which are absent in the ^{1}H NMR spectra of the respective homopolymers. In addition, signals are seen between 3.1 and 2.0 ppm associated with the backbone protons of poly(VPA) and poly(MA). The number of signals observed in the ^{1}H NMR spectra shown in Figure 2b may be interpreted as a fingerprint of the sequences present in the copolymer. In a first attempt to interpret the NMR spectra of the copolymer, one needs at least to consider triad sequences. The resonances located between 1.0 and 3.0 ppm

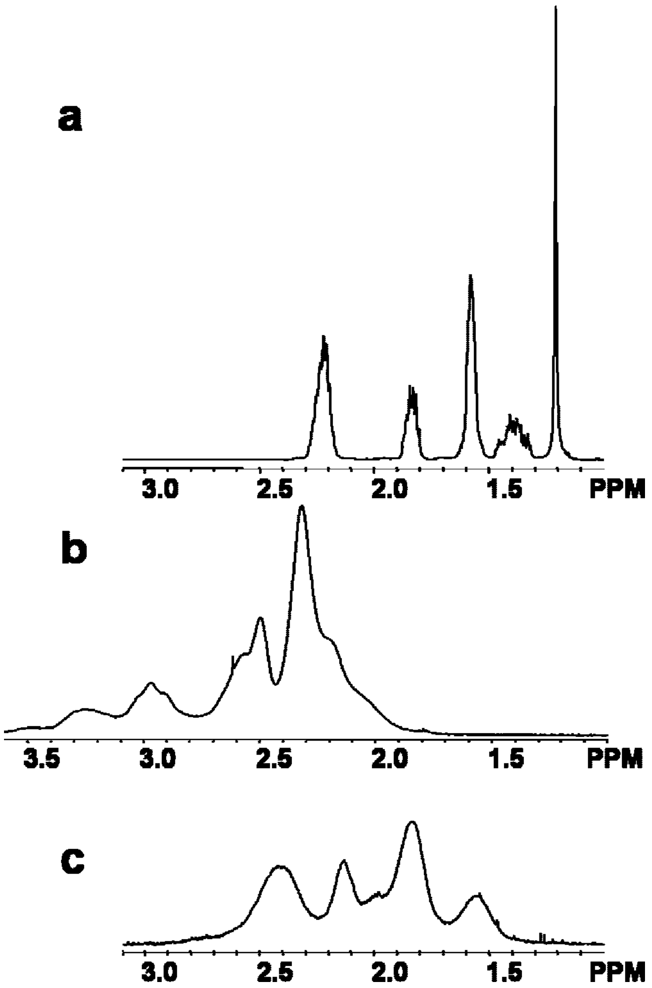
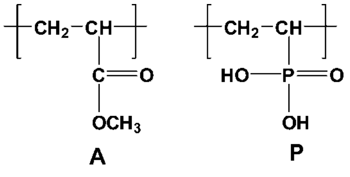


Figure 2. ^{1}H NMR spectra of (a) unpurified poly(MA) in $CDCl_3$, (b) poly(VPA-*co*-MA) with 47 mol % of VPA in D_2O after purification, and (c) poly(VPA) in D_2O after purification.

Scheme 1. Chemical Structures of Repeating Units of Poly(MA) and Poly(VPA)



are assigned to the sequences AAA and PPP (A and P represent MA and VPA repeat unit, respectively, as shown in Scheme 1). In these sequences, the monomer unit in the middle does not sense the presence of unlike species in the vicinity. Therefore, signals with the most similar chemical shift to the resonances in the respective homopolymers in the ^{1}H NMR spectrum of poly(VPA-*co*-MA) are assigned to the protons belonging to the triad sequences AAA and PPP. The middle monomer unit in the triad sequences of PAA, APA, PPA, and APP is in close proximity to at least one monomer unit of the other kind. Therefore, protons due to these sequences are expected to have signals at a different chemical shift compared to the protons of the sequences AAA and PPP. Thus, resonances between 3.0 and 4.0 ppm in the ^{1}H NMR spectra of the copolymer are tentatively assigned to the triad sequences PAA, APA, PPA, and APP. The fraction of these sequences is obtained as 22% by comparing the intensities of the signals due to these sequences with the integral over all signals.

