

# Recent Trends in Advanced Polymer Materials in Agriculture Related Applications

Amrita Sikder,\* Amanda K. Pearce, Sam J. Parkinson, Richard Napier,\* and Rachel K. O'Reilly\*

Cite This: *ACS Appl. Polym. Mater.* 2021, 3, 1203–1217

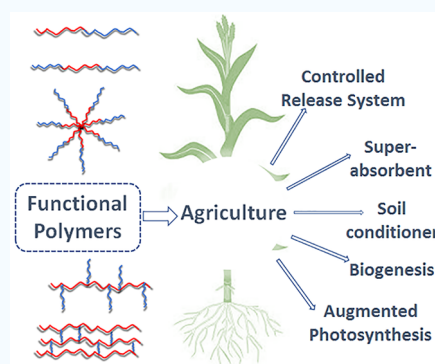
Read Online

ACCESS |

Metrics &amp; More

Article Recommendations

**ABSTRACT:** Over the past few decades, advanced polymeric materials have gained popularity in the development of sustainable agricultural applications. Smart polymeric systems have extensively contributed to the agricultural industry by increasing the efficiency of pesticides, herbicides, and fertilizers by facilitating controlled release systems and, therefore, enabling lower doses to be used. Superabsorbent polymeric materials have been used as soil conditioners to control the impact of drought, whereas polycationic polymers have been utilized for plant bioengineering. These functions in the environment are complemented by applications within plants as part of the developing range of tools for genetically transforming plants in order to increase productivity and disease resistance. This Review will summarize and discuss the recent developments in the design and application of advanced polymeric systems for precision agriculture related applications. The design criteria of the polymers employed to date, such as polymer structure, as well as the properties of polymer nanoparticles including shape and size will be discussed, and the key findings in the related area will be highlighted. Finally, we will identify future directions for the exploration of functional polymers with the ultimate aim of advancing sustainable agriculture.



**KEYWORDS:** functional polymers, stimuli-responsive, controlled agrochemical delivery system, superabsorbent material, plant bioengineering, sustainable agriculture

## 1. INTRODUCTION

Agriculture represents one of the most important contributors to good health, environmental pollution, sufficient nutrition, and economic development.<sup>1</sup> Initially, the driving force for agricultural development worldwide was to increase the productivity per unit area of land used for crop production, and over the years, this has been achieved through extensive use of fertilizers and pesticides and the exploitation of natural resources such as soil and water.<sup>2</sup> In response to the accumulating environmental impacts, recently, the world has begun striving toward more sustainable agricultural practices<sup>3</sup> for a better tomorrow. Some of the current issues now facing global agriculture are the needs to control the delivery of agrochemicals and to cope with soil degradation, water pollution, climate change, and ever-evolving plant pathogens and disease.<sup>4–7</sup> As scientific capabilities increase, new polymeric materials are proving to be potent and promising candidates for effectively addressing these issues.

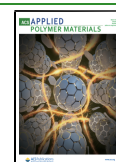
Polymers<sup>8–10</sup> are a class of versatile materials that have been used extensively in agriculture, as their properties such as structure, functionality, and biodegradability can be tailored to specific applications. More recently, research has started exploring bespoke and stimuli-responsive smart polymeric systems<sup>11</sup> for various plant applications. The continued development in technology and the use of advanced functional

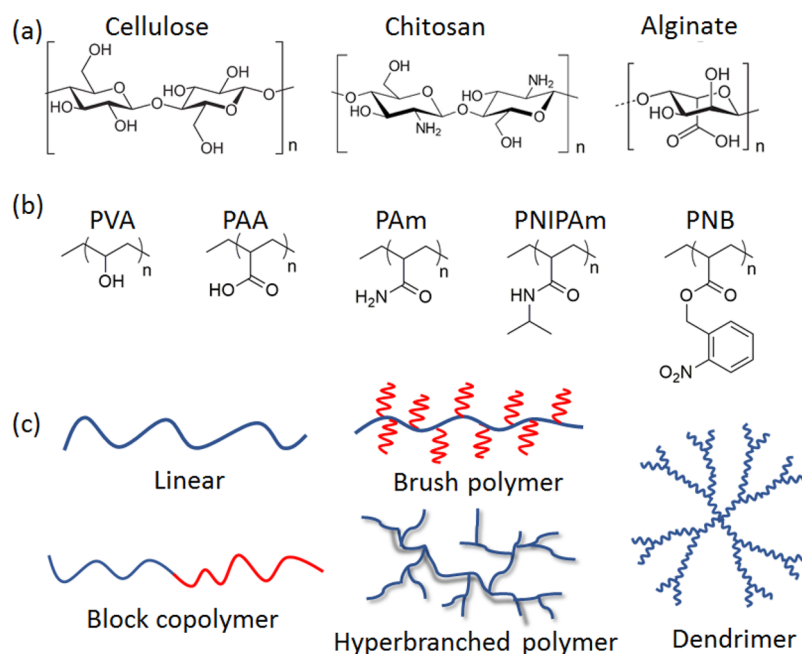
polymeric materials have together contributed to improvements in the controlled delivery of agrochemicals, soil conditioners, nutrients, water management, genetic engineering, and more.<sup>12–16</sup> To the best of our knowledge, no comprehensive reviews have been published thus far covering the breadth of research “hotspots” in advanced polymers for agriculture. In this regard, we have compiled a detailed Review focusing on the impacts that synthetic polymers have made in farming with a discussion on the structure and design aspects of these materials and key literature findings in a comprehensive manner. We will first introduce the general concept of functional polymer materials, their structure and uses, and then focus on several prominent research directions for these materials which include (i) controlled delivery of agrochemicals; (ii) water utilization by superabsorbent polymers; (iii) other applications inside plants and organisms. Furthermore, we will consider the most significant challenges that need to be overcome in order to increase the efficiency

Received: September 3, 2020

Accepted: January 28, 2021

Published: February 17, 2021



Scheme 1. Different Aspects of Advanced Polymers Used in Agriculture Related Applications<sup>a</sup>

<sup>a</sup>(a) Natural functional groups and (b) synthetic functional polymers discussed in this Review. (c) Different polymer architectures possible through various synthetic techniques.

and commercialization of these polymeric materials. Finally, we will indicate potential new opportunities and applications of novel functional polymers that can contribute to the development of sustainable agricultural practices.

## 2. FUNCTIONAL POLYMERS

A functional polymer<sup>17–19</sup> is any polymer that contains additional functional groups that differ in their chemistry to the backbone chain (Scheme 1a). These polymers often possess unique properties that can be tuned by altering these groups along the backbone. Furthermore, “smart” polymers contain functional groups that are responsive to stimuli, such as pH, light, or temperature,<sup>20–22</sup> which can further alter the polymer properties. There are many naturally occurring functional polymers (Scheme 1a) such as agar,<sup>23</sup> starches,<sup>24</sup> alginates,<sup>25</sup> chitosan,<sup>26</sup> and cellulose.<sup>27</sup> Synthetic functional polymers were first developed in the 1960s by Szwarc, Bywater, and Morton.<sup>28</sup> Since then, these materials have occupied an eminent place in modern science with rapidly growing interest due to the potential applications of these materials in biomedical science,<sup>29,30</sup> materials science,<sup>31</sup> and energy and the environment.<sup>32,33</sup> One niche area of research has focused on developing functional polymers for sustainable agriculture.<sup>34</sup>

