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Research Article

Direct Synthesis of Hyperbranched Poly(acrylic acid-co-3-hydroxypropionate)

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Hyperbranched poly(acrylic acid-co-3-hydroxypropionate) (PAcHP) was synthesized by base-catalyzed hydrogen transfer polymerization of acrylic acid through one step. The copolymers obtained through solution and bulk polymerization were insoluble in water and all organic solvents tried. Structural and compositional characterizations of hyperbranched PAcHP were performed by using FTIR, solid ^{13}C-NMR, TGA, and titrimetric analysis. Acrylate fraction of the hyperbranched PAcHP obtained via bulk polymerization was determined as 60–65% by comparing TGA curves of hyperbranched PAcHP and pure poly(3-hydroxy propionate) (PHP). However, analytical titration of the same sample revealed that acrylic acid units were about 47.3%. The results obtained from TGA and analytical titration were used to evaluate the chemical structure of the copolymer. Hyperbranched PAcHP exhibited hydrogel properties. Swelling behavior of the copolymer was investigated at a wide pH range and ionic strength. The dynamic swelling profiles of hyperbranched PAcHP exhibited a fast swelling behavior in the first hour and achieved the equilibrium state within 12 h in PBS. Depending on the conditions, the copolymers exhibited swelling ratios up to 2100%. As the copolymer has easily biodegradable propionate and versatile functional acrylic acid units, it can be used as not only biodegradable material in medical applications but also raw material in personal care commodities.

1. Introduction

Base-catalyzed hydrogen transfer polymerization (HTP) is an anionic polymerization route applied to vinyl monomers containing loose hydrogen atom(s). Strong bases as an initiator, a radical polymerization inhibitor, and an aprotic solvent (in case of solution polymerization) are used to perform the polymerization. Base-catalyzed HTP was reported for the first time by Breslow et al. [1] to obtain poly-β-alanine from acrylamide. Breslow et al. [1] revealed that base-catalyzed HTP of acrylamide, methacrylamide, crotonamide, and so forth resulted in the corresponding aliphatic polyamides. Then, many scientists reported kinetics [2, 3], mechanism [4–6], and application of base-catalyzed HTP to various acrylamide derivatives [7–11]. Base-catalyzed HTP was not interesting for scientists possibly due to the low degree of polymerization (DP) [2–8], uncontrolled branching [12, 13], sometimes low yield [7, 8], and applicability to limited monomers.

Saegusa et al. [14] reported that base-catalyzed HTP of acrylic acid yielded oligomeric poly(3-hydroxy propionate) which is a biodegradable thermoplastic polyester. Yamada et al. [15] reported that poly(3-hydroxy propionate) with higher molecular weight might be synthesized by HTP of acrylic acid in the presence of crown ether as a cocatalyst. In the study, Yamada et al. [15] fractionated the polymerization products as firstly ether-soluble and ether-insoluble (chloroform soluble) and then ether-insoluble fraction as water-soluble and water-insoluble. Yamada et al. [15] have isolated an insoluble fraction in all organic solvents as a product of HTP for long reaction times and attributed it to vinyl polymerization product (polyacrylic acid). But some points still remained unclear. Rozenberg et al. [3, 16] have recently published many detailed studies on mechanism and kinetics of base-catalyzed HTP of hydroxyethyl (met) acrylate [16] and some acrylamide derivatives [3]. Rozenberg et al. elicited complex mechanism of HTP and well-characterized the structures of the hyperbranched products.

Table 1: Base-catalyzed HTP of acrylic acid at different experimental conditions.

[M] moles	[I] moles	Temperature (°C)	Time (h)	Solvent	$f1$ %	$f2$ %	$f3$ %	$f4$ %
0.1	0.001	60	72	N/A	79.4	20.3	0.3	—
0.1	0.001	100	240	N/A	3.2	13.2	2.1	81.5
0.1	0.001	100	240	Pyridine	1.7	16.0	5.5	76.8
0.1	0.001	60	240	Pyridine	58.6	34.6	0.9	5.9

Our study aims to reveal the structure and swelling properties of insoluble fraction obtained HTP of acrylic acid and to propose possible application field(s). In this study, HTP of acrylic acid was carried out in bulk and solution phase for long reaction times. Chemically distinct fractions of both (bulk and solution) polymerization products were isolated successfully. Insoluble fraction of bulk polymerization product was characterized by using spectroscopic, thermal, and analytical methods. Swelling behavior of the insoluble fraction was investigated at a wide PH range and ionic strength.