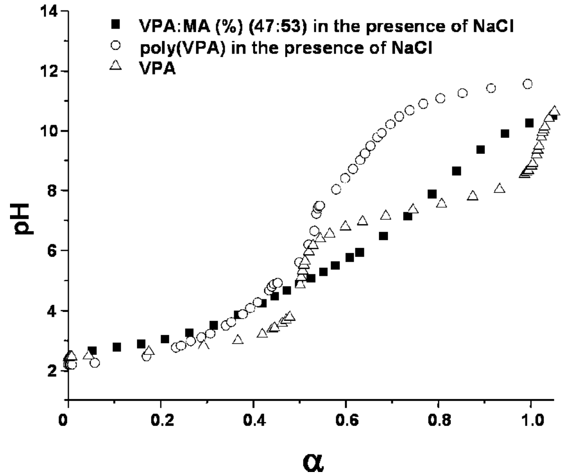


Figure 3. Titration curves of poly(VPA-*co*-MA) with 47 mol % of VPA and poly(VPA) in the presence of NaCl and titration curve of VPA. α is the nominal degree of neutralization in terms of equivalents of the bases added per phosphonic acid group.

Although one could be tempted to calculate the fraction of these triads, applying the rules of copolymer statistics this would give utterly incorrect results in the present case. As indicated above, free radical polymerization of VPA seems to occur via cyclopolymerization of the VPA anhydride. This in turn brings propagating radicals of different structures into play,[16] which results in a rather complex kinetic scheme for the copolymerization even if one does not consider penultimate effects, etc.

The titration curve of poly(VPA-*co*-MA) containing 47 mol % of VPA was investigated using potentiometric titration. The development of pH as a function of nominal degree of neutralization is displayed Figure 3 for (a) a solution of a copolymer, (b) poly(VPA) with nearly equimolar composition of the comonomer, and (c) for comparison, the titration curve of VPA.[16] It is worth noting that the nominal degree of neutralization of the copolymer was calculated by taking the analytical composition of the copolymer revealed by NMR studies into account. Thus, the molar mass of a hypothetical monomer composed of 47 mol % of VPA and 53 mol % of MA was calculated by

$$m_{\text{(hypothetical monomer)}} = (\text{molar mass})_{\text{VPA}} \times \text{fraction}_{\text{VPA}} + (\text{molar mass})_{\text{MA}} \times \text{fraction}_{\text{MA}}$$

All solutions contained NaCl at a concentration of 0.85 M. The titrations were carried out with 0.1 N NaOH. Titration curves of this copolymer indicate a linear increase in pH up to degree of neutralization 0.61. This is followed by a steeper increase in pH with increasing nominal degree of neutralization until the limiting value of pH is reached. The copolymer (with 47 mol % VPA) exhibits the same starting pH as the poly(VPA), and the two titration curves also show similar behavior up to degree of neutralization of 0.27, indicating a presence of acidic groups of similar strength in poly(VPA) and in poly(VPA-*co*-MA). After this point, the absolute value of pH observed in the curve of the copolymer is smaller than in the curve of poly(VPA), indicating that additional protons, as in the case of the VPA monomer,[16] are removed from the copolymer. It is expected that the phosphonic acid groups in the triad sequence PPP and in poly(VPA) are similar in their acidity, whereas the acidic groups in the triad sequences PAA, APA, PPA, and APP exhibit dissimilar acidity. The titration curve of the copolymer does not exhibit a well-defined end point. However, it is obvious that the titration curve of the copolymer bears resemblance to the titration curve of the VPA as shown in Figure 3, albeit the distinctively separate neutralization steps seen in the VPA are