The two major criteria for polymeric materials to be commercially viable in field-based agricultural applications are cheap and readily available raw materials and polymer biodegradability. Natural polymers meet these criteria; however, they have two major drawbacks: (i) the properties of natural polymers in their native state often do not fit the needs of specific applications and (ii) modification of these polymers is often difficult due to their lack of suitable functional groups as well as insolubility in organic solvents for common organic reactions.<sup>35,36</sup> These drawbacks can eventually cause an undesirable excess use of natural polymers to improve agricultural production. This has led to research into

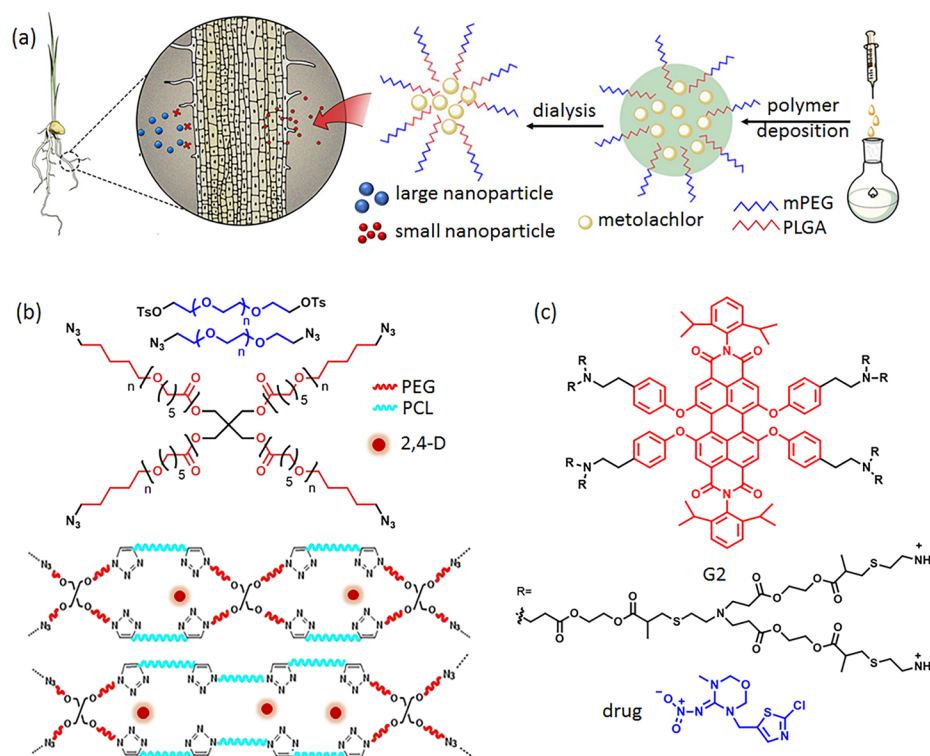
synthetic polymers as an alternative strategy. In recent years, controlled radical polymerization techniques such as atom-transfer radical polymerization,<sup>37</sup> nitroxide-mediated polymerization,<sup>38</sup> and reversible addition–fragmentation chain-transfer polymerization<sup>39</sup> have enabled the facile synthesis of polymers with a wide range of functional groups (Scheme 1b). In addition to the control over polymer functional groups, various synthetic techniques can also give access to a wide range of polymer architectures (Scheme 1c) such as block copolymers,<sup>40</sup> dendrimers,<sup>41</sup> bottle-brush polymers,<sup>42</sup> and hyperbranched polymers,<sup>43</sup> further expanding the range of materials that can be used in agriculture. However, the common drawbacks to synthetic polymers—high costs of production and lack of biodegradability—will likely limit their immediate implementation until they can be addressed. For example, biodegradability can be introduced by incorporating biodegradable polymers<sup>44</sup> such as poly(caprolactone), poly(lactide), poly(glycolic acid), or poly(vinyl alcohol) into the polymer backbone. Synthetic–natural hybrid polymers<sup>45–47</sup> have also emerged as potential materials, as they are based on cheap, natural polymers but also have properties of synthetic functional polymers. Through the concerted efforts of polymer chemists, synthetic polymers have been successfully used across a broad range of applications in agriculture, contributing powerful new tools for the agricultural and food industries, which will be discussed in the following sections.

## 3. CONTROLLED AGROCHEMICAL DELIVERY

Agrochemicals such as fertilizers, herbicides, and pesticides are essential in agriculture; however, they are also associated with undesirable environmental impacts, including bioaccumulation in the food chain and contamination of ecosystems. Controlled release techniques that combine agrochemicals with functional polymers have emerged as a strategy to deliver the required agrochemical at its active field rate over a long time period without unwanted leaching into the environment. This strategy

Table 1. Examples of Different Polymers Used for Controlled Agrochemical Delivery

polymer used	agrochemical used	nature of carrier	release property	ref
poly(PEG-co-PLGA)	metolachlor	micelle	diffusion control	48
PEG-aliphatic diacid conjugate	imidacloprid	micelle	diffusion control depends on diacid	49
poly(lactic-co-glycolic acid)	imidacloprid	nanoparticle	diffusion control	50
PCA-PEG-PCA triblock copolymer	imidacloprid	nanoparticle	diffusion control depends on PEG length	51
PLGA-PEG-PLGA terpolymer	metazachlor	nanoparticle	diffusion control depends on PEG length	52
cross-linked polymer (PCL-PEG)	2,4-D	gel	diffusion control	53
cross-linked polymer (acrylamide-itaconic acid)	potassium nitrate	cross-linked nanoparticle	depends on the nature of cross-linker	54
PDI containing fluorescent dendrimer	thiamethoxam	micelle	diffusion control	55
PHB, PHBV, poly(vinyl alcohol)	ametryn	particle formed by emulsion	release depends on surface property of the particle	56
poly( $\epsilon$ -caprolactone)	atrazine	nanocapsule/nanosphere	release depends on morphology and loading content	57
chitosan-poly lactide graft copolymer	imidacloprid, flusilazole	micelle	diffusion control	63, 47
DPPE conjugated chitosan-co-PLA	chlorpyrifos	nanoparticle	diffusion control	64
N-phthaloyl acylated chitosan cross-linked by suberoyl chloride	NPK, plant growth regulator	nanocapsule	diffusion control	65
poly( $\gamma$ -glutamic acid), chitosan	avermectin	nanoparticle-electrostatic complexation	pH responsive	45
azidobenzaldehyde-functionalized chitosan	methomyl	nanocapsule	pH responsive	67
poly(glycidyl methacrylate-co-acrylic acid)	abamectin	functionalized silica nanoparticle	pH responsive	69
PNIPAm-polydopamine	imidacloprid	core-shell microsphere	NIR-light and temperature responsive	70
pesticide conjugated polymer (PEG/acrylate)	2,4-D	micelle	light responsive	71, 72



**Figure 1.** Representation of active ingredient-loaded nanoparticles. (a) Schematic representation of the preparation of metolachlor-loaded polymer nanoparticles. Reproduced from ref 48. Copyright 2017 American Chemical Society. (b) Structure of the azide and alkyl functional precursors and schematic representation of forming multicomponent amphiphilic networks. Reproduced with permission from ref 53. Copyright 2019 John Wiley & Sons. (c) Structure of a PDI-cored cationic dendrimer and the hydrophobic drug thiamethoxam. Reproduced with permission from ref 55. Copyright 2015 Royal Society of Chemistry.

may also reduce degradation, evaporation, and wash-away of the active agents into the soil, improving efficiency while reducing environment toxicity and thereby enhancing practical applicability and human health. The desirable properties of suitable delivery systems for sustainable agriculture should (i)

control release of the agrochemicals at the lowest effective concentration, (ii) protect the agrochemical from degrading environments such as light and pH, (iii) possess lower cytotoxicity than the conventional pesticides, and (iv) have long lasting validity of the nanocarriers, which will reduce the

frequency of pesticide application and treatment by extending the lasting validity period. Some examples of functional polymers that have been used for agrochemical delivery are summarized in Table 1.