2. Materials and Methods

2.1. Polymerization. Anhydrous acrylic acid (99%, Sigma), potassium tert-butoxide (≥99.0%, Aldrich), and anhydrous pyridine (99% Acros Organics) were purchased commercially and used as obtained. Polymerization reactions were tabulated in Table 1. Reaction mixtures in Schlenk flask were stirred under argon atmosphere in dark. Reaction mixture was poured into excess amount of diethyl ether to precipitate out. Ether-soluble fractions (fraction 1) were isolated by evaporation of ether using rotary evaporator. Ether-insoluble white crystals were then treated with chloroform to extract poly(3-hydroxy propionate) (PHP) which is named as fraction 2. Chloroform insoluble part was then filtrated, dried, and treated with methanol to extract polyacrylic acid (fraction 3). Methanol insoluble fraction (fraction 4), which is insoluble in water and all organic solvents tried, was dried at 60°C in vacuum oven.

2.2. Characterization. Polymerization products were characterized using FTIR, ^{1}H-NMR, ^{13}C-NMR, solid ^{13}C-NMR, TGA, and titrimetric method. FTIR spectra of PHP and PAcHP samples were recorded using Shimadzu IRAffinity-1. FTIR data processing was carried out using Shimadzu IRSolution 1.50 provided by Shimadzu Corporation. ^{1}H-NMR and ^{13}C-NMR spectra of PHP in $CDCl_3$ were recorded using 500 MHz Varian NMR spectrometer. Solid ^{13}C-NMR spectra of insoluble products were recorded using Varian Mercury 300. NMR data was processed using MestReNova 6.0.2-5475 software. TGA thermograms of polymer samples were obtained using TA instrument Hi-Res TGA 2950 with 10°C min^{-1} heating rate under nitrogen flux. Insoluble fraction (PAcHP) samples were titrated using standardized 0.05 N NaOH to determine the degree of acrylic acid units in the copolymer samples.

2.3. Swelling Ratios of Hydrogels. Swelling behavior of the hyperbranched PAcHP copolymer obtained from bulk polymerization was investigated in phosphate-buffered saline (PBS) solutions with different pH values (4, 6, 7, 8, 10, and 12). Completely dry, irregular shaped hydrogels were weighed and then immersed in 25 mL of PBS solutions with different pH at room temperature. At a predetermined time point, the hydrogel was removed from the solution and weighed after wiping with a filter paper for the removal of the free solution on the surface. After each weighing, the samples were returned to the containers with refreshed buffer solution. All experiments were performed in triplicate.

Swelling ratios (SRs) of samples were calculated as follows:

$$\mathrm{SR} = \left(W_t - W_d\right) * \frac{100}{W_d}, \tag{1}$$

where W_d is the weight of dry samples and W_t is the weight of wet samples at time t.

Na_2SO_4 solutions with different ionic strengths (0.025, 0.010, 0.25, and 1.000 M) were used to evaluate the salt effect on the swelling of PAcHP hydrogels at room temperature. The same swelling protocol and calculation route were applied as mentioned above.

2.4. Swelling-Deswelling Behavior of the Hydrogels. Swelling-deswelling behavior of the PAcHP hydrogels was examined using pH = 2.0 and pH = 12.0 buffer solutions. Swelling ratios of the hydrogels were determined according to (1) at consecutive time intervals. The experiments were performed in triplicate and the average of results was reported.

3. Results

3.1. Base-Catalyzed Hydrogen Transfer Polymerization of Acrylic Acid. As shown in Table 1, hyperbranched polymer was not formed at the first stage (in a few days) of the polymerization. At this stage, HTP and uncontrolled radical vinyl polymerization occurred. One of the most important results is formation of hyperbranched polymers at elevated temperature and in longer reaction time. This may be due to (i) conversion of living PHP chains to hyperbranched PAcHP through addition of new monomers to the propagating PHP chains as acrylic acid units and then branching and (ii) viscous reaction medium hindering proton transfers to carbanion atom and thus carbanion atom getting involved in anionic vinyl polymerization instead of proton transfer.

