pH-Responsive Controlled-Release Fertilizer with Water Retention via Atom Transfer Radical Polymerization of Acrylic Acid on Mussel-Inspired Initiator

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ABSTRACT: This work reports a polydopamine-*graft*-poly(acrylic acid) (Pdop-*g*-PAA)-coated controlled-release multi-element compound fertilizer with water-retention function by a combination of mussel-inspired chemistry and surface-initiated atom transfer radical polymerization (SI-ATRP) techniques for the first time. The morphology and composition of the products were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), gel permeation chromatography (GPC), and inductively coupled plasma (ICP) emission spectrometry. The results revealed that the stimuli-responsive layer formed by a Pdop inner layer and a PAA outer corona exhibit outstanding selective permeability to charged nutrients and the release rate of encapsulated elements can be tailored by the pH values. At low pH, the Pdop-*g*-PAA layer can reduce nutrient loss, and at high pH, the coating restrains transportation of negative nutrients but favors the release of cations. Moreover, PAA brushes provide good water-retention property. This Pdop-*graft*-polymer brushes coating will be effective and promising in the research and development of multi-functional controlled-release fertilizer.

KEYWORDS: controlled-release fertilizer, polydopamine, pH-responsive, poly(acrylic acid), atom transfer radical polymerization

INTRODUCTION

Fertilizers have been used for vital input material to supply nutrients in growing media and play an important role in increasing and sustaining an optimal crop yield for many years. However, various environmental problems and drawbacks associated with the use of conventional fertilizers received extensive attention.[1−3] To ensure the proper use of fertilizer to both crop production and the environment, researchers have tried to find ways to achieve the novel defined goal of fertilizer use, that is, improving fertilizer nutrient efficiency and minimizing environmental impacts.[4,5] One possible way to overcome these shortcomings is using slow- and controlled-release fertilizers.[6−8] Recent research and developments on technology for slow- and controlled-release delivery of plant nutrients in the water or soil is an active area in agriculture.[9−12]

Slow- and controlled-release fertilizers have many obvious and great advantages compared to the conventional type, such as reduction of plant toxicity and stress, substantial reduction in pollution of soil and water, reduction of fertilizer application costs, reduced seed or seedling damage from high local concentrations of salts, etc.[13−17] Coated fertilizer, encapsulating traditional fertilizers with polymeric material, is one of the basic approaches to improve nutrient uptake of crops and to reduce environment pollution resulted from overdosage of fertilizers. Many kinds of polymeric coating have been widely chosen and studied, such as wheat straw,[17] cellulose,[18,19] starch,[20] chitosan,[7,21] superabsorbent polymers,[22−24] etc. However, few coated fertilizers have been reported, which can provide a

tunable barrier and control the release rate of nutrients according to different ambient conditions. As we known, the crops need for nutrients in acidic soil is different from that in alkaline conditions. In this sense, designing a stimuli-responsive release coating for encapsulated fertilizer according to different acid and basic environments seems interesting and urgent.

Among the polymeric layer, superabsorbent-coated fertilizers have attracted more and more attention. The possibility of their application in the cultivated field has been studied to alleviate agricultural problems, such as reducing irrigation water consumption and improving nutrient retention in medium.[25] Acrylic acid (AA) is most frequently used in the superabsorbent material industrial production.[26,27] Moreover, poly(acrylic acid) (PAA), a biodegradable water-soluble polymer with various industrial applications, with significant pH response, is mainly due to high concentrations of −COOH groups.[28−30] However, most of the fertilizers with water-retention function were prepared by a cross-linked technique, which give a network coating on the fertilizer. The thickness of PAA coating, playing a key role for release behavior of nutrients, is roughly controlled by the ration of AA and fertilizer. However, atom transfer radical polymerization (ATRP) is a well-established controlled/"living" radical polymerization technique that has been
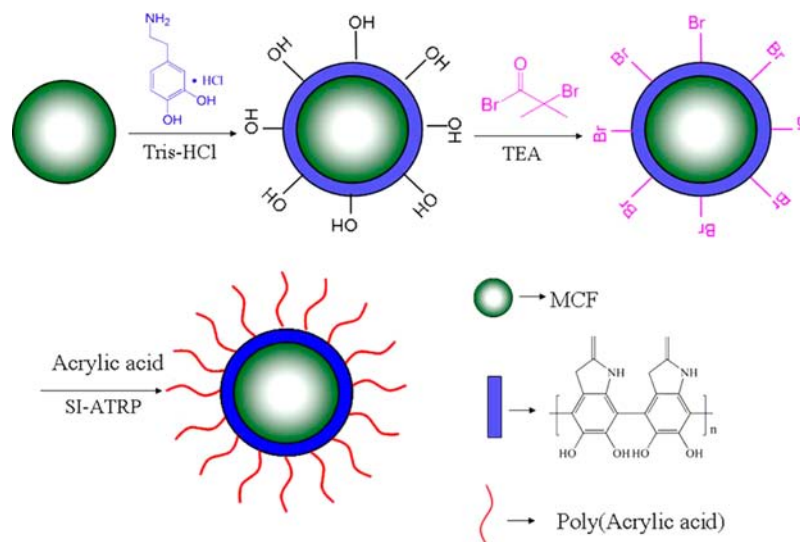
Scheme 1. Schematic Illustration of the ATRP of PAA from PCMCF

successfully applied to monomer systems, including acrylate and methacrylate.[31−33] Using the surface-initiated (SI)-ATRP technique for polymerization of AA to confer pH-response controlled-release fertilizer with water-retention properties has not been reported. The main reason is that few fertilizers can be as direct as an initiating platform of PAA and linear PAA cannot encapsulate effective nutrients, which cannot realize a slow and controlled role.