### 3.1. Synthetic Polymers as Nanocarriers. 3.1.1. Encapsulation and Noncovalent Loading of Polymer Assemblies.

One of the most versatile methods for preparing nanocarriers is the physical encapsulation of an active agent within amphiphilic polymers as they form self-assembled nanoparticles in aqueous media. One such nanocarrier system was reported by Tong et al.,<sup>48</sup> who demonstrated the self-assembly of a block copolymer of biocompatible poly(ethylene glycol) (PEG) and biodegradable poly(lactic-co-glycolic acid) (PLGA). These blocks were selected to generate amphiphilicity-driven nanoparticles in water with the hydrophobic core providing a loading space for the herbicide metolachlor, while the hydrophilic shell could shield the herbicide and improve its solubility in water (Figure 1a). These nanoparticles were shown to have a lower toxicity to nontarget human cells compared to the free herbicide. They also showed that the particle size could be tuned by changing the loading amount of metolachlor and found that the copolymer/metolachlor ratio of 4:1 was ideal for producing nanoparticles small enough for rapid uptake into root cells. A higher herbicidal activity was observed in rice and hairy crabgrass when using the metolachlor-loaded nanoparticles compared to the free herbicide.

Adak et al.<sup>49</sup> have reported a series of amphiphilic copolymer micelles synthesized from PEG-*b*-poly(aliphatic acid) for the controlled delivery of imidacloprid. PEG 300, 600, and 1000 were selected as the hydrophilic moieties, whereas various aliphatic diacids, namely, glutaric acid, adipic acid, pimelic acid, and suberic acid, were used as the hydrophobic headgroup. The effect of PEG chain length and the nature of the hydrophobic headgroup on the critical aggregation constant, size of micelles, imidacloprid encapsulation efficiency, and release rate were investigated. The release rate of imidacloprid from these micelles (size ~ 170–250 nm) was found to be slower than from the commercially available formulations; however, no uniform trend could be observed for the polymers having different hydrophilic–hydrophobic segments. The same pesticide was also encapsulated into 5–10  $\mu\text{m}$  sized particles composed of an amphiphilic diblock polymer poly(lactic-co-glycolic acid).<sup>50</sup> It was demonstrated that the concentration of imidacloprid required when using such functional microdispensers was 200 times lower than for commercial formulations against crop pests.

Along with amphiphilic diblock polymers, triblock copolymers have also been utilized to prepare agrochemical delivery systems. Memarizadeh et al.<sup>51</sup> synthesized ABA triblock linear dendritic copolymers composed of poly(citric acid) (PCA) as the dendritic A block and poly(ethylene glycol) (PEG) as the linear B block. This triblock polymer self-assembled to form nanoparticles in water, and imidacloprid was loaded through hydrophobic interactions. Experimental results revealed that imidacloprid nanoencapsulation was associated with increased mortality of *Glyphodes pyloalis* larvae and a reduced LC<sub>50</sub> (50% lethal concentration) compared to the free imidacloprid.

The rate of release of agrochemicals is highly dependent on the nature of the polymer, i.e., hydrophilic/hydrophobic ratio, linear/branched nature, degree of cross-linking, and various noncovalent interactions (H-bonding, ionic interaction etc.) and can be effectively tuned by modifying any of these

parameters. Rychter et al.<sup>52</sup> examined the influence of a relatively small PEG block content in poly(L-lactide-co-glycolide)–poly(ethylene glycol)–poly(L-lactide-co-glycolide) (PLGA–PEG–PLGA) with respect to polymer degradation and herbicide release. They found that the presence of even a short PEG block in the terpolymer chain increased the overall hydrophilicity of the polymer, thereby increasing its susceptibility to hydrolytic and enzymatic degradation in the soil environment. The introduction of the PEG block within PLGA–PEG–PLGA terpolymers also decreased the degree of crystallinity, which facilitated rapid biodegradation. The authors further prepared a series of herbicide-loaded polymers by varying the ratio of PEG to demonstrate tunable release properties.

In an interesting report by Dabbaghi and Rahmani,<sup>53</sup> a series of multicomponent amphiphilic cross-linked networks were synthesized (Figure 1b) from various combinations of azide- and alkyne-functionalized precursors (azido-terminated star-shaped poly(caprolactone), azido-terminated PEG, alkyne-terminated PEG) by a combination of ring-opening polymerization and click chemistry. The swelling behavior, biodegradability, and encapsulated 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide release was tuned by changing the ratio of hydrophobic segments and hydrophilic segments as well as by varying the cross-linking density. A higher cross-linking density and increased hydrophilicity resulted in less swelling and a slower degradation rate, giving a desirable release profile of the encapsulated agrochemical.

The nature of the cross-linker can also have a significant effect on agrochemical release properties. One study demonstrated this by preparing poly(acrylamide-co-itaconic acid) hydrogels cross-linked with either ethylene glycol-dimethacrylate (EGDMA) or *N,N'*-methylenebis(acrylamide) (NMBA).<sup>54</sup> The authors then evaluated the controlled release of a potassium nitrate fertilizer and demonstrated that the cross-linker provided distinct active sites to interact with the nitrate ions and pore sizes that allowed both its retention and also continuous and controlled release. A change in the cross-linker resulted in a different hydrophobic/hydrophilic balance, which affected the hydrogels swelling and release rates. A higher swelling percentage as well as faster release rate were observed for the more hydrophilic EGDMA cross-linked hydrogel in water compared to the NMBA cross-linked gels. The authors observed that swelling kinetics were affected in saline solution for the EGDMA cross-linked polymer due to ionic interactions with the EGDMA moiety, whereas a negligible effect was observed on the NMBA cross-linked polymer.

Liu et al.<sup>55</sup> introduced fluorescently-labelled nanocarriers for agrochemical delivery and release that could enable facile tracing in the food chain through the simple detection mode of fluorescence. They developed a unique type of pesticide nanocarrier using a water-soluble cationic dendrimer, which consisted of a fluorescent perylene diimide (PDI) core connected to dendritic hydrophobic polyesters and peripheral amino groups (Figure 1c). A hydrophobic insecticide, thiamethoxam, was loaded and immobilized via synergistic electrostatic and hydrophobic interactions. The dendrimer-based nanocarriers could efficiently deliver the drug into live cells, increasing the cytotoxicity of the drug and the larval mortality.