Scheme 2. Schematic Representation of Poly(VPA) Cross-Linked with EGDA

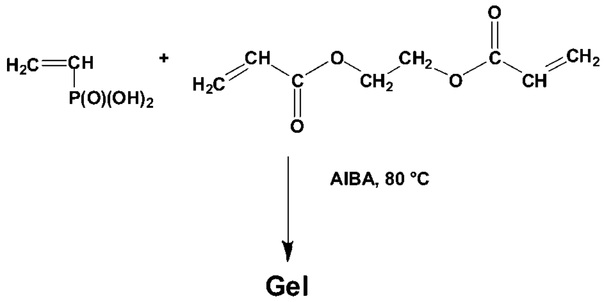


Table 3. Swelling Step Sequence and Mass Swelling Ratios of the Poly(VPA-*co*-EGDA) Hydrogel

step sequence	pH of swelling medium	mass swelling ratio
1[a]	7	14.05
2[b]	3	7.72
3[a]	7	12.71
4[b]	5	8.61
5[a]	7	17.73
6[b]	9	9.50
7[a]	7	19.40

[a] Pure water. [b] See Experimental Section.

rather smeared out in the copolymer. This indicates that the copolymer possesses more protons that can be neutralized than the homopolymer.

VPA-Based Hydrogels. Given that VPA can be copolymerized with MA, VPA-based hydrogels were synthesized by polymerization of VPA in the presence of a relatively small amount of a difunctional cross-linker having a similar chemical structure as MA, namely EGDA (Scheme 2). AIBA was used as the initiator, and the polymerization was carried out at 80 °C. The molar ratio of VPA to EGDA was 9:1 in the feed. As expected, the product was a gel. It was washed with water to remove the nonreacted VPA. The yield of the copolymerization of VPA with EGDA was calculated as 10% by comparing the mass of the monomers in the feed with the dry mass of the hydrogel.

The first step in the characterization of a hydrogel is to determine its equilibrium swelling ratio since most of the properties of the gel are influenced by the swelling ratio.[2] To investigate the influence of external conditions on the swelling ratio, hydrogels obtained from the copolymerization of VPA with EGDA were tested in various buffer solutions. The swelling of the hydrogels was followed by gravimetry as a function of the pH of the swelling medium. In consequence, the gel was exposed to 0.5 M phosphoric acid buffer solutions of pH 3, 5, and 9 as well as to pure water. The swelling ratio was obtained by comparing the mass of the wet and dry hydrogel. The mass swelling ratios of poly(VPA-*co*-EGDA) are given in Table 3. It reveals that the VPA-based hydrogel absorbs significant amount of water. For example, the mass swelling ratio for this hydrogel was found as 8 (step sequence named as 2 in Table 3) after exposing the gel to the phosphoric acid buffer with a pH of 3 for 1 h at 25 °C. Exposing the same gel to phosphoric acid buffers each one fixing a different pH (Table 3) clearly indicates that the swelling ratio displays low dependence, if any, on pH. The swelling ratio obtained after equilibrating the sample in water before exposing it to another buffer solution was higher (step sequence named as 1) than any previous value in the sequence of exposures. Comparing the mass swelling ratios of the hydrogel determined after equilibrating the sample with pure water before it was immersed to the next buffer solution (step sequences names as 3, 5, and 7 in Table 3) clearly indicates an increase in the mass swelling ratio as a consequence of the prolonged exposure of the gel to more basic conditions. For instance, a swelling ratio of 19 was observed (step sequence named as 7 in Table 3) after equilibrating the gel in water after it had been exposed to the buffer with a pH of 9 for 12 h. The increase in the mass swelling ratio after exposing the sample to more basic conditions is tentatively explained by the change of the cross-link density of the gel. Since EGDA was used as the cross-linking agent, hydrolysis of the ester groups upon prolonged exposure to basic conditions may be at the origin of the observed effect. The variation of the cross-linking density will influence the balance between different forces leading to a change in the equilibrium swelling ratio.[16] The hydrolysis of the carboxylic esters under acidic or alkaline conditions is well-known in the literature.[20] The experimental observations imply that the hydrolysis takes place to a greater extent when the hydrogel was allowed to equilibrate with an alkaline medium.