Polydopamine (Pdop), a facile and reliable cross-linked coating with lots of advantages, helps us to circumvent this problem. Adhesive mechanisms and behaviors of dopamine show that the cross-linked Pdop layer can deposit on various surfaces by self-polymerization in an aqueous solution, even on itself.[34−36] What is important is that it was reported that Pdop shows excellent biocompatibility and low cytotoxicity, making it a versatile platform for bioapplications.[37−39] Moreover, Pdop coatings have been explored as a versatile platform for secondary reactions and polymerization.[40−43]

On the basis of our previous work,[12] we design a "crosslinked coating-*graft*-polymer brushes" structure to realize stimuli-responsive release and water-retention properties at the same time. The cross-linked Pdop layer was deposited on the double copper potassium pyrophosphate trihydrate, providing three essential nutrients (Cu, K, and P). Subsequently, the SI-ATRP was employed to graft PAA on the Pdop layer. The effect of pH on the release behavior of elements (Cu, K, P, and N) is systematically studied in water. The water absorbency and water-holding capacity of the resultant fertilizer are also investigated. The results revealed that Pdop-*g*-PAA coating has bifunctions with pH-responsive release and tunable water retention. This technology will be effective and promising in the research and development of slow- and controlled-release fertilizer.

■ MATERIALS AND METHODS

Materials. Dopamine hydrochloride and copper(I) bromide were purchased from Aldrich. 2-Bromoisobutyryl bromide (BIBB) and *N,N*-dimethylaminopyridine (DMAP) were provided by Alfa Aesar. 2,2′-Bipyridine (bpy) was provided by J&K Chemical, Ltd. and used without further purification. AA (Chengdu Kelong Chemical Reagent Factory, Sichuan, China) was purified by vacuum distillation. Triethylamine (TEA, Tianjin ShengMiao Chemical Industry Limited

Company, Tianjin, China) was dried over calcium hydride for 12 h prior to distillation under nitrogen. All of the water used was deionized. All other chemicals were analytical-grade and used as received.

Preparation of Multi-element Compound Fertilizer (MCF). The procedure for the synthesis of the double copper potassium pyrophosphate trihydrate is in accordance with the reported procedure.[44] The synthesis was carried out by adding the copper sulfate solution (0.1 M) to the potassium pyrophosphate solution (0.1 M) under vigorous stirring at room temperature. The suspension was left for 24 h for aging, and then the precipitate was filtered and dried under vacuum at 60 °C.

Preparation of Pdop-Coated Multi-element Compound Fertilizer (PCMCF). A total of 200 mg of dopamine hydrochloride was dissolved in 200 mL of Tris-HCl. A total of 2 g of MCF powder was added to the solution. The mixture was stirred for 24 h at room temperature. The solid was centrifuged/water-washed and dried under vacuum at 45 °C. To obtain Pdop-coated fertilizers with a certain thickness of Pdop film, the number of deposition cycles was designed for 3 times. The deposition procedure was repeated in the same way as mentioned above.

Preparation of PCMCF-Supported Initiator. A 100 mL flask containing 2 g of PCMCF, 20.0 mL of CH₂Cl₂, 1 mL of TEA, and 0.5 g of DMAP was evacuated and filled with Ar 3 times. Then, 1 mL of BIBB dissolved in 20 mL of CH₂Cl₂ was added dropwise at 0 °C for 60 min. The resulting mixture reacted at room temperature for 23 h to produce the supported initiator. The solid was centrifuged and thoroughly washed with acetone and then with a methanol/water (1:1, v/v) mixture prior to being dried under vacuum at room temperature. These initiator-coated fertilizers were denoted as PCMCF−Br.

Preparation of Pdop-*g*-PAA-Coated Multi-element Compound Fertilizer (PPCMCF). A total of 1.0 g of PCMCF−Br, 0.14 mmol of CuBr, and 0.28 mmol of bpy were placed in a Schlenk flask with a magnetic stirring bar, which sealed with a rubber plug and subsequently evacuated and filled with argon 3 times. A series of AA monomer (20, 30, and 40 mmol) neutralized with NaOH was added to deionized water (20 mL) in another flask. The mixture was degassed by freeze−pump−thaw cycles, followed injection to the Schlenk flask with double-ended needles performed under argon. The mixture was stirred at room temperature for 24 h. The substrates were exhaustively rinsed and dried. The resulting products were denoted as PPCMCF-1, PPCMCF-2, and PPCMCF-3.