Grillo et al.<sup>56</sup> demonstrated that the surface properties of a polymeric carrier can also affect its release. They prepared two

different biodegradable microparticles using the emulsion/solvent evaporation technique for the sustainable release of the herbicide triazine. Poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-valerate) (PHBV) were used as the hydrophobic core materials for loading the herbicide, while hydrophilic poly(vinyl alcohol) was used as an emulsifier to increase their solubility in aqueous medium. SEM analysis revealed that both microparticle formulations were spherical but had different surface porosities (a smooth surface for PHB microparticles whereas a rough surface with pores for PHBV microparticles), and the herbicide release profiles differed according to the different surface properties. The release efficiencies were calculated to be  $\sim 74\%$  and  $\sim 85\%$  for the PHB and PHBV microparticles, respectively. The authors explained that the interaction of the PHB moiety with valerate in PHBV caused polymer plastification by reducing the free volume and crystallinity, resulting in a faster release compared to PHB microparticles. In addition, the morphology of the nanocarriers has been shown to have a major impact on their controlled release properties. Pereira et al.<sup>57</sup> studied the effects of two different types of poly( $\epsilon$ -caprolactone) particles, nanocapsules and nanospheres, for the delivery of the herbicide atrazine in target and nontarget plant species. Nanospheres were produced by an oil-in-water method using the polymer alone, whereas the nanocapsules were prepared using the same method but further adding the surfactant capric triglyceride along with the polymer. The nanocapsules were found to have a lower physiological stability compared to nanospheres, with the nanospheres remaining stable throughout a 90-day period, whereas the size of the nanocapsules increased with time, indicating aggregation. The authors provided a possible hypothesis that the instability of the nanocapsules was due to oxidation of the oil used in the preparation method, which then further interacts with the surfactants in the medium, eventually increasing interparticle interactions and resulting in aggregation. However, both types of nanoparticles were loaded with atrazine at over 90% encapsulation efficiency and showed prolonged release into water while being less genotoxic than free atrazine.

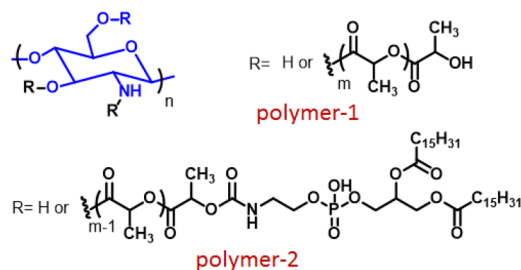
Liu et al.<sup>58</sup> prepared three types of delivery systems using poly(lactic acid): microcapsules, microspheres, and porous microcapsules for delivery of the insecticide  $\lambda$ -cyhalothrin. The release of the pesticide was found to be controlled mainly by diffusion and matrix degradation. By manipulating the process parameters, they were able to construct nanocarrier systems with tunable sizes as well as different loading contents. They noted that the weight ratios of poly(lactic acid)/ $\lambda$ -cyhalothrin and the size of the microcapsules affected the release of the pesticide, with smaller microcapsules having faster release rates. Similarly, pellet and microgranule shaped nanocarriers were prepared using a poly-3-hydroxybutyrate-co-3-hydroxyvalerate copolymer to evaluate the impact of the carrier shape for sustainable herbicide release.<sup>59</sup> Depending on shape as well as polymer/pesticide mass ratio, these nanoparticles showed different kinetic profiles of polymer degradation (whereby the polymer pellet showed a faster degradation profile than the granules) with an overall controlled release of the pesticide in soils, and demonstrated excellent killing efficiency against creeping bentgrass.

**3.1.2. Covalent Polymer–Agrochemical Assemblies.** Thus far, we have discussed literature examples describing the noncovalent incorporation of agrochemicals into the hydrophobic interiors of amphiphilic polymer assemblies. However,

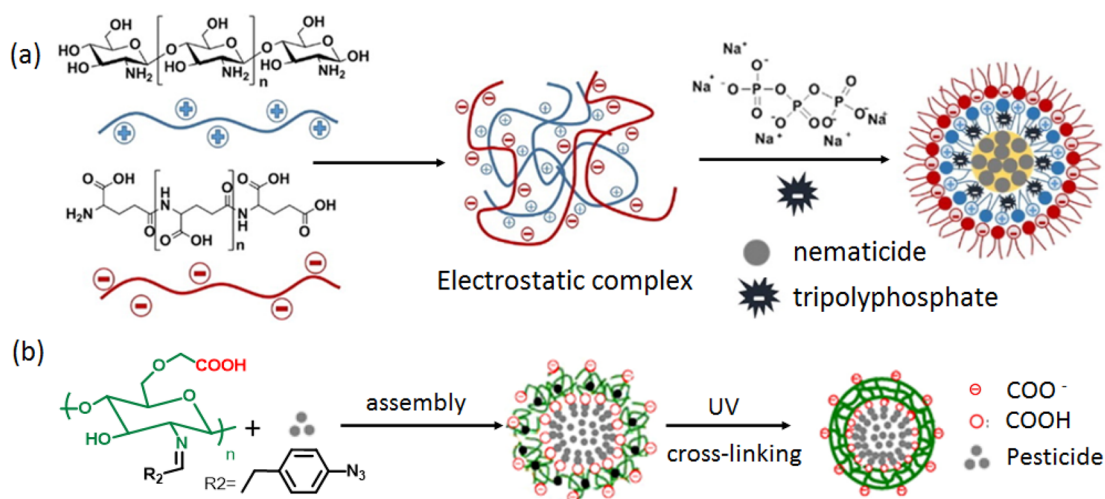
there are major concerns for noncovalent encapsulation, including generally poor loading efficiency and instability after encapsulation, resulting in undesirable premature release of the active agent in biological systems. As an alternative, polymer–agrochemical conjugates have been investigated to address the aforementioned issues. Kwiecien et al.<sup>60</sup> synthesized a bioactive polymer by conjugating the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). The resultant polymer–drug conjugate was then blended with poly(lactide) (PLA) and poly(butylene adipate-co-terephthalate) at different ratios to prepare a biodegradable mulch. Their system exhibited slow release of the herbicide from the mulch for broadleaf weed suppression, on account of the slow degradation of the mulch film under glasshouse conditions. Biological targeting and activity of the MCPA–PHBV conjugate was investigated using the fava bean as a model crop, and the authors observed complete suppression of weed growth. In a later report,<sup>61</sup> an in-depth study of the same mulch system through energy-dispersive X-ray spectroscopy analysis suggested that the release of even 1% MCPA could effectively suppress weed growth; however, higher concentrations of the herbicide adversely affected several physiological parameters of the nontarget fava bean growth.

One further important option for controlled delivery is to enhance the stability of the active agent through precise modification. Shang et al.<sup>62</sup> demonstrated improved pesticide photostability of emamectin benzoate following the formation of polymer nanoparticles. The nanoparticles were prepared by copolymerizing an N-acylated emamectin benzoate monomer with butyl acrylate and methyl methacrylate using an emulsion polymerization technique. Experimental results showed that the obtained nanoparticles exhibited greatly improved photostability compared to the commercially available emamectin benzoate formulation. Additionally, laboratory toxicity tests demonstrated that the insecticidal effects of the pesticide–polymer conjugate were improved over those of the control formulation.

**3.2. Synthetic-Biopolymer Hybrids.** One major drawback to the economic use of synthetic polymers is the residual material, which may be harmful to the environment. Attempts have been made to address this issue by preparing hybrid nanocarriers that combine synthetic polymers with natural polymers. In this regard, chitosan is one of the biopolymers widely explored due to its natural abundance and inherent antimicrobial properties. For example, Li et al.<sup>63</sup> studied the efficacy of an amphiphilic chitosan–poly(lactide) graft copolymer, where poly(lactide) was grafted onto the water-soluble chitosan to improve insecticide loading (Figure 2,



**Figure 2.** Synthetic-biopolymer hybrids: structure of chitosan grafted polymers as mentioned in refs 63 and 64.



**Figure 3.** Representation of pH-responsive polymers. (a) Schematic illustrations of the preparation of nanoparticles via electrostatic complexation. Reproduced with permission from ref 45. Copyright 2018 Elsevier. (b) Schematic representation of the assembly process of methomyl-loaded shell cross-linked nanocapsules. Reproduced with permission from ref 67. Copyright 2014 Elsevier.

polymer-1). The resultant amphiphilic polymer formed submicron nanoparticles that could encapsulate imidacloprid, giving a sustained release profile. In a later report, the same nanocarrier was utilized as a fungicide delivery system with the fungicide flusilazole loaded into the polymeric micelles via a modified nanoprecipitation method.<sup>47</sup> The authors reported that flusilazole was released by diffusion through the polymer matrix and that the nanoparticles successfully enhanced the activity of flusilazole by providing better penetration through grape leaves.