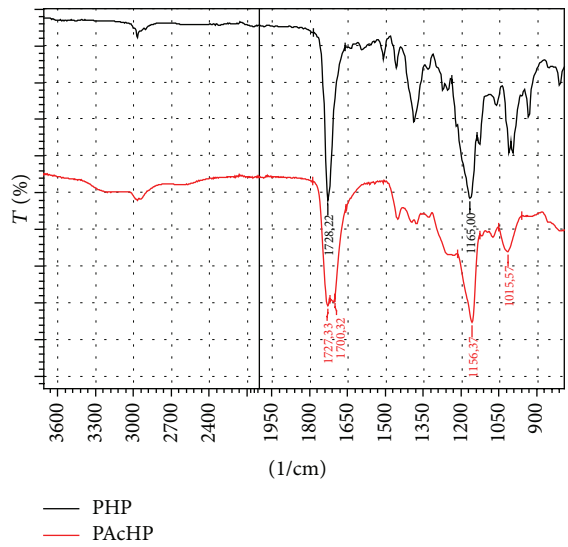

Figure 1: FTIR spectra of PHP (black line, upper) and PAcHP (red line, bottom) obtained from bulk polymerization.

Pyridine, which was the best solvent for HTP of acrylamide [1], exhibited positive effect on formation of PHP (an increment from 13.2% to 16.0%). This may be due to contribution of the basic solvent to the hydrogen transfer from monomers or propagating chain-ends.

3.2. Characterization of Polymerization Products

3.2.1. FTIR Spectroscopy. FTIR spectra of fraction 2 and fraction 4 obtained from bulk polymerization were recorded to understand the differences in functional groups in both fractions 2 and 4. Although spectrum (a) in Figure 1 has only a characteristic ester carbonyl stretching band at about 1728 cm^{-1}, spectrum (b) has two carbonyl stretching bands at about 1727 and 1700 cm^{-1}. The band at about 1700 cm^{-1} may be attributed to acid carbonyl which is commonly seen in the 1690–1720 cm^{-1} range. Furthermore, broad band at asymmetric OH stretching region (3000–3500 cm^{-1}) in spectrum (b) intensifies the existence of carboxylic acid units in fraction 4. This approach may be outlined as follows: fraction 2 is a polyester (PHP) and fraction 4 has both ester units and carboxylic acid units.

3.2.2. NMR Spectroscopy. ^{1}H-NMR spectrum of fraction 2 in Figure 2 was recorded to ensure that it was a linear homopolymer of 3-hydroxypropionate (PHP). Two triplets at 2.9 and 4.6 ppm belong to methylene protons next to the oxygen atom and carbonyl group, respectively. Peak groups at about 6.2 ppm were attributed to the olefinic end-group protons shown in Figure 2. Considering the peak intensities belonging to chain-ends, it may be concluded that fraction 2 consisted of oligomeric PHP.

Since fraction 4 was not soluble in water and all organic solvents tried, solid ^{13}C-NMR spectrum of fraction 4 was recorded and compared to ^{13}C-NMR spectrum of fraction 2

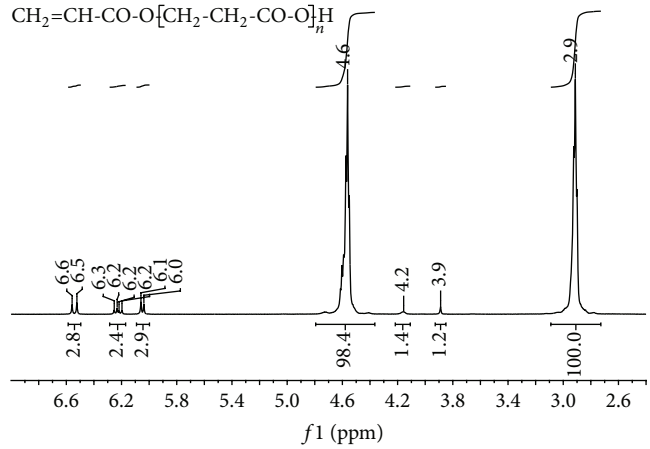

Figure 2: ^{1}H-NMR spectrum of PHP.