Techniques of Characterization. Transmission electron microscopy (TEM, Hitachi H-600) was used to observe the morphology of products. Fourier transform infrared (FTIR) spectroscopy studies were carried out using Nicolet AVATA360. Thermal stability was determined by thermogravimetric analysis (TGA, Netzsch STA449F3)
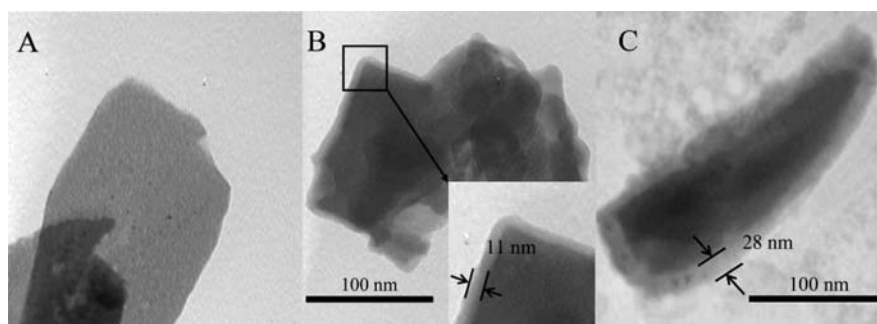
Figure 1. TEM image of (A) MCF, (B) PCMCF, and (C) PPCMCF-3.

over a temperature range of 25–1000 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Relative molecular weights and molecular weight distributions were determined by a gel permeation chromatography (GPC) system performed with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min in a thermostatted oven at 40 °C, using columns in serial connection (PLgel 5 μm Mixed-C, 300 × 7.5 mm) and equipped with a Waters 1515 isocratic high-performance liquid chromatography (HPLC) pump and a Waters 2414 refractive index detector. The contents of K, Cu, P, and N were analyzed by an inductively coupled plasma (ICP) emission spectrometer (Thermo Scientific 6000 Series).

Measurement of Water Absorbency of PPCMCF. An accurately weighed product (0.2 g) was immersed into a certain amount of deionized water and allowed to soak at room temperature for 24 h. The swollen polymers were filtered and weighed. The water absorbency (WA) was calculated using eq 1

$$WA = (M - M_0)/M_0 \qquad (1)$$

where M and M_0 refer to the weights of the swollen and dried superabsorbent-coated fertilizer, respectively.

Measurement of Water-Holding Capacity of Soil with PPCMCF. A total of 0.2 g of products was mixed with 20 g of dry soil (below 26 mesh) and placed in a 5 cm diameter beaker. Then, 20 g of deionized water was added to the tube and weighted (marked W_1). The tube was maintained at room temperature and weighted every 2 days (marked W_i) over a period of 20 days. The water evaporation ratio (WE, %) of the soil was calculated from eq 2.

$$WE\,(\%) = (W_1 - W_i) \times 100/20 \qquad (2)$$

Release Behavior of PPCMCF-3 in Water. The release behavior of potassium (K_2O), copper (Cu), nitrogen (N), and phosphorus (P_2O_5) from different kinds of fertilizers in water was determined as follows: A total of 0.2 g of products was enclosed in dialysis bags [molecular weight cut-off (MWCO) = 15 000]. Then, the bags were put into conical bottles with 200 mL of aqueous solution with well-defined pH values of 5, 7, and 9 (adjust pH to 5–9 using a dilute solution of HCl and NaOH). During 30 days, 5.0 mL of the solution was withdrawn at a predetermined time and the same volume of fresh medium was added to the system to maintain a constant amount of solvent. After microwave-assisted digestion in the presence of a catalyst, the contents of K, Cu, and P released from fertilizers in the solution were determined with an ICP emission spectrometer.

■ RESULTS AND DISCUSSION

Morphology and Characteristics of PPCMCF. The fabrication strategy is shown in Scheme 1. The stimuli-responsive fertilizers were successfully prepared by two-step polymerization. The PCMCF was prepared by spontaneous polymerization of dopamine on MCF. The bromoalkyl initiators were then immobilized on the Pdop coating, followed by ATRP of AA to produce the fertilizers with grafted PAA brushes from the Pdop layer.
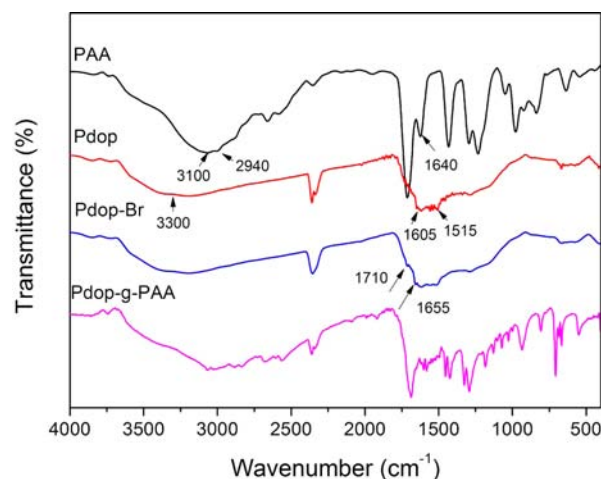

Figure 2. FTIR spectra of samples.

TEM images of the evolution of the surface morphology of products are shown in Figure 1. In comparison to MCF (Figure 1A), Figure 1B shows that the light outer shell is obviously on the boundary of dark flaky crystals, which indicates that the MCF was homogeneously coated with Pdop and the encapsulation boundary is clear. The average thickness of the Pdop film is about 11 nm after 3 deposition cycles. The growth profile of Pdop is in agreement with our previous work.[45] Figure 1C shows the TEM image of PPCMCF-3 with a typical core/shell structure. After PAA grafting, the wall thickness became larger, as seen from TEM images, and the thickness of Pdop-g-PAA coating is about 28 nm.

Figure 2 shows the FTIR spectra of PAA, Pdop, Pdop−Br, and Pdop-g-PAA coating without the MCF core. Ethylenediaminetetraacetic acid (EDTA) was used to remove the salt core, which interferes with the the fringe transmission spectrum. For the IR spectrum of PAA, the peaks observed at 3100 cm^{-1} are attributed to −OH groups and the water peak. The peak at 2940 cm^{-1} corresponds to the −CH stretching of acrylate units. The peak at 1640 cm^{-1} corresponds to −C=O stretching of acrylate units. Pdop has discernible bands at 1515 and 1605 cm^{-1} and at 3200–3500 cm^{-1} because of the indole or indoline structures and nitrogen−hydrogen/oxygen−hydrogen bonds, as reported previously.[46] A weak absorbance at around 1710 cm^{-1} could be indicative of esters formed by the reaction of BIBB with catechol hydroxyl groups, whereas a shoulder at 1655 cm^{-1} suggests the presence of amides formed by the reaction of BIBB with the dopamine primary amine.[47] For the FTIR spectrum of Pdop-g-PAA, the IR analysis results show that the characteristic groups of both PAA and Pdop exist

Table 1. Characteristics of Controlled-Release Fertilizers

	K$_2$O (g/g)		Cu (g/g)		P$_2$O$_5$ (g/g)		N (mg/g)	
fertilizers	calculated[a]	measured[b]	calculated	measured	calculated	measured	calculated	measured
MCF	0.070	0.076	0.412	0.421	0.286	0.287		
PCMCF	0.054	0.060	0.318	0.316	0.221	0.228	20.08	22.100
PPCMCF-3	0.043	0.046	0.255	0.269	0.177	0.180		21.324

[a]Calculated values. [b]Measured values determined by an ICP emission spectrometer.
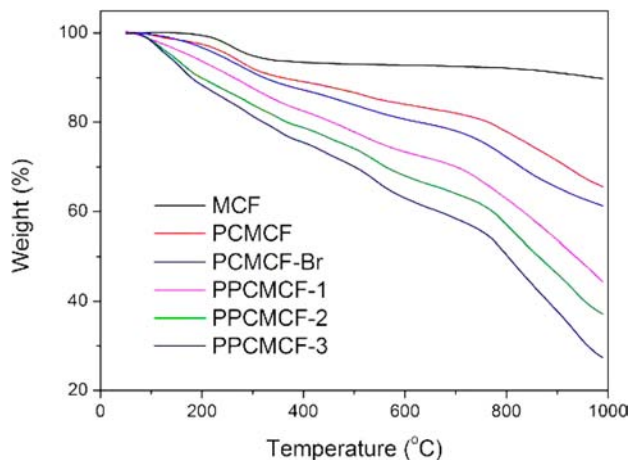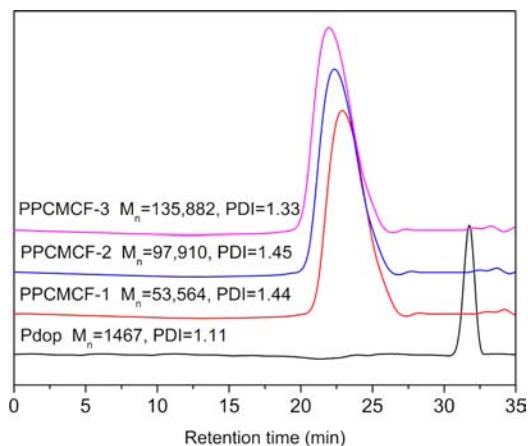

Figure 3. TGA curves of samples.

Figure 6. Water absorbencies of samples.

Figure 4. GPC traces of polymer peeled from controlled-release fertilizers.
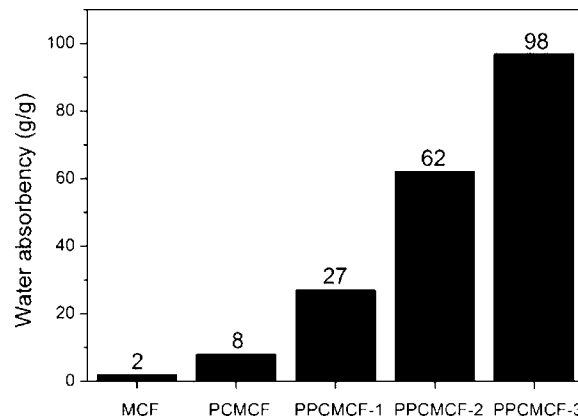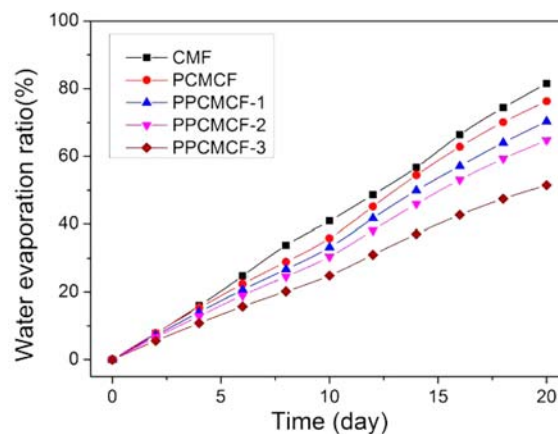

Figure 7. Water-retention behavior of soil with samples.

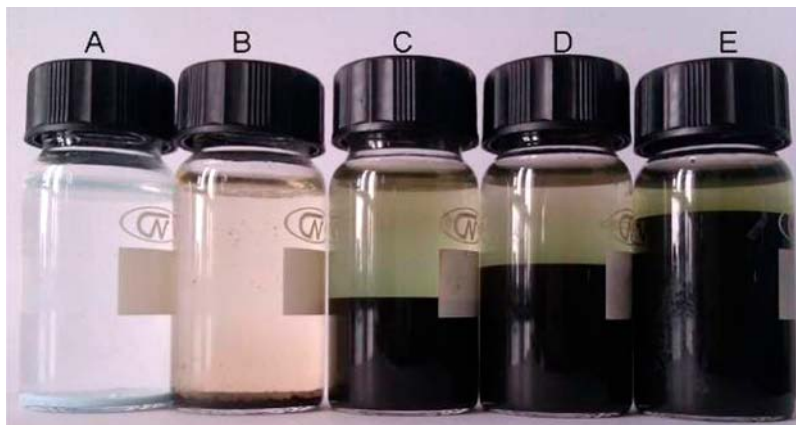in the products, indicating that the PAA chains were successfully grafted from Pdop coating.

Figure 5. Photographs of swollen (A) MCF, (B) PCMCF, (C) PPCMCF-1, (D) PPCMCF-2, and (E) PPCMCF-3 in deionized water.
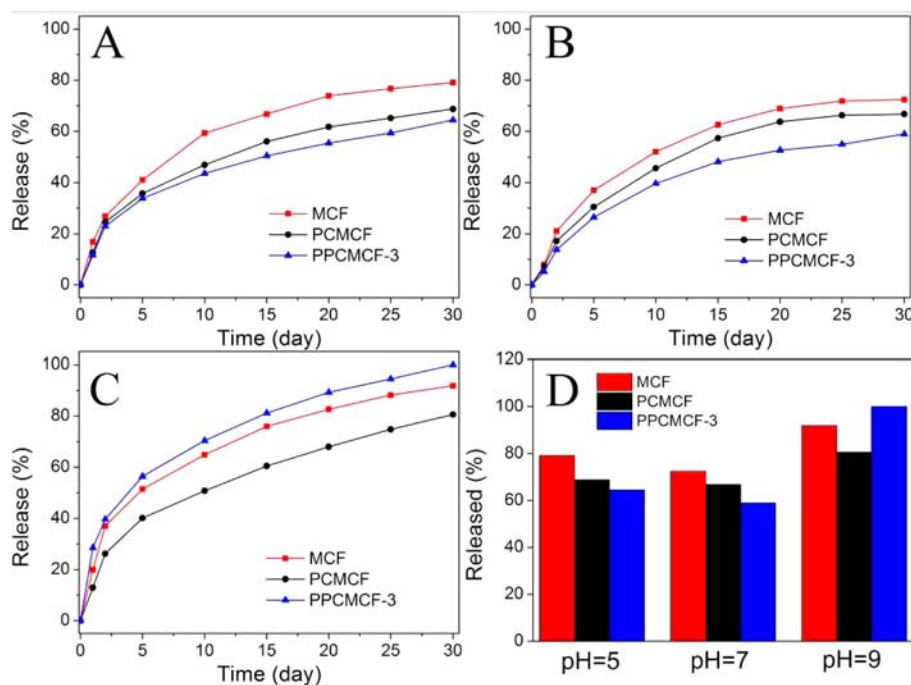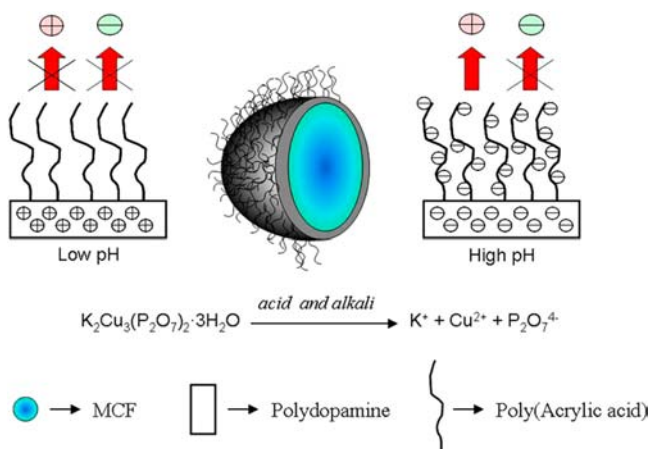
Figure 8. Controlled-release behavior of K from fertilizers in (A) pH 5, (B) pH 7, and (C) pH 9. (D) Comparison of the release rate of potassium from fertilizers in different pH solutions after 30 days.

Scheme 2. pH-Responsive Behaviors of the Pdop-*g*-PAA Coating in Different pH Solutions

The total amount of salt contained was determined using a sample digestion method for evaluating nutrient contents in PPCMCF. After microwave-assisted digestion in the presence of the catalyst, the contents of K, Cu, and P in the PPCMCF were determined with an ICP emission spectrometer. The release behaviors of nutrients from fertilizer were determined as mentioned above. The release percentage was calculated using eq 3

$$W = M_i/M_0 \qquad (3)$$

where M_i refers to the amount of nutrients released during study period days and M_0 refers to the total amount of nutrient.

The characteristics of products are listed in Table 1. The determined contents of K_2O, Cu, and P_2O_5 are almost consistent with the calculated values.

TGA was used to determine the relative amount of Pdop coating and grafted PAA brushes. As shown in Figure 3, the weight loss of MCF is 10.19% at 1000 °C, the weight loss of PCMCF is 35.79% at 1000 °C, and the weight loss of PCMCF−Br is 38.83% at 1000 °C. The difference between PCMCF and PCMCF−Br corresponds to 0.166 mmol of initiator groups/g of initiator-coated fertilizers. The weight losses of PPCMCF-1, PPCMCF-2, and PPCMCF-3 are 55.33, 64.75, and 72.21 wt % at 1000 °C, respectively. The results prove that the successful grafting of PAA brushes from the surface of PCMCF and the chain length of PAA can be tuned by the amount of monomer. It is noted that the weight loss of PPCMCF-3 is about 72%; however, in TEM images, the thickness of the polymer is 28 nm. We think some linear PAA may exist in the controlled-release fertilizer, although we rinsed these many times. However, it is reasonable from the ratio of AA to PCMCF.

The results of grafting polymerization were further obtained, as confirmed by GPC (Figure 4), after an alkaline-etching method (1 M NaOH).[48,49] The GPC curve with a narrow molecular weight distribution ($M_w/M_n < 1.5$) confirmed the successful ATRP. The result demonstrated that PAA brushes are grafted on the PCMCF successfully and the relative molecular weights of PAA can be tuned by the amount of monomer.

Effect of AA Monomer on Water Absorbency. One of the vital properties of PPCMCF is the water absorbency because of the superabsorbent layer. Figure 5 shows the photographs of the swollen samples. The MCF (A) and PCMCF (B) exhibit low water absorbency. Dramatically, the swollen images of PPCMCF fertilizers indicate that the PAA brushes could greatly enhance the water absorbency of fertilizers and the ability increases with an increasing molecular weight of PAA.

To investigate the water absorbency of samples, the samples were immersed in deionized water to reach swelling equilibrium. As shown in Figure 6, the MCF and PCMCF exhibit low water absorbency of 2 and 8 g g^{-1} in water,

Figure 9. Controlled-release behavior of Cu from fertilizers in (A) pH 5, (B) pH 7, and (C) pH 9. (D) Comparison of the release rate of Cu from fertilizers in different pH solutions after 30 days.
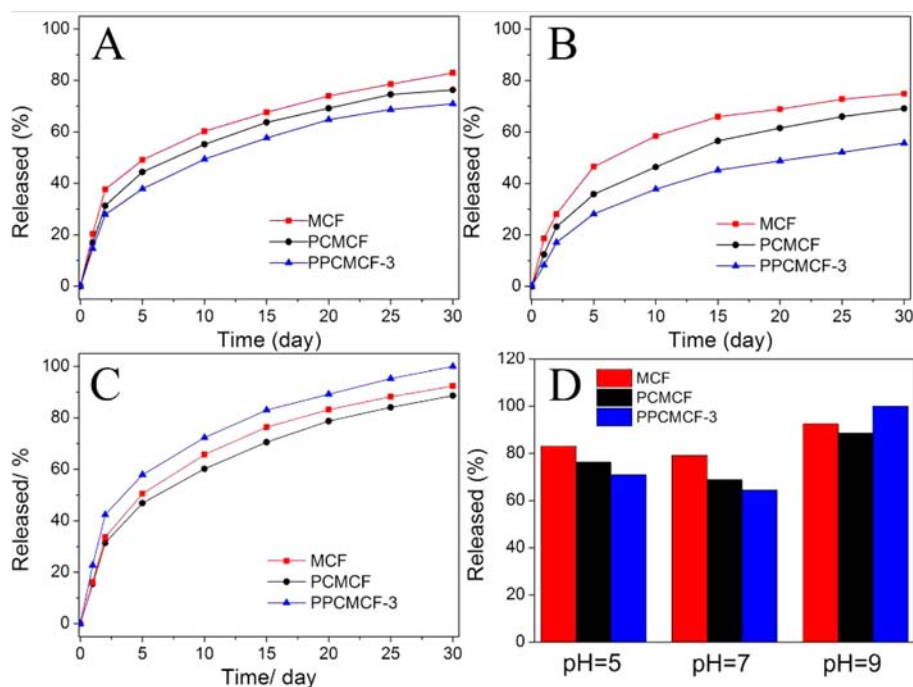

Figure 10. Controlled-release behavior of P from fertilizers in (A) pH 5, (B) pH 7, and (C) pH 9. (D) Comparison of the release rate of P from fertilizers in different pH solutions after 30 days.
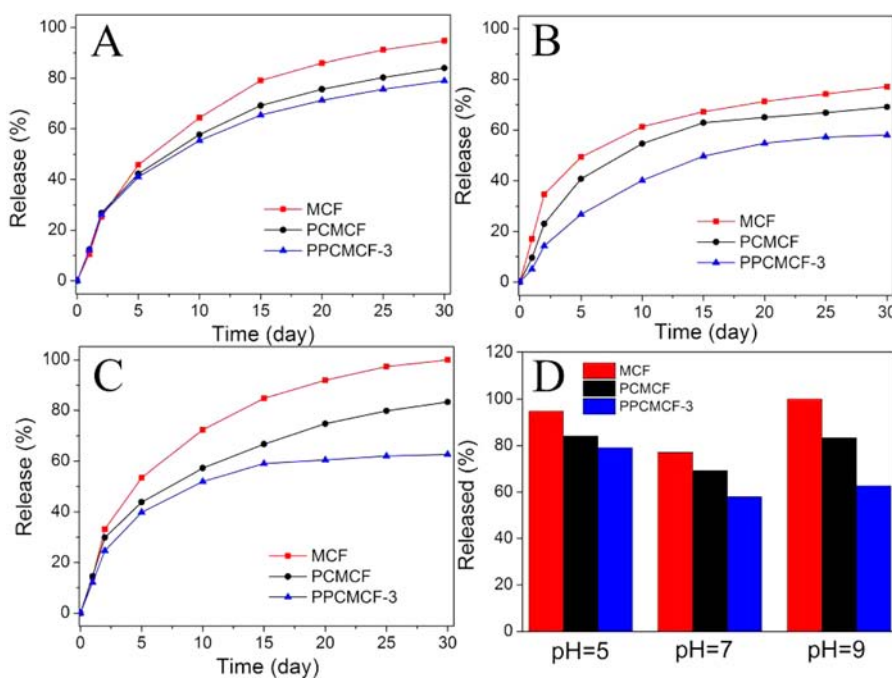
respectively. The water absorbencies of the superabsorbent-coated fertilizers were up to 27, 62, and 98 g g^{-1} for PPCMCF-1, PPCMCF-2, and PPCMCF-3, respectively. Clearly, the introduction of PAA brushes on the PCMCF could greatly enhance the water absorbency of fertilizers, and the ability of absorbing water of PPCMCF increases with an increasing length of PAA chains.

Water-Retention Behavior of PPCMCF in Soil. Another principal property of PPCMCF is its water-retention capacity. Figure 7 shows the water-retention properties of soil with or

without PPCMCF. It can be found that the water transpiration ratio of soil with MCF reached 81.53 wt % on the 20th day. For PCMCF, the water evaporation of the soil reached 76.29 wt %. Interestingly, after 20 days, the water transpiration ratio of soil with PPCMCF-1, PPCMCF-2, and PPCMCF-3 decreased to 70.32, 64.75, and 51.44 wt %, respectively. The results indicate that the MCF and PCMCF could not contribute much to improve the property of water retention. However, the addition of PPCMCF to soil could obviously increase the water retention and decrease the water evaporation. Moreover, the
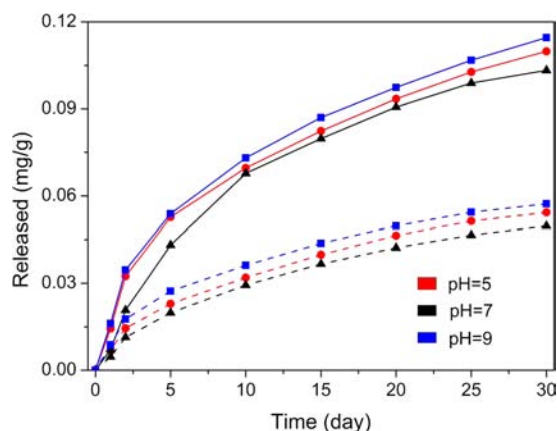
Figure 11. Release behavior of N from PCMCF (dot lines) and PPCMF-3 (solid lines).

water-retention properties of PPCMCF increase with the increasing length of PAA chains.

Controlled-Release Behavior of MCF, PCMCF, and PPCMCF-3. To obtain the best estimation of release behavior, PPCMCF-3 was selected as a model to study the pH-responsive controlled-release behavior of fertilizers. The release rate of all fertilizers is very slow and does not reach equilibrium after 30 days, because the MCF has relatively low water solubility. The release curve was obtained by plotting the concentration of nutrition normalized with the highest value versus time. The results indicate these series fertilizers have an excellent controlled-release behavior.

Figure 8 shows the controlled-release behavior of potassium from fertilizers at room temperature in different pH solutions. The accumulative release rate of potassium from MCF, PCMCF, and PPCMCF-3 is 80.32, 72.41, and 64.15 wt % within 30 days, in acidic solution (Figure 8A). The release behavior in neutral solution (Figure 8B) has the same trend; after 30 days, the release rate is 76.95, 71.01, and 60.14 wt %, respectively. For basic solutions (Figure 8C), the accumulative release of K from MCF reaches 89.79 wt % and PCMCF is 86.54 wt %; however, PPCMCF-3 is 100 wt %. Figure 8D shows the accumulative release rate of potassium from fertilizers after 30 days. For MCF, the release rate is faster in acid/basic solution than that in neutral solution because a faster hydrolysis of MCF may occur. Furthermore, the release kinetics of K from PCMCF based on the relative intensity is lower than that from MCF in different buffer solutions. This result is reasonable because the Pdop-based inner layer acts as an impermeable film, preventing the release of nutrients. On the basis of this, the accumulative release rate of potassium from PPCMCF-3 should be smaller than PCMCF, because the diffusion resistance increases after PAA chains are grafted on the Pdop film. However, it is noted that the nutrients released from PPCMCF-3 exhibit a large difference in permeability according to pH compared to MCF and PMCF. After 30 days, at low pH, the accumulative release rate of potassium of PPCMCF-3 is lower than that of PCMCF. In contrast, it is the reverse in basic solution.

The probable proposal may be illustrated in Scheme 2. The Pdop inner layer exhibits zwitterionicity because Pdop molecules have a great deal of amino and phenolic groups.[50,51] However, the effect of zwitterionicity of the Pdop layer on the hydrolytic ions of MCF is negligible because of the Pdop-based film with a low-charge density. The main role of the Pdop film

is restraining the transportation of molecules. However, for the polymer brush outer corona, the layer has a net negative charge at high pH that excludes anions but lets cations pass; in contrast, the brushes are uncharged at low pH, which are used just as a hindrance. The double layer with a Pdop inner layer and a PAA outer corona presents strong electrostatic attraction with positive nutrients and results in pH-responsive release behavior. At a weak acid media, the Pdop-g-PAA coating was used as a hindrance with an uncharged outer corona and the release rate of the positively charged nutrient was restricted. At an alkaline solution, the active groups (included phenolic groups of Pdop and carboxylic groups of the grafted PAA brushes) of the Pdop-g-PAA coating are deprotonated. Strong electrostatic attraction exists between the deprotonated coatings and positive nutrients, and the encapsulated positive nutrients may pass through the coating quicker in an alkaline environment. According to this proposal, the release behavior of copper is the same as potassium and the release behavior of P is reverse, because it is negative charged as $P_2O_7^{4-}$. The next investigation further verifies this proposal.

Figure 9 shows the controlled-release behavior of copper from samples. The accumulative release rate of Cu from MCF, PCMCF, and PPCMCF-3 is 81.27, 70.57, and 63.68 wt % for 30 days in acidic solution, respectively (Figure 9A). The accumulative release is 77.45, 70.06, and 55.89 wt % in pH 7 solution, respectively (Figure 9B). The release of Cu from PPCMCF-3 reaches 100 wt %, while MCF is 85.68 wt % and PCMCF is 80.95 wt % in alkaline solutions (Figure 9C). The accumulative release rate of copper is shown in Figure 9D and the same as the release trend of potassium.

In contrast, the release rate of phosphorus from samples is different. Figure 10A shows that the release rate of P ($P_2O_7^{4-}$) from MCF, PCMCF, and PPCMCF-3 is 97.48, 85.19, and 80.11 wt % within 30 days in an acid environment, respectively. At pH 7, the accumulative release of phosphorus is 79.44, 71.08, and 63.67 wt %, respectively (Figure 10B). At pH 9 (Figure 10C), the release of P encapsulated in MCF, PCMCF, and PPCMCF-3 is 100, 91.44, and 65.71 wt %, respectively. The opposite trend is obtained from Figure 10D. The release of phosphorus from polymer-brush-grafted fertilizers exhibit a stimuli-responsive release of nutrients. Just as we presented in Scheme 2, the Pdop-g-PAA coating acts as an impermeable cap, preventing the release of $P_2O_7^{4-}$ in the closed state, with existing electrostatic repulsions between the deprotonated Pdop-g-PAA and negative nutrients. Therefore, the negative ions difficultly pass through the coating in alkaline media.

To investigate the degradation of Pdop film in buffer, the accumulative release of nitrogen is measured as a sign of collapse of Pdop. As shown in Figure 11, the release of N from the coating gradually climbs up in solution with different pH values. The results of the release of nitrogen against time are almost the same trend for PCMCF and PPCMCF-3. However, what should be noted is that the release rate of nitrogen from PPCMCF-3 is faster than that from PCMCF. It is attributed to the fact that PAA has a hydrophilic portion and the swelled PAA may promote the Pdop decomposition.

PPCMCF with water-retention function via mussel-inspired initiator ATRP was successfully prepared. The composite layer formed by a Pdop inner layer and a PAA outer corona exhibits stimuli-responsive permeability for charged nutrition depending upon the pH. At low pH, the Pdop-g-PAA layer can reduce nutrient loss, and at high pH, the coating restrains the transportation of negative nutrition but favors the release of

cations. The result showed that the product with excellent controlled-release and water-retention properties could be expected to be promising in the research and development of coated fertilizer.

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Notes
The authors declare no competing financial interest.

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