

VIP Frontal Copolymerization Synthesis and Property Characterization of Starch-graft-poly(acrylic acid) HydrogelsQing-Zhi Yan, Wen-Feng Zhang, Guo-Dong Lu, Xin-Tai Su, and Chang-Chun Ge*^[a]

Abstract: Recently, a considerable amount of research has centered on uniquely structured polymers synthesized through self-propagating frontal polymerization. The obtained polymer materials have better features than those obtained by using the classical batch route. The additional advantages are short reaction times and low cost. This work describes the first frontal polymerization synthesis of a graft copolymer superabsorbent hydrogel of acrylic acid onto starch at high monomer and initiator concentration. The

effects of varying the relative amounts of the reaction components on the most relevant parameters relating to frontal polymerization were explored. The front velocity dependence on initiator concentration could be fit to a power function. The temperature profiles were found to be very sharp with

a maximum temperature below 150 °C, which was responsible for high monomer conversion. The ultimate properties of the product appear to depend on the polymerization front velocity and the temperature. The high-temperature and rapid temperature increase at the polymerization front led to products with interconnected porous structures caused by the evaporation of water. So, a fast-swelling, highly absorbing hydrogel with respect to batch polymerization was obtained.

Keywords: frontal polymerization • graft copolymerization • microporous materials • polymers • superabsorbent hydrogels

Introduction

There are various methods through which polymers can be synthesized from monomers. The most common method uses stirred batch reactors, in which case, due to mixing, both the chemical compounds and the temperature are homogeneous in space, so that the polymerization reaction occurs simultaneously at each point in the reactor. To avoid runaway polymerization, the reactions are usually performed at low monomer and initiator concentration. Under these reaction conditions, the rates of polymerization are slow, requiring longer reaction times and continuous heating to synthesize products. The possibility of triggering off a polymerization reaction and achieving high monomer conversion in a short time often represent desirable features. This is particularly true in some cases that need to circumvent phase separation and sedimentation. Also, metastable

materials with unique structures may be required that would not be accessible from a homogeneous process. In these situations, frontal polymerization (FP) might represent a valid alternative.

FP is a way of converting a monomer into a polymer which exploits the heat released by the reaction itself. This heat causes the polymerization of monomer close to the hot zone, releasing more heat. If heat loss is not too large, the result is a self-sustaining hot front which propagates step by step through the reaction vessel.

FP was first discovered by Chechilo, Enikolopyan et al. in 1972. They studied methyl methacrylate frontal polymerization in adiabatic reactors at high pressure.^[1–4] Pojman et al. later demonstrated the feasibility of FP for a variety of monomers at ambient pressure.^[5,6] Because of the high temperatures reached by the propagating fronts, polymerization runs can be performed without removing the inhibitor from the monomers. Some experiments successfully produced polymers with specific desired properties.

Pojman et al. reported on the advantageous application of FP for the obtainment of interpenetrating polymer networks^[7] and thermochromic composites (changes color with changes in temperature).^[8] It was found that the polymers prepared by FP were characterized by reduced phase separation and sedimentation when compared with those ob-

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tained by traditional homogeneous methods. A similar result was reported by Tredici et al.,^[9] who found that more homogeneous composites can be obtained by such a route. In these studies, phase separation was limited by the high conversion rate, which “freezes” the various components of the mixture in a metastable situation.

To extend the number and type of both chemical systems and practical applications, Mariani et al.^[10] studied frontal ring-opening metathesis polymerization. Polyurethanes have been recently prepared by using FP.^[11] Now FP with thiol-ene systems has been achieved.^[12]

Furthermore, the application of FP to synthesize copolymers has been investigated.^[13,14] In these cases, the temperatures reached by the fronts makes the ratio of monomers equal to unity. As a consequence, all copolymer chains were characterized by the same composition, independent of monomer conversion and with no need of feed correction during the reaction.

Recently, FP was used by Washington and Steinbock for the preparation of temperature-sensitive hydrogels of improved homogeneity,^[15] and by Pujari et al. for the obtainment of macroporous polymers without porogen.^[16]

In addition to the above features of interest, it should be underlined that FP has several potential advantages over traditional methods of polymer synthesis. Because reactions become self-propagating after an initial input of heat, continuous heating during polymerization is avoided; this can decrease energy and processing costs. By eliminating post-polymerization solvent removal, waste production can be reduced. The additional advantage is the avoidance of charring from thermal runaway polymerization.