Another interesting system<sup>64</sup> was prepared by conjugating the lipid 2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine (DPPE) to a chitosan-*co*-PLA graft copolymer for the controlled delivery of the organophosphate insecticide chlorpyrifos (Figure 2, polymer-2). DPPE was chosen due to its high biocompatibility and ability to load the lipophilic chlorpyrifos with high efficiency. The nanoparticle size could be tuned by using either emulsion/solvent evaporation (218–283 nm) or nanoprecipitation (132–180 nm) techniques as well as by increasing the loading content, whereby size increased with higher loading due to a larger volume of the hydrophobic core.

Chen et al.<sup>65</sup> demonstrated that it was possible to improve the mechanical properties and permeability of a cross-linked membrane of chitosan nanoparticles. The hydrophobic cross-linker suberoyl chloride was used to cross-link *N*-phthaloyl acylated chitosan, where the permeability of the chitosan membrane could be regulated by varying the degree of cross-linking (0 to 7.4%). Permeability was found to decrease gradually with an increase in cross-linking density due to a decrease in free volume in the cross-linked network. This system proved to be an excellent candidate for controlled release of various plant nutrients, including macroelements (N, P, K), microelements (Zn<sup>2+</sup> and Cu<sup>2+</sup>), and a plant growth regulator (1-naphthylacetic acid).

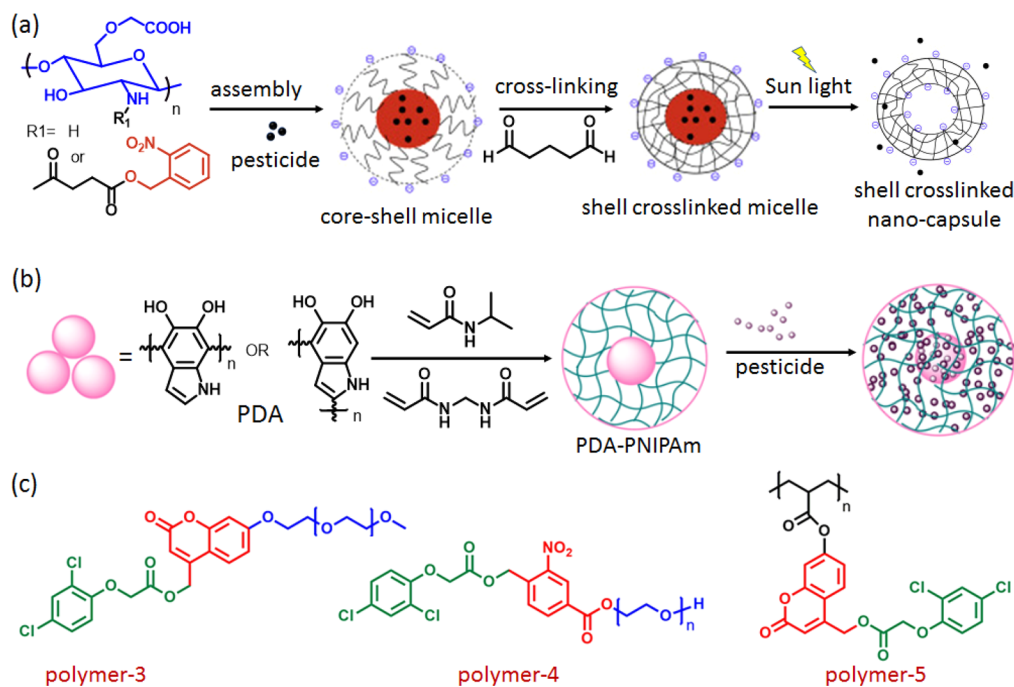
Using a similar concept, pesticide-loaded nanoparticles were prepared by cross-linking chitosan with two different cross-linking agents, namely, glutaraldehyde (GLA) and tripolyphosphate (TPP).<sup>66</sup> Chitosan was cross-linked covalently with GLA, whereas TPP was incorporated noncovalently via electrostatic interactions. It was observed that the stability of

the covalently cross-linked GLA–chitosan nanoparticles was higher than the noncovalently TPP cross-linked ones, but there was no significant difference in pest-control activity between the two.

**3.3. Stimuli-Responsive Polymers.** With continually emerging developments in nanotechnology, stimuli-responsive polymeric smart materials have received considerable attention for their ability to deliver agrochemicals under specific microenvironment conditions in a self-regulated manner. Liang et al.<sup>45</sup> developed a pH-responsive system through electrostatic complexation between  $\gamma$ -polyglutamic acid and chitosan, followed by noncovalent cross-linking with TPP for the transport of the nematocide avermectin. At lower pH, the nanocarrier exhibited higher stability facilitated by strong electrostatic interactions between chitosan and the carboxyl groups of  $\gamma$ -polyglutamic acid, which subsequently diminished with an increase in pH (Figure 3a). The system showed an initial pH-independent release of 20% with an additional 69.5% release at pH 8.5, 60.4% at pH 7, and 57.5% at pH 5.5.

Sun et al.<sup>67</sup> demonstrated a light-stimulated synthesis and pH-responsive release of an insecticide from methomyl-loaded chitosan nanocapsules to control armyworm larvae (Figure 3b). The nanocapsules were prepared by encapsulating hydrophilic methomyl inside the aqueous lumen of self-assembled nanocapsules of photo-cross-linkable azidobenzaldehyde-functionalized amphiphilic carboxymethyl chitosan, followed by UV irradiation to cross-link the membrane. More than 90% encapsulation efficiency of the nanocapsules was obtained at pH 4, attributed to the hydrogen bonding between methomyl molecules and carboxylic groups present on the inner surface of the polymer nanocapsules, whereas at higher pH (pH 6), disruption of H-bonding led to the diffusion-controlled release of methomyl, preventing burst release. The authors further varied the degree of cross-linking of the nanocapsules and found that the release rate was affected, whereby an increased degree of membrane cross-linking showed a slower release profile.

Similarly, another chitosan-based photocontrolled agrochemical delivery system<sup>68</sup> was prepared by conjugating photolabile 2-nitrobenzyl functional groups to carboxymethyl chitosan. The modified polymer formed micelles in water and



**Figure 4.** Representation of photoresponsive polymers. (a) Schematic illustration for the synthesis of pesticide-loaded, light-activated nanoparticles. Reproduced with permission from ref 68. Copyright 2015 Elsevier. (b) Schematic representation for the preparation of core-shell PDA-PNIPAm nanocomposites. Reproduced from ref 70. Copyright 2017 American Chemical Society. (c) Structure of the 2,4-D-conjugated photoresponsive polymer as described in refs 71 and 72 (Color code: green, drug; red, photolabile group; blue, hydrophilic chain; black, hydrophobic chain).

could be further cross-linked with dialdehyde to enhance the stability of the system (Figure 4a). Transmission electron microscopy (TEM) images and dynamic light scattering (DLS) analysis confirmed the formation of micelles with a core-shell structure and an average diameter of 140 nm, and a herbicide could be encapsulated in the nanocapsules with very high encapsulation efficiency (~92%). Experimental results revealed that the micelles were stable in aqueous solution at pH 7.0 with no detectable release in the absence of light irradiation, whereas upon exposure to solar irradiation, there was sustained release, showing 97% release over 8 h in pH 7.0 buffer solution.