The phase diagram of a polymer/solvent mixture and specifically the presence of a lower critical (LCST) or upper critical solution temperature (UCST) determine whether the polymer expands or contracts upon changes in temperature. For that reason it was investigated whether poly(VPA) in an aqueous solution exhibits LCST or/and UCST behavior. It could be observed that the aqueous solutions of poly(VPA) in concentration range from 25 to 6.5 wt % showed no difference in the appearance upon increasing the temperature from room temperature to 85 °C. The solutions became more transparent upon dilution. The poly(VPA) solutions of 11.0 and 6.5 wt % were kept at 4 °C for overnight, but no change of the physical appearance of the solutions was observed. These experimental observations indicate the physical appearance of aqueous poly(VPA) solutions did not change as a function of temperature and that the persistence of turbidity in concentrated aqueous solutions of poly(VPA) implies that water is a poor solvent for poly(VPA) at these conditions.

Conclusions

It was the aim of this investigation to probe whether hydrogels could be prepared from VPA and a conventional bifunctional cross-linker, namely EGDA by free radical copolymerization. VPA is an interesting monomer and an analogue of acrylic acid. Unlike poly(acrylic acid), poly(VPA) has found little attention in polymer science so far as consequence of difficulties encountered with the polymerization of VPA or its esters. These could only be overcome very recently[16] with the demonstration that high molecular weight poly(VPA) can be synthesized via a free radical mechanism and with involvement of VPA anhydride as a possible intermediate. The latter forms spontaneously in the monomer feed under suitable polymerization conditions. Copolymerization of VPA and other monomers is a virtually unexplored field. Copolymerization of VPA with bifunctional comonomers would open a route to novel hydrogels. Along these lines of thought, the copolymerization of VPA with MA needed to be investigated first to probe the copolymerization behavior of VPA with a monomer that is structurally akin to EGDA. The copolymers serve as model to study the interaction of the network chains with water and more importantly their response to changing pH conditions. Therefore, it was important to record the titration curves of the copolymers with respect to the homopolymers behavior.

VPA was copolymerized successfully with MA via free radical polymerization at temperatures between 60 and 80 °C in aqueous medium. The copolymerization diagram implies that the polymerization of VPA with MA follows a nonideal behavior with dependence of the copolymer composition on temperature at high fractions of VPA in the feed. The deviations from the ideality probably arise from the nature of the polymerization mechanism of VPA, which involves the participation of cyclopolymerization of VPA anhydride as a potential precursor as was shown for the homopolymerization of VPA.[16] Solubility studies of the resulting polymers proved that true copolymers of VPA and MA have been obtained and not mixtures of homopolymers. Titration curves of the poly(VPA-*co*-MA) indicated the presence of functional groups of other acidity than the ones on poly(VPA), and from the ^{1}H NMR spectra of the purified copolymers the presence of different triads could be inferred. VPA-based hydrogels were prepared by copolymerization of VPA with EGDA via free radical polymerization at 80 °C. Swelling studies revealed that VPA-based hydrogels absorb significant amount of water. Moreover, the swelling ratio of the VPA-based hydrogels displayed low dependence on pH.

There is a recent interest in poly(VPA) related to its possible application in fuel cells as the key constituent of polymer electrolyte membranes (PEM). Employing of poly(VPA) as proton solvents in the fuel cell membranes requires cross-linked poly(VPA). Cross-linking of poly(VPA) is crucial for fuel cell applications in order to cope with problems encountered with the water management of the PEM. The present work can be considered as a preliminary study to demonstrate that well-defined poly(VPA) gels can be prepared. Further work will concentrate on their potential application for fuel cell construction. There is a recent study concerning the cross-linking of poly(VPA). However, materials prepared in this study are ill-defined.[21]

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