On the basis of what is summarized above, it is evident that FP is a very promising technique and one to be widely explored. We expected that similar benefits could be achieved if this approach was applied to the graft polymerization synthesis of polymers.

Grafting has been used as an important technique for modifying the physical and chemical properties of polymers. Chemical modification of starch through grafting of vinyl monomers has been a subject of academic as well as industrial interest for the past few decades.^[17–21] Besides its low cost and availability, the biodegradability of starch has given it even more importance in this environmentally concerned era.

Graft copolymerization of starch with acrylic acid has found extensive commercial application, especially as superabsorbent hydrogels for personal-care products,^[8–20] drug-delivery systems,^[17] and agricultural applications.^[21,22] Preparation of chemically modified starch-based superabsorbent materials is normally accomplished by batch polymerization. To avoid runaway polymerization, these graft copolymers are usually produced at low monomer and initiator concentration, requiring longer reaction times and continuous heating. Moreover, the resulting polymers can exhibit less porous, noncellular structures with the deposition of homopolymers on starch particle surfaces, leading to low absorbing capacity and rate in saline solution.^[19–22] However, de-

sired features of superabsorbent materials are high absorbing capacity and high absorbing rate. We suspected that we could apply FP to the synthesis of chemically modified starch-based superabsorbent hydrogels with improved properties.

For a new suitable system, a thorough systematic study on the influence of the relative ratios among all components of the reaction mixture has to be carried out. Specifically, front velocity and its maximum temperature are the parameters of main interest. Indeed, as mentioned above, most of the advantages of FP are a direct consequence of the high conversion rate due to high front temperatures. But excessively high velocity and temperature can have undesirable effects on conversion and, ultimately, on the properties of products.

Herein, we report on our recent results devoted to setting up experimental conditions for the first synthesis of starch-grafted polyacrylic acid superabsorbent hydrogels by using the FP technique. We determine the dependency of the frontal velocity on the initiator concentration and on other components of the reaction system, as well as the effects of the propagating front on morphology, conversion, water absorbency, and absorption rate. Furthermore, a comparison with some samples obtained by using batch polymerization is reported.

Results and Discussion

Frontal polymerization synthesis of graft copolymers:

Starch-*graft*-poly(acrylic acid) superabsorbent hydrogels were synthesized frontally through graft copolymerization of acrylic acid (AA) onto starch in test tube. In general, to make a starch-grafted hydrogel, the starch was mixed with an appropriate amount of distilled water and then heated to form a gelatinized starch slurry. A glass test tube was filled with the appropriate amounts of gelatinized starch, partially neutralized AA solution, initiator ammonium persulfate solution, and cross-linker methylene bisacrylamide solution. The graft polymerization process was initiated by application of a soldering iron to the top of the test tube until the formation of a hot propagating front began (Figure 1). Front propagation occurred at a constant velocity and the position of the front was obvious because of the difference in the op-

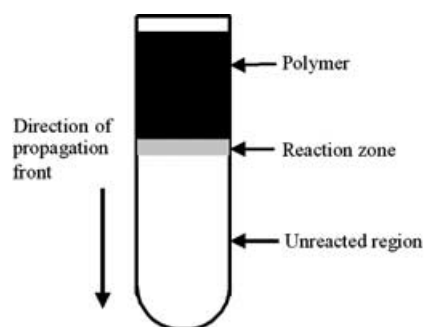


Figure 1. Schematic representation of frontal polymerization.

tical properties of the polymer and raw materials. A plot of the front position versus time produces a straight line, the slope of which is the front velocity. The temperature profiles were measured by using a K-type thermocouple connected to a digital thermometer.

The propagating behavior of the copolymerization front and the corresponding properties of the copolymers were investigated by making changes to the conditions of graft polymerization. The weight ratios of starch/AA, water (total amount added)/AA, initiator/AA, and the neutralization degree of AA were varied. The features of the process and the observed property measurements for all the polymerizations are given in Table 1.

In each case there was a range in which a steady-state polymerization front was observed. Both lower and higher relative amounts of components excluded the existence of a steady-state propagation front. For example, for series with different neutralization degrees, reproducible FP data were obtained only in the range between 30 and 65% mol mol⁻¹. For higher neutralization degrees, no FP was observed. Conversely, for lower neutralization degrees, the gelatinized starch separated from the monomers. Also, for the series of reactions with different initiator/AA ratios, at lower ratios the propagating front was not able to be self-sustainable, whereas with a greater initiator content, spontaneous polymerization occurred.