Using a completely different design strategy, Gao et al.<sup>69</sup> developed a pH-responsive system based on silica nanoparticles coated and functionalized with a poly(glycidyl methacrylate-acrylic acid) copolymer. The nanocarrier showed base-mediated agrochemical release due to the transformation of the surface carboxylic acid groups to carboxylate groups. The insecticide abamectin was loaded into the nanocarriers, and the release profile revealed that after 15 days at pH 5 and 7 there was 14–15% release, whereas at pH 10, the release of the insecticide reached 39% after 5 h and 87% after 15 days. Thus, the payload could be conserved on the crop surface but released rapidly upon ingestion by insect larvae, which have a basic midgut.

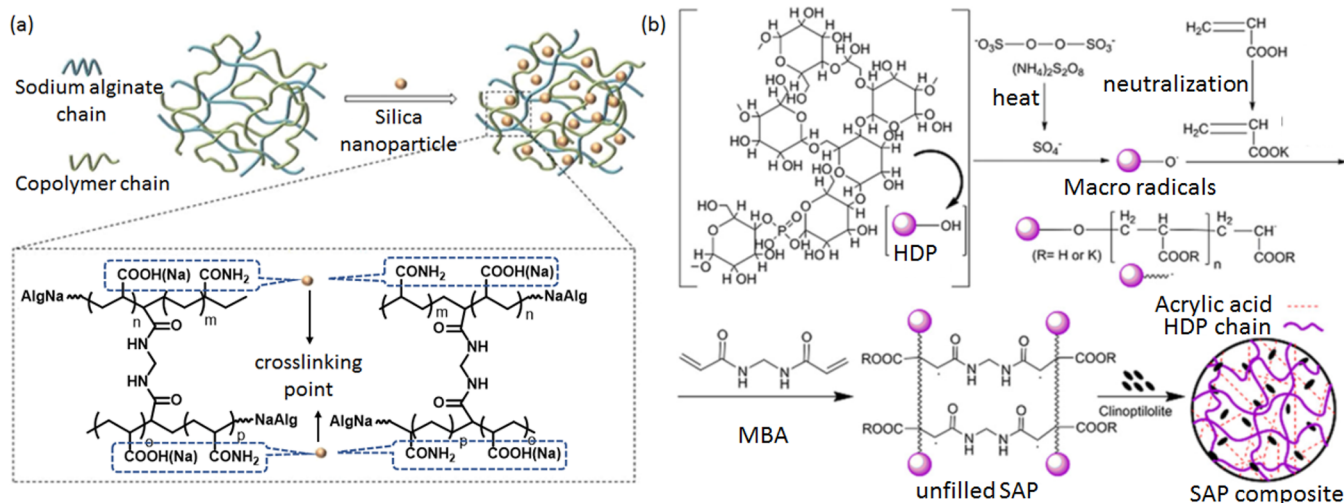
Xu et al.<sup>70</sup> reported a dual responsive (NIR-light and temperature-sensitive) nanocarrier (Figure 4b) using poly(*N*-isopropylacrylamide) (PNIPAm)-capped poly(dopamine) (PDA) microspheres. The release rate of imidacloprid was found to be strongly dependent on the temperature owing to the well-reported thermoresponsive nature of the NIPAm unit, with negligible release at 15 °C but increased release with rising temperature. It was also found that in the presence of NIR light irradiation, PDA experienced efficient photothermal

conversion with a cumulative drug release (15.7% after 0.5 h compared with 5.2% without light). Such a dual stimuli-responsive drug release profile may be beneficial for identifying the best surrounding environmental conditions for the field application of these nanoformulations.

Ding et al. developed<sup>71</sup> a photoresponsive system for the controlled delivery of herbicides, by conjugating 2,4-D with PEG (PEG 4000/PEG 10000) via the photoresponsive spacer arm 3-nitro-4-bromomethylbenzoic acid (Figure 4c, polymer-3). The amphiphilic polymer-pesticide conjugate could self-assemble into core-shell micelles in water, and subsequently release 2,4-D upon exposure to UV irradiation due to photolysis of the polymer chains.

Coumarin-based polymers, as light responsive smart delivery systems, also hold great interest for field applications. Atta et al.<sup>72</sup> synthesized two different types of polymers: the first by conjugating a coumarin-2,4-D unit onto PEG and the second by polymerizing an acrylate-based coumarin-2,4-D conjugate monomer (Figure 4c, polymer-4 and polymer-5, respectively). These polymers presented extended herbicidal activity with controlled release of 2,4-D under UV light.

Overall, it is apparent that polymeric material-based nanoformulations have led to improved properties over conventional pesticides in terms of sustainable release,<sup>63,65</sup> stimuli-responsiveness,<sup>45,67–72</sup> solubility,<sup>48,64</sup> stability,<sup>62,66</sup> and targeted delivery.<sup>60</sup> It has become clear from these reported materials that the release rate of the active ingredients can be tuned by changing the hydrophobic/hydrophilic balance (an increase in hydrophilicity increases the release rate)<sup>52,54</sup> or by varying the degree of cross-linking (an increase in cross-linking leads to slower release).<sup>53,54</sup> In addition, the size (generally a small size demonstrates faster release),<sup>49,58</sup> shape (no general conclusion can be made),<sup>57–59</sup> and surface porosity<sup>56</sup> of the polymer nanoparticles can all have significant effects on the



**Figure 5.** SAPs for water retention. (a) Illustration of proposed reaction mechanism for the synthesis of the RHA/superabsorbent composite. Reproduced with permission from ref 93. Copyright 2017 Elsevier. (b) Schematic representation of the proposed mechanism for the synthesis of HDP-g-AA/clinoptilolite SAPs. Reproduced with permission from ref 95. Copyright 2019 John Wiley & Sons.

agrochemical loading content and subsequent release properties.

#### 4. SUPERABSORBENT POLYMERS

Superabsorbent polymers (SAPs) are three-dimensional cross-linked polymer networks that have the potential to absorb a large amount of fluid.<sup>73</sup> These materials are of growing interest in the agriculture sector, as they can effectively improve water retention and soil texture by regulating the evaporation and infiltration rates of water, and can also release water and nutrients to the plants.<sup>74–77</sup> In general, effective SAP materials should possess features such as (i) high fluid absorption capacity, (ii) high fluid retention, and (iii) high or regulated absorption rate. These features are reflected in the swelling capacity of the SAP materials and are greatly influenced by the mechanical strength of the material, cross-linking type, and extent of cross-linking.<sup>78</sup> There has been substantial focus on developing SAPs from natural polymers such as starch, cellulose, chitosan, and alginate due to their abundant raw resources; however, these polymers have poor mechanical strength and insufficient water capacity.<sup>79</sup> On the other hand, synthetic SAPs offer improved mechanical properties and facile tunability through changing the functional monomers. However, an SAP material for use in agricultural land for practical agriculture application should have a number of additional desired properties including (i) the highest absorption capacity with maximum equilibrium swelling in saline, (ii) the maximum absorption capacity under load, (iii) high durability and stability in the swelling environment and storage conditions, (iv) the ability to degrade without producing toxic byproducts, (v) not changing the pH of the soil, and (vi) cost-effective production.