(oligomeric PHP) as shown in Figure 3. Considering that the ^{13}C-NMR spectrum of polyacrylic acid [17] reported previously has three peaks for CH_2 (32 ppm), CH (39 ppm), and COOH (184 ppm), ^{13}C-NMR spectrum of fraction 4 may be attributed to combination of acrylic acid and 3-hydroxypropionate units. The peak with low intensity at about 94.5 ppm corresponds to olefinic carbons at chain-ends.

3.2.3. TG Analysis. Figure 4 shows derivative curves of TG thermograms for fraction 2 and fraction 4. Although fraction 2 (PHP) decomposes at temperature interval of 150–275°C through one step, fraction 4 begins to decompose at about 150°C through two steps. First step is completed at about 300°C by a mass loss of 51.9%. Second step takes place at a temperature range of 325–475°C by a mass loss of 31.9%. As easily shown, first step overlaps completely with the decomposition of fraction 2 (PHP).

As is well known, poly(acrylic acid) decomposes through two steps [18]. At the first step, 27.4% of poly(acrylic acid) decomposes at a temperature interval of 142–301°C. At the second step, 55.2% of poly(acrylic acid) decomposes at a temperature interval of 335–425°C. In the light of the literature, at first step in the DTG curve of fraction 4 is related to both complete ester (PHP) units and partial acrylic acid units. Considering the peak areas in the DTG curve, acrylate ratio in fraction 4 may be estimated roughly as 60–65% by a simple calculation.

3.2.4. Titrimetric Analysis. The relative amount of acrylic acid units was determined as 47.3% by titration of fraction 4 samples with standardized NaOH solution. Considering that the result obtained from titration was lower than that of DTG (60–65%), structure of fraction 4 (hyperbranched PAcHP) was proposed as shown in Figure 5. The hyperbranched structure consists of four types of units: (1) acrylic acid units shown by red color, (2) acrylate units as branching points shown by green color, (3) propionate units shown by black color, and (4) propionic acid units at chain-ends shown by

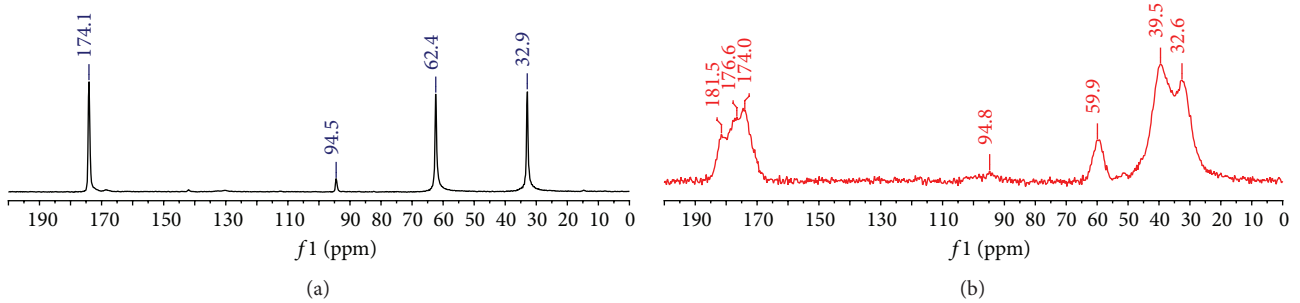

Figure 3: ^{13}C-NMR spectra of (a) PHP and (b) PAcHP obtained from bulk polymerization.