Spectroscopic characterization: The FTIR spectrum (Figure 2) of the reaction product indicates the presence of starch, starch-g-poly(acrylic acid), and partially neutralized starch-g-poly(acrylic acid). The bands at about 3426 (broad), 2921 (weak), 1467 (weak), 1369 (weak), and 974 cm⁻¹ (strong) are related to the O–H stretching, C–H stretching, C–H bending, O–H bending, and C–O stretching for starch, respectively. The bands appearing at 1560 (strong), 1216

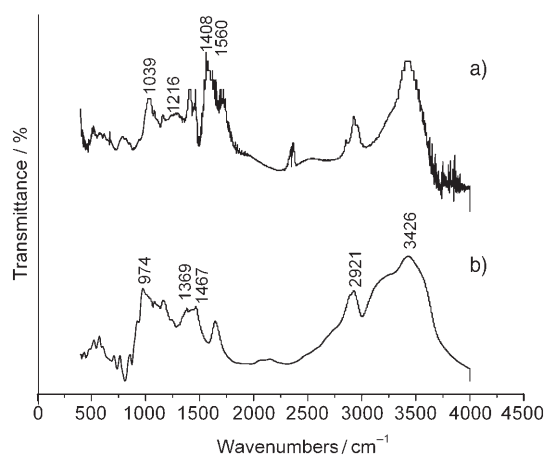


Figure 2. IR spectra of a) starch and b) starch-g-poly(acrylic acid).

(weak), and 1039 cm⁻¹ (weak) are characteristics of acrylic acid stretching modes for O–H and C=O groups. The strong band at 1408 cm⁻¹ could be attributed to the presence of carboxylate ions in the acrylate groups.

Frontal velocity: The variation of front velocity with differing relative amounts of the reaction components is presented in Table 1. The frontal velocity decreased from 0.57 to 0.36 cm min⁻¹ as the starch/AA ratio was raised from 0 (no starch added) to 0.4 (for starch/AA > 0.4, no FP was observed), rapidly from 1.4 to 0.25 cm min⁻¹ as the water/AA was raised from 1 to 2.4 (for water/AA > 2.4, no FP existed), and from 1.27 to 0.28 cm min⁻¹ as the neutralization degree of AA was raised from 30 to 65%. Conversely, the frontal velocity increased from 0.44 to 1.04 cm min⁻¹ as the initiator/AA ratio was raised from 0.008 to 0.055 (Table 1). The water concentration in the reaction system had a large effect

Table 1. The propagating features of the polymerization front and the absorption characteristics of copolymer for different conditions.

Run no.	Starch/AA ratio [wt/wt]	Water/AA ratio [wt/wt]	Neutralization degree [% mol mol ⁻¹]	Initiator/AA [wt/wt]	Frontal velocity [cm min ⁻¹]	T _{max} [°C]	Conversion [%]	Water absorption [g g ⁻¹]
FP1	0	1.8	35	0.008	0.57	120	86.7	1980
FP2	0.1	1.8	35	0.008	0.5	114	88.9	1487
FP3	0.2	1.8	35	0.008	0.46	113	92.3	837
FP4	0.3	1.8	35	0.008	0.43	110	94.6	620
FP5	0.4	1.8	35	0.008	0.36	108	95.8	473
FP6	0.3	1.0	35	0.008	1.4	147	79.6	318
FP7	0.3	1.5	35	0.008	1.15	141	86.3	362
FP8	0.3	1.8	35	0.008	1.02	133	91.8	410
FP9	0.3	2.2	35	0.008	0.41	110	95.1	616
FP10	0.3	2.4	35	0.008	0.25	102	97.5	697
FP11	0.25	1.3	30	0.008	1.27	144	94.3	443
FP12	0.25	1.3	35	0.008	1.04	139	97.6	425
FP13	0.25	1.3	40	0.008	0.87	130	95.7	403
FP14	0.25	1.3	50	0.008	0.45	120	98.6	281
FP15	0.25	1.3	65	0.008	0.28	111	98.0	297
FP16	0.3	1.8	35	0.008	0.44	111	94.1	627
FP17	0.3	1.8	35	0.010	0.48	113	91.0	619
FP18	0.3	1.8	35	0.015	0.61	116	87.5	587
FP19	0.3	1.8	35	0.028	0.77	122	83.7	503
FP20	0.3	1.8	35	0.042	0.92	129	76.0	427
FP21	0.3	1.8	35	0.055	1.04	131	70.4	348

on the front temperature, and a 140 percent increase of water concentration resulted in a 5.6-fold decrease in front velocity.