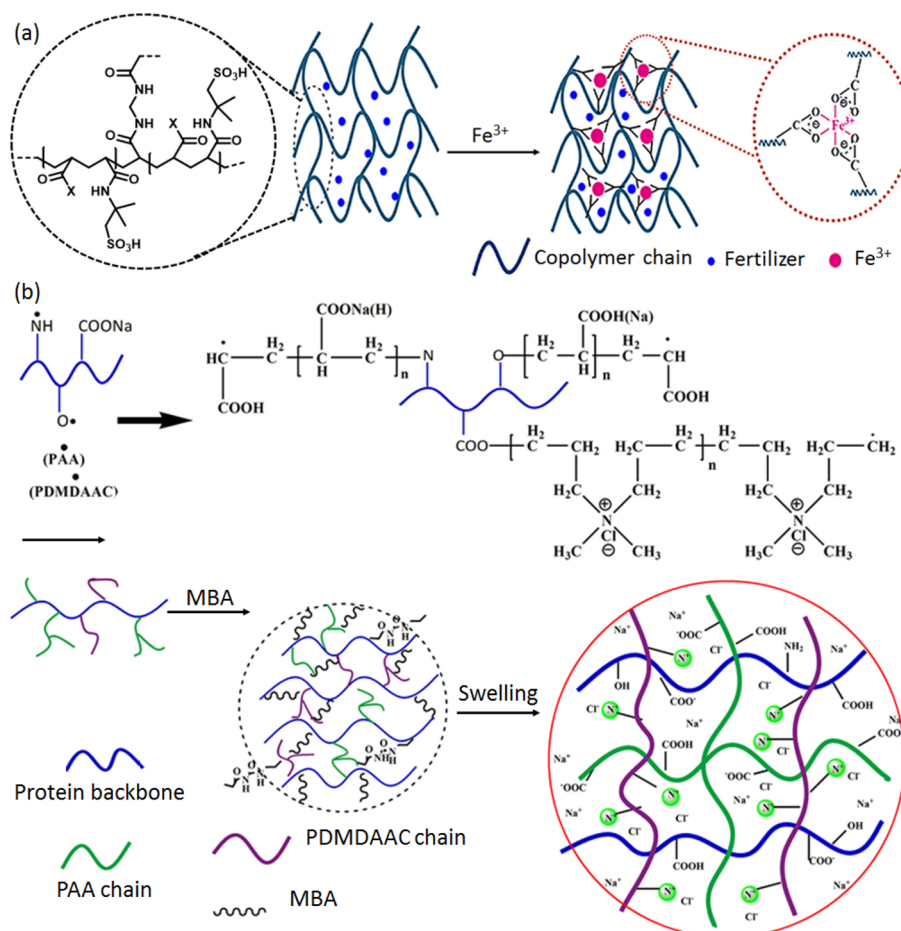
**4.1. Synthetic SAP.** In 1984, Erickson<sup>80</sup> first reported the application of SAPs prepared from various poly(alkyl acrylates) and poly(alkyl methacrylates) as soil conditioners, and ever since, scientists have continued to explore various superabsorbent polymers, including stimuli-responsive smart systems,<sup>81</sup> to improve their reversible water retention capacity. Synthetic polymers like poly(acrylamide)- and poly(vinyl alcohol)-based hydrogels have been utilized for field applications (mixed into soil/seed coating) and were found

to be very effective for water retention over long periods with a greater survival rate of plants.<sup>82–85</sup> Dabbaghi et al.<sup>86</sup> reported a unique superabsorbent material prepared using functionalized tannic acid (TA), which is well known for its antimicrobial properties. Alkene-functionalized TA was used as an internal cross-linker for poly(acrylic acid), while epoxy-functionalized TA was used as the external cross-linker. A series of materials were prepared by varying the amount of internal and external cross-linker, and then their various properties were evaluated such as free swelling, absorbency under load, and gel content. These materials were confirmed as potential candidates for agricultural applications due to the additional advantage of excellent antibacterial activity against Gram-positive and Gram-negative bacteria. Cheng et al.<sup>87</sup> prepared a low-cost SAP by polymerizing acrylic acid (AA) in the presence of *N,N'*-methylenebis(acrylamide) and urea cross-linkers. By varying the mass ratio of each component, they optimized the material and found the highest water absorption (909 g/g) when using a 0.02% MBA to AA mass fraction with a 1.0 mol urea/mol AA ratio. They also evaluated the absorption behavior in the presence of different salt concentrations as well as the effect of SAP on different types of soils. The results highlighted that the addition of SAP to soils could significantly improve the water absorption and retention capacity of soils (20–25 times higher compared to the untreated soil).

Biodegradability is one of the important criteria of SAP materials for field applications in order to fulfill human economic necessities without amplifying waste accumulation. Researchers have sought to improve the biodegradability of such materials by the incorporation of biobased cross-linkers, hydrophilic segments, or charged functional groups. Stahl et al.<sup>88</sup> synthesized poly(acrylamide–acrylate) copolymer hydrogels and studied the rate of biodegradability of this superabsorbent material, and they observed superior biodegradation properties in soils compared to pure poly(acrylate). In another report,<sup>89</sup> poly(aspartic acid)-based polymer networks were studied and found to have an elevated capacity for biodegradation.

**4.2. Synthetic-Biopolymer Hybrid SAP.** Although there has been a lot of research developing SAPs, their application has been limited due to their high cost, incipient toxicity, and





**Figure 6.** SAPs for water retention as well as controlled agrochemical delivery. (a) Schematic representation for the preparation of collagen-g-p(AA-co-AMPS)-Fe(III) polymer. Reproduced with permission from ref 97. Copyright 2019 John Wiley & Sons. (b) Synthesis mechanism of collagen-g-poly(acrylic acid). Reproduced with permission from ref 81. Copyright 2020 John Wiley & Sons.

detrimental effects on the environment. In recent years, SAPs prepared by combining synthetic polymers with natural polymers have gained popularity as they successfully address most of the aforementioned issues. One notable example reported poly(acrylamide) grafted onto chitosan, followed by cross-linking with MBA.<sup>90</sup> The properties and swelling profile of the material were optimized by changing the ratio of chitosan, MBA, and other reaction parameters. It was found that the maximum equilibrium swelling was achieved using a cross-linker ratio of 1% relative to the acrylamide. Like chitosan, polysaccharides are another important class of natural polymer that have been utilized for preparing SAP. For example, Mukerabigwi et al.<sup>91</sup> prepared a SAP by grafting poly(acrylic acid) onto xyloglucan polysaccharide chains and employing MBA as a cross-linker, and observed excellent water absorbance capacity under optimal conditions. Ahmed et al.<sup>92</sup> reported the synthesis of a superabsorbent hydrogel formed via graft copolymerization of carboxymethyl cellulose, acrylic acid, and acrylamide using MBA as cross-linker. This polymer conjugate demonstrated outstanding superabsorbent properties, having a swelling ratio of 190 g g<sup>-1</sup>. They further demonstrated the practical utility of this material by cultivating green peas in pots, whereby mixing 0.7% of the superabsorbent hydrogel with sand reduced water requirements by up to 25%. Importantly, there was improved plant growth in the presence of the SAP hydrogel under both full irrigation and drought.

An alternate method to improve the mechanical properties of SAPs is to add fillers, such as the inclusion of inorganic or organic nanoparticles into polymer networks. One example describes the preparation of an SAP nanocomposite via the grafting of acrylic acid and acrylamide onto sodium alginate loaded with rice husk ash (RHA), a silica-based filler.<sup>93</sup> H-bonding interactions between the hydroxyl groups of the polymer and RHA provided additional cross-links within the 3D-hydrogel network, improving the mechanical strength of the hydrogel (Figure 5a). The swelling ability and salt resistance properties of the RHA-nanocomposite were higher than that of the hydrogel in the absence of filler; however, the swelling of both materials was significantly affected by solution pH and temperature.