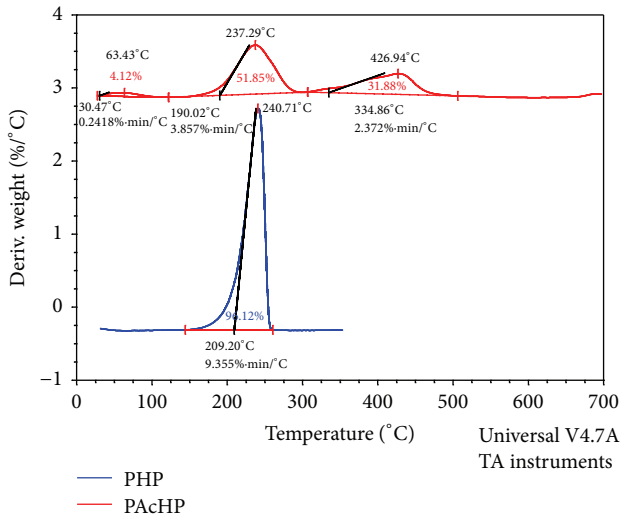

Figure 4: TGA curves of PHP (blue line, bottom) and PAcHP (red line, upper) obtained from bulk polymerization.

blue color. Units 1 and 4 contribute to the result obtained from titration (47.3%) since they contain acidic protons. Similarly, units 1 and 2 contribute to the result obtained from DTG (60–65%).

3.3. Swelling Study of Hyperbranched PAcHP Samples

3.3.1. pH Effect. The swelling behavior of the hyperbranched PAcHP was investigated over a period of 5-6 days in PBS with pH ranging from 4.0 to 12.0 at room temperature. The dynamic swelling profiles of hyperbranched PAcHP exhibited a fast swelling behavior in the first hour and achieved the equilibrium state within 12 h in PBS as shown in Figure 6. The initial fast swelling of hydrogels was due to the osmotic pressure difference. Since the copolymer was composed of acrylic acid groups which can dissociate or get protonated at suitable pH of the swelling media, swelling ratio of the copolymer underwent appreciable change with external pH. At pH of 4.0, a slight swelling capacity of the copolymer was observed due to the protonation of carboxylic groups. The carboxylic groups on the hyperbranched structure were converted to the protonated acid form which resulted in the decreased swelling ratio of the copolymer. As pH exceeded 6.0, some carboxylate groups were ionized and the electrostatic repulsion between the carboxylate groups resulted in an enhancement of the swelling ratio [19]. Moreover, the ionization also causes an increase in ion osmotic pressure. These two factors were thus responsible for a higher degree of swelling in the medium of pH range from 6 to 12.

3.3.2. Ionic Strength Effect. The effect of the ionic strength on the swelling ratios of the hyperbranched copolymer is shown in Figure 7. It shows that an increase in the ionic strength within the range of 0.025–1.000 M yields a significant decrease in the swelling ratio of the copolymer. This is because of the "salting-out" effect, which is a characteristic of the aqueous solutions of many polymers [20]. The addition of salts in polymer aqueous solutions results in a partial dehydration of polymer chains and decreases the hydrophilicity of the polymer chains [21]. Thus, the presence of salt reduces the hydrophilicity and equilibrium swelling ratio of PAcHP hydrogels.

3.3.3. Swelling-Deswelling Behavior. To investigate the time-dependent swelling behavior of PAcHP hydrogels, dynamic swelling studies were performed. The hydrogels were tested in buffer solutions with pH values of 12.0 and 2.0. Figure 8 presents the swelling ratios of hydrogels in buffer solutions with pH values of 12.0 and 2.0 at ambient temperature as a function of time. The reversible swelling-deswelling behavior of the hydrogel was observed. At pH 12.0, the hydrogel swells within 150 minutes up to 2700% due to anion-anion repulsive electrostatic forces, while at pH 2.0 it shrinks within 90 minutes due to protonation of the carboxylate groups. This pH-dependent reversible swelling behavior (on-off switching behavior) of the hydrogel makes it possible candidate for controlled drug delivery systems.