In the exothermic reaction of AA grafting copolymerization onto starch, water and starch act as a diluent, reducing the concentration of AA. An increase in the neutralization degree of AA decreased the concentration of AA. A decrease of monomer or initiator concentration reduced the rate of polymerization, and thus, of the propagating front velocity.

To investigate the front velocity functional dependence on initiator concentration, we carried out additional experiments at different temperatures. Figure 3 shows the velocity

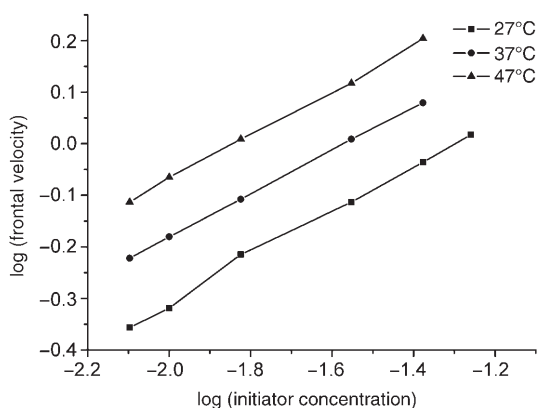


Figure 3. Logarithm of front velocity versus logarithm of initiator concentration.

dependence on initiator concentration at three different temperatures (27, 37, and 47 °C). The dependence is reported on a double logarithmic scale. All the investigated runs show a substantial linear trend with a gradient of 0.4. Pojman et al.^[23] studied triethylene glycol dimethacrylate polymerization fronts and showed the power functional dependence for velocity versus initiator concentration is different for azobisisobutyronitrile (AIBN, 0.20), benzoyl peroxide (0.23), and lauroyl peroxide (0.31). Tonoyon et al.^[24] found a 0.50 power dependence with *tert*-butyl peroxide. It is expected that the dependence should be between 0.25 and 0.50, reflecting the extremes of an infinitely narrow reaction zone and bulk polymerization.^[23] The grafting copolymerization front results fit in this range.

Temperature profile: Figure 4 shows a typical temperature profile in a graft copolymerization front of acrylic acid onto starch (corresponding to experiment FP2 in Table 1). The temperature increases from 27 to 114 °C over a distance of 1.5 cm. This corresponds to a local region complete conversion in about 3 min.

The propagating front temperature (T_{\max} , Figure 4) dependence on the relative amounts of the components was similar to the corresponding frontal velocity trend (Table 1). The polymerization front is a hot wave, and a higher front

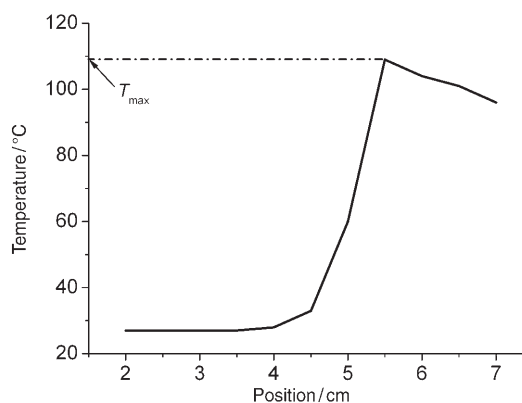


Figure 4. Temperature profile obtained during the frontal copolymerization of acrylic acid grafting onto starch: starch/AA = 0.1; water/AA = 1.8; initiator/AA = 0.008; 35% neutralization degree.

velocity decreases the time for heat loss, resulting in a higher front temperature.

Conversion: The conversion ranged from 70.4 to 98.6% within the range of the experimental conditions studied (Table 1). The conversion dependence on the relative amounts of the components was the reverse of the corresponding T_{\max} trend, except for that of the neutralization degree series. The lower front temperature led to higher conversion. For the neutralization degree series no trend was observed.