In another instance, Zhou et al.<sup>94</sup> synthesized a collagen-graft-poly(acrylic acid)/attapulgite superabsorbent composite by cross-linking acrylic acid-grafted starch with MBA in the presence of an attapulgite filler, which is known for its inherent water absorption properties. Similarly, clinoptilolite zeolites were used as the filler in a SAP prepared by the graft copolymerization of hydroxypropyl distarch phosphate (HDP) with acrylic acid (Figure 5b).<sup>95</sup> The study revealed that the surface morphology of the superabsorbent polymer could be improved with the incorporation of clinoptilolite, and as a result, the water absorbance was maximized (1210 g/g). Moreover, water retention experiments revealed that the optimum SAP in 100% sand had higher water retention,

while SAP in 50% sand lost its absorbed water 49 days later than the control sample.

**4.3. Controlled Release SAP.** SAPs have also attracted considerable attention as release formulations, as the combination of fertilizer/nutrients and superabsorbent properties can aid plant nutrition, along with soil conditioning by reducing the frequency of irrigation. Zhan et al.<sup>96</sup> reported the synthesis of a SAP by reacting phosphoric acid with poly(vinyl alcohol), where the resultant material was able to absorb and retain water and provide controlled release of phosphate as a fertilizer. In another example,<sup>97</sup> phosphorus was loaded onto smart SAP materials prepared by the polymerization of collagen, 2-acrylamido-2-methyl-1-propanesulfonic acid, and acrylic acid. The obtained polymer was then coordinated with Fe(III), where iron chelation caused additional noncovalent cross-linking, which reduced the water absorption capacity but enhanced the controlled release property of the loaded phosphorus fertilizer (Figure 6a). In an interesting report, Xu et al.<sup>81</sup> demonstrated an effective approach to prepare SAPs with high salt tolerance and pH responsiveness by grafting zwitterionic groups onto the polymer backbone (Figure 6b). Specifically, they prepared an amphoteric superabsorbent polymer by grafting acrylic acid onto collagen, a natural polymer, followed by cross-linking with dimethyldiallylammonium chloride (DMDAAC). This material showed pH-dependent, reversible swelling with responsive herbicide release properties.

All these reports highlight the ability of SAPs to effectively improve soil water retention,<sup>92–94,98</sup> soil condition,<sup>87,99</sup> and water-use efficiency. Furthermore, the carbon fixation rate in the early stage of plant growth and utilization efficiency of granular fertilizer<sup>81,96,97</sup> can also be improved. On the basis of the literature analysis, it is apparent that to improve SAP water capacity, more ionic functional groups (i.e.,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ) need to be included,<sup>100,101</sup> whereas to improve the salt resistance, zwitterionic groups are needed.<sup>81,102</sup> Along with total absorption capacity and salt resistance, other important factors for ideal SAP such as good absorption under load, higher mechanical properties, and absorption rate have been investigated, and synthetic factors affecting these have been correlated in Table 2.

## 5. OTHER APPLICATIONS: INSIDE PLANTS AND ORGANISMS

One of the leading challenges in agriculture is the growing demand for food, and plant bioengineering is one of the emerging strategies to address this need, by providing an effective pathway for breeding new varieties of crops with higher yields as well as qualities such as enhanced resistance to herbicides, insects, diseases, and drought.<sup>103,104</sup> There is also interest in polymer materials as vehicles for nanosensors, which can report on plant responses at a far greater level of detail than ever achieved previously.<sup>105</sup> A set of reports show convincing evidence that nanoparticles with hydrodynamic radii up to 100 nm are taken up into plants through the roots and are distributed by the plant vasculature. It is likely that the sites of ingress are the stomata in leaves, or the areas of damage around abrasions and tissue restructuring in roots when lateral roots push through living tissues to reach the soil. Evidence that nanoparticles can be transported within plants shows that the effective delivery of functionalized polymers is viable.<sup>106</sup>

**5.1. Gene Transfection.** Although considerable progress has been achieved with regards to bioengineering techniques,

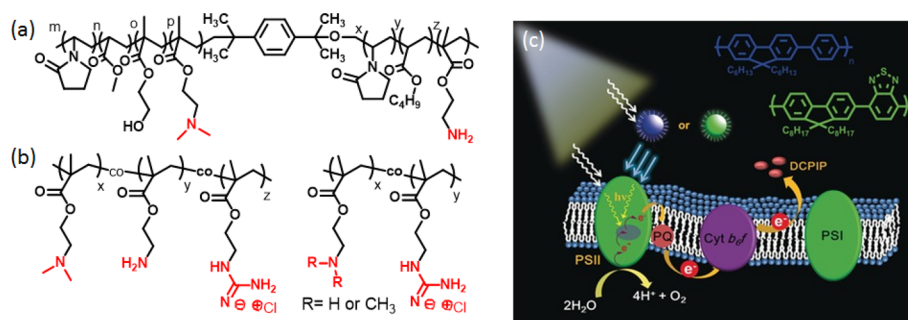
**Table 2. Effect of the Main Synthetic (Internal, Structural) Factors Affecting SAP Material Properties<sup>a</sup>**

variation in synthetic factor	absorption capacity	absorption rate	swollen gel strength or absorbance under load	soluble fraction
increase in cross-linker concentration	–	–	+	–
increase in initiator concentration	+	–	–	+
increase in monomer concentration	–	+	–	+
increase in reaction temperature	+	–	–	+
increase in particles porosity	NA	+	–	–+
surface cross-linking	–	–+	+	–+

<sup>a</sup>Table reproduced from ref 74, Copyright 2008 Springer Nature. +, increasing; –, decreasing; –+, varied, depending on the reagents and/or techniques employed.

the genetic transformation of plant species still remains a challenging task, primarily due to a lack of efficient delivery vectors that can transport genetic material into plant cells through their rigid and multilayered cell wall.<sup>107</sup> Polymeric materials have been widely explored as delivery vectors for biomedical applications,<sup>108</sup> whereas their potential for plant systems remains understudied, and only a few examples have been reported so far. Silva et al.<sup>109</sup> demonstrated the potential of conjugated polymer nanoparticles for effective siRNA delivery to target specific genes in the cellulose biosynthesis pathway. This study was performed using tobacco BY-2 protoplasts (plant cells from which the cell wall has been removed) as a cell model; further investigations are required with intact plant cell walls. Jiang et al.<sup>110</sup> first reported the activity of a polymeric gene carrier in plants. They prepared different generations of polycationic dendrimers containing a central hydrophobic chromophore and evaluated the delivery efficiency *in vivo*, exploiting the fluorescent chromophore to track the nanoparticles within the plant. They chose two different double-stranded RNAs (dsRNAs), namely, shoot meristemless (dsSTM) and werewolf (dsWER), as these are expressed in the shoot apical meristem and are required for meristem formation and maintenance throughout the plant lifecycle. The dsRNA and dendrimer polyplexes were able to penetrate through the root wall into the plant cells, leading to a significant reduction in shoot apical meristem size and increased lateral roots. In another report,<sup>111</sup> a number of dimethylaminoethyl methacrylate (DMAEMA)-based cationic polymers (Figure 7a) were evaluated for plasmid DNA binding capacity, protection against nuclease degradation, and transfection efficiency to *Ceratodon purpureus* moss as well as *Nicotiana tabacum* protoplasts. However, in general, the exploration of functional polymers in this