4. Discussion

HTP of acrylic acid at elevated temperature and in longer reaction times yields an insoluble product. The study revealed that the product has hyperbranched structure composed of hydrophobic ester (3-hydroxy propionate) and hydrophilic acid (acrylic acid) units. PHP is known to be easily biodegradable [22, 23] and poly(acrylic acid) is one of the most popular components used for controlled drug delivery [24–26] and

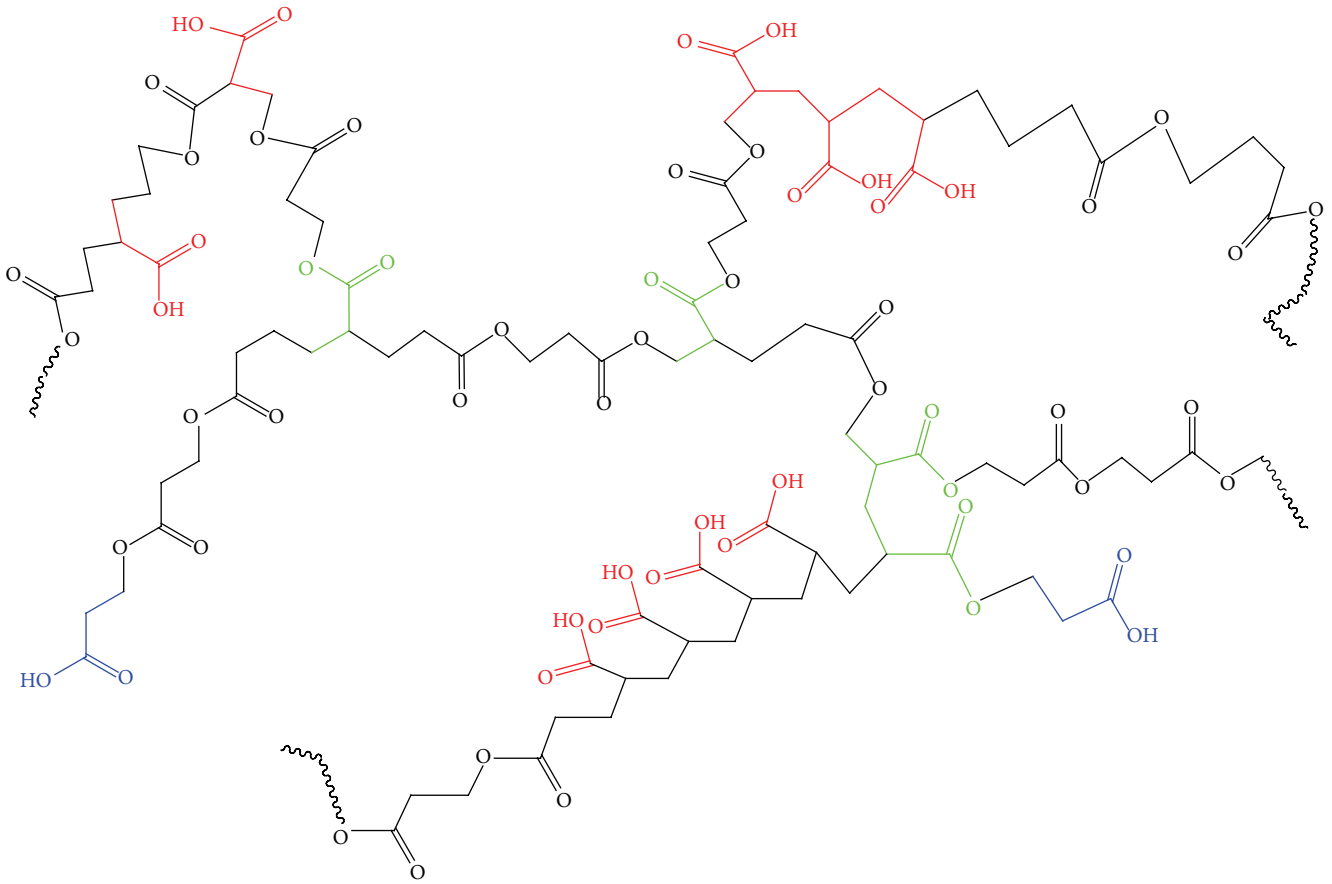

Figure 5: Chemical structure of hyperbranched PAcHP.

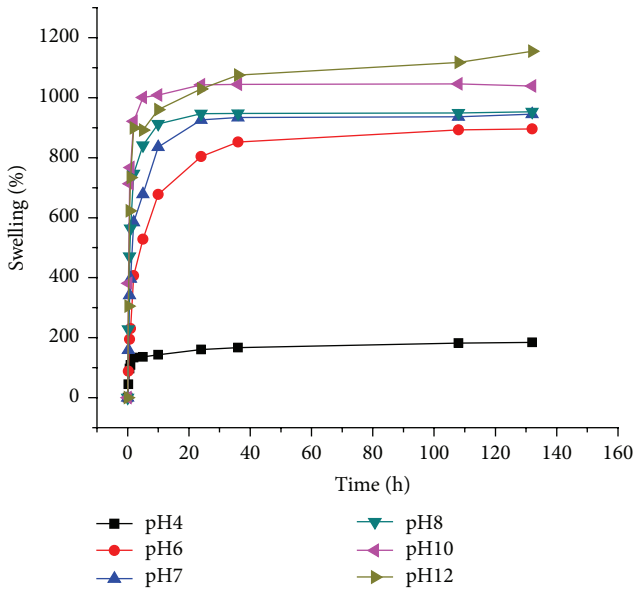

Figure 6: Time dependence of swelling ratio for hyperbranched PAcHP obtained from bulk polymerization at a wide range of pH.

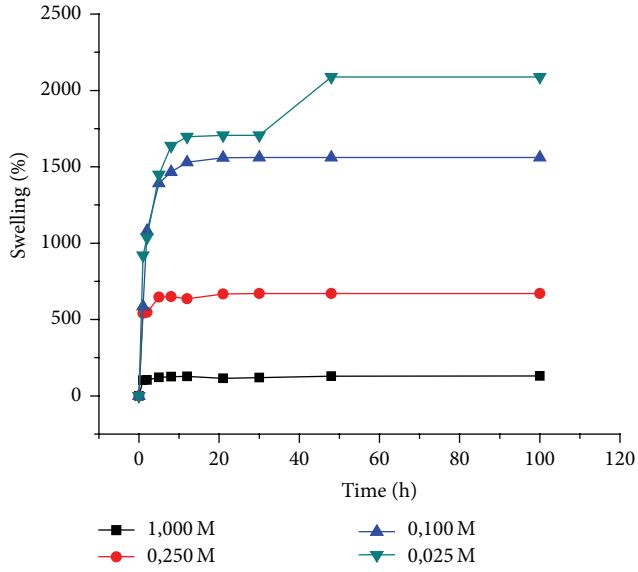

Figure 7: Time dependence of swelling ratio for hyperbranched PAcHP obtained from bulk polymerization (ionic strength).

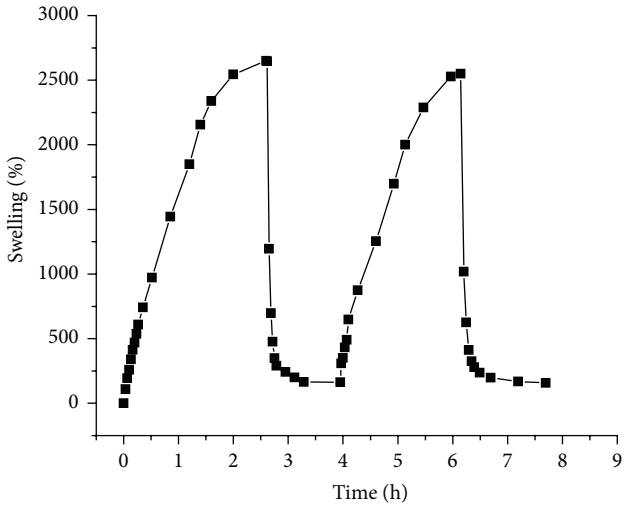

Figure 8: Dynamic swelling (pH 12.0)/deswelling (pH 2.0) behavior of PAcHP hydrogels obtained from bulk polymerization.

tissue scaffolding [24]. Our study shows that hyperbranched PAcHP exhibits hydrogel properties and hence may be considered biodegradable polymer matrix for drug delivery and (or) hydrogel scaffold for tissue engineering applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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