High temperature results in the complete decomposition of the initiator before the monomer is completely consumed, a condition known as initiator “burnout”.^[25] Methacrylic acid fronts, where the front temperature reaches 260 °C, can have conversions as low as 65%.^[23] The acrylamide front temperature was lowered to 165 °C by diluting the reaction mixture, resulting in 76% conversion.^[25] In all sets of our experiments, the front temperature was below 150 °C (Table 1) and high conversion could be achieved.

In addition, increasing the initiator concentration increased the radical concentration, which produced a large number of water-soluble molecules,^[26] leading to low conversion.

Water absorption: From Table 1 it can be seen that the water absorption decreased rapidly from 1980 to 473 g g^{-1} as the starch/AA ratio was raised from 0 to 0.4, but increased from 318 to 697 g g^{-1} as the water/AA ratio was increased from 1 to 2.4. When the neutralization degree of AA was increased from 30 to 50%, the absorption initially decreased. Above neutralization degrees of 50%, the absorption increased. For the initiator series, the water absorption decreased from 627 to 348 as the initiator to monomer ratio was increased from 0.008 to 0.055.

Superabsorbents are polymers with hydrophilic cross-linked networks that absorb water as a result of the swelling of hydrophilic chains due to the charge repulsion. This swelling stops when the swelling force is equal to the elastic force of the cross-linked network.^[27] This indicates that the

water absorption is influenced by the hydrophilic group as well as by the cross-linking density. In addition, the microstructure of hydrogels plays an important role in the absorbency of polymers.^[28,29]

Decreasing the starch/AA ratio enhances the absorbency by increasing the hydrophilic group and ionic charge content of the polymer backbones, resulting in an increase in absorbency of the superabsorbent material. The scanning electronic microscope (SEM) images (Figure 5) revealed a striking difference in the microscopic morphology of the products prepared at different starch/AA ratios. For all samples (FP1–FP3 in Table 1) porous structures were observed, but the porosity and interconnectivity increased as the starch/AA ratio was decreased, as shown in Figure 5.

The well-defined pores can be attributed to the high synthesis temperature and rapid temperature increase at the polymerization front; this evaporates water to produce gas bubbles. The increase of front temperature with the decrease of starch/AA ratio (Table 1) results in more bubbles. Some gas bubbles escape from the reaction system, the remaining gas bubbles are trapped by the sticky reaction mixture and consequently form interconnected capillary channels. Higher porosity would increase the available space for water in the swollen state.^[28]

The existence of primary cyclization could be mostly responsible for the water absorption dependence on the water/AA ratio and the degree of neutralization of AA. In this work, starch-grafted poly(acrylic acid) superabsorbent hydrogels were prepared by free-radical FP. In a free-radical chain polymerization, the existence of primary cyclization has been observed repeatedly in cross-linked polymerizations.^[30–32] Primary cyclization causes small loops to be formed in the network, which leads to a reduction in the effective cross-linking density, so increasing water absorbency in the polymers.

Superabsorbent materials polymerized with more water have a higher degree of primary cyclization, which creates a less cross-linked mesh. This is because the rate at which a propagating radical consumes double bonds is reduced (less monomer in solution), thus the propagating radical will spend more time in the proximity of pendant double bonds (created by cross-linker) attached to the polymer chain.

The increase of neutralization degree of AA with the addition of NaOH decreases the extent of cyclization because the negatively ionized acrylic acid chains are extended fur-

ther during the polymerization, forcing the pendant double bond and propagating radical further apart. This effect was observed when the neutralization degree was raised from 30 to 50%. Above this neutralization degree most of the carboxylic acid groups were ionized and the addition of NaOH served to increase the ionic strength of the reaction mixture. The addition of more ions causes ion shielding, diminishing the degree to which the negative carboxylic acid groups will repel each other.^[33] This change in conformation brings the pendant double bond and propagating radical in closer proximity to each other and allows more primary cyclization.

Increasing the initiator/AA ratio increases the radical density, and radical recombination can occur.^[34,35] So only a few free radicals are available at active grafting sites on the starch backbones. Most radicals undergo recombination or initiate homopolymerization.^[36] The increase of homopolymerization and oligomers lead to the decrease in the water absorption.

Comparison between samples obtained by using frontal and batch polymerization:

To compare the macroscopic as well as microscopic properties of hydrogels obtained from frontal and conventional batch polymerization (BP), reference hydrogels with the same nominal composition were synthesized in a batch reactor at 60 °C. Table 2 gives the typical

Table 2. Reaction and absorption characteristics of some hydrogel samples obtained by using FP and batch polymerization.

Sample	Reaction time [min]	Conversion [%]	Water absorption [g g ⁻¹]	Water absorption ^[a] [g g ⁻¹]	Equilibrium time ^[b] [min]
FP1	15	86.7	1980	131	2.4
FP2	17	88.9	1487	88	3.1
FP3	21	92.3	837	55	3.5
BP1 ^[c]	64	80.8	1383	89	20
BP2 ^[c]	46	86.2	1205	75	24
BP3 ^[c]	54	84.6	529	53	27

[a] In 0.9% wt NaCl solution. [b] Time to reach equilibrium absorption. [c] Samples obtained by batch polymerization with the same components as samples FP1, FP2, and FP3, respectively.

comparative data. Samples BP1, BP2, and BP3 were synthesized by the usual batch technique, starting from the same components as samples FP1, FP2, and FP3, respectively. These data reveal that the high-temperature synthesis of FP does affect properties of the obtained samples. Note that a significant increase in the conversion and the absorbing rate and capacity can be observed.

Higher conversion obtained in the FP may be attributed to a shorter reaction time (Table 2) and the hot front propagating step by step, which led to a decrease in the loss of acrylic acid monomer

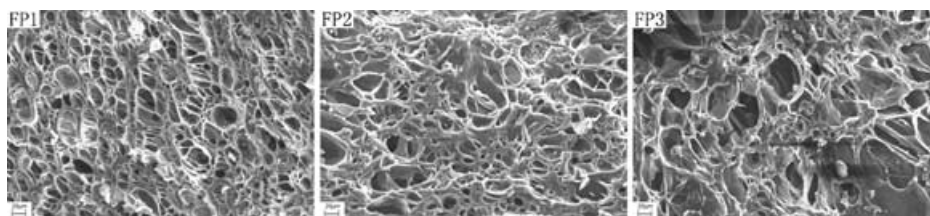


Figure 5. Scanning electron micrographs of hydrogels produced by frontal polymerization at different starch/AA ratios: FP1, ratio=0; FP2, ratio=0.1; FP3, ratio=0.3. The scale bar at the bottom left of each image represents 20 μm.

caused by gasification during polymerization.

The dramatic enhancements in absorbing behavior could be attributed to structural improvements in the hydrogel produced by FP. This presumption was confirmed by SEM images. Figure 6 shows the inside of a sample (BP1 in Table 2) prepared by BP, and the inner surfaces of samples (FP1 in Table 1) produced by using FP at different magnifi-

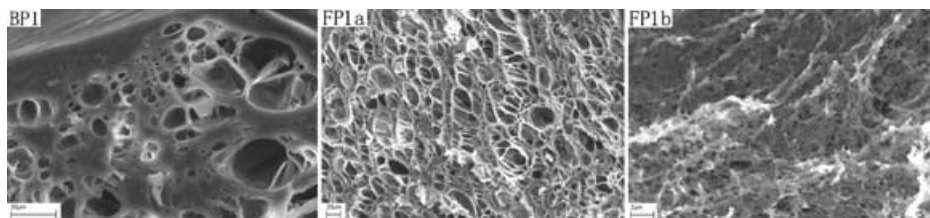


Figure 6. Scanning electron micrographs showing a conventional batch polymerization hydrogel (BP1, scale bar = 20 μm) and frontal polymerization hydrogels (FP1 a and b, scale bar = 20 and 2 μm , respectively) at different magnifications.

cations. The hydrogel synthesized by using FP displays a spongelike porous structure, and most of the pores are connected to each other to form capillary channels. The BP-produced samples, however, present a dense mass structure with fewer pores. Other samples in Table 2 also showed similar images.

As mentioned above, the interconnected capillary channels can be obtained in the FP because of the high synthesis temperature and rapid temperature increase at the polymerization front. When a dried superabsorbent with interconnected capillary channels was placed in water or an aqueous solution, water flowed through the interconnected channels by means of a capillary effect, instead of diffusion of water through the glassy layer (as observed in the BP samples). This resulted in extremely fast swelling and high absorption of the superabsorbents.^[37]

On the basis of the comparative results shown above, FP can be considered a reliable alternative approach to be used for the synthesis of starch graft copolymers with short reaction times, at relatively low cost (no energy has to be provided except for that igniting the polymerization reaction), and with properties superior to those of the corresponding materials synthesized by the classical method.

Conclusion

The first synthesis of starch-graft-poly(acrylic acid) superabsorbent hydrogels by using frontal copolymerization has been successfully carried out. In this model system, the relative amounts of reaction components have been varied in order to find their influence on the polymerization parameters and polymer properties.

The obtained graft copolymer is characterized by conversion and water absorbing features better than those obtained by using the classical batch route. In particular,

higher absorbing rate and capacity in saline solution have been reached. The unique microstructure of hydrogels produced by FP is critical for better absorbing features.

The above results allow us to conclude that FP can be exploited as an alternative means of starch graft copolymer synthesis with additional advantages of short reaction times and low cost.

Further studies with the aim of extending this technique to other graft copolymers or other superabsorbent formulations, including interpenetrating polymer networks and stimuli-sensitive superabsorbents, are in progress.

Experimental Section

Materials: The materials used in this study were potato starch containing 5.3% moisture, acrylic acid mono-

mer, methylene bisacrylamide cross-linker, ammonium persulfate initiator, and sodium hydroxide. All materials were used as received from Beijing Chemical Company, China.

Instruments: The infrared experiments of grafted and ungrafted starch were run by using KBr pellets on a 670 FTIR spectrophotometer in the frequency range of 4000–600 cm^{-1} . The structures of the superabsorbents obtained were examined by using a LEO-1450 scanning electronic microscope (SEM). The samples used for the SEM measurements were immersed in distilled water after synthesis to allow maximum swelling, dehydrated in ethanol, and then air-dried at 60°C. Dried samples were cut to expose their inner structure and coated with a layer of carbon.

Frontal polymerization: Potato starch (0–4.4 g) and distilled water (0–15 g) were mixed and then heated at around 60°C to form gelatinized starch. Acrylic acid (11 g in 4 g water) was partially neutralized with varying amounts of a solution of sodium hydroxide (1.8–4 g) in water (4.6–10 g). Solutions of ammonium persulfate (0.088–0.605 g) and methylene bisacrylamide (0.0015 g) in water (2 g) were prepared. Then the monomer solution and the initiator and cross-linking agent solution were added to the gelatinized starch. The mixture was stirred (magnetic stirrer) at room temperature for 30 min and then poured into a 200 mm-long test tube (inner diameter 18 mm). A K-type thermocouple connected to a digital thermometer was utilized to monitor the temperature change. The junction was immersed at about 6 cm from the free surface of the mixture. The front position was recorded as a function of time and temperature.

The upper layer of the mixture was then heated by using a soldering iron until a hot propagating front formed. Front propagation occurred at constant velocity by conversion of monomer and starch to copolymer with a number of homogeneous bubbles on the propagating front.

After the reaction was complete, the tubes were cooled to room temperature. The reaction product was removed and cut into small pieces (2–5 mm) which were immersed in a solution (60 vol%) of aqueous methanol for 24 h to remove water-soluble materials. Then the pieces were dehydrated with methanol and dried in a vacuum oven at 65°C until the weight of the specimen was constant. The dried polymer product was weighed. The total amount of polymer obtained from the weight of monomer and starch charged was calculated to yield the percentage conversion.

Batch polymerization: Several batch runs were performed in order to compare the resultant samples with the corresponding ones obtained by FP. In typical syntheses, the same amounts of each component as quoted

above were mixed in a 400-mL beaker, immersed in a water bath set at 60°C, and allowed to react.

Absorption measurements: Water absorption measurements were performed by using a filtration method. For dried superabsorbent polymers, a fixed amount ($0.2\text{ g} \pm 0.001$) of fractionated (160–180 μm) product was dispersed in distilled water (500 mL) or aqueous sodium chloride solution (200 mL, 0.9 wt %) for 30 min. The swollen samples were filtered through a 200 mesh wire gauze until they no longer slipped from the gauze when it was held vertically. The degree of absorption was determined from the weight gain on the gauze after immersion in water per unit weight of absorbent before immersion. To measure the absorption rate, the water-absorbed samples were taken from the solution at prescribed periods and their absorbing capacity was examined through the above procedure. To obtain a reliable value for absorbing at any time, three values were averaged, although the value of the standard deviation for this method is ± 5.3 g of water absorbed per gram of dry hydrogel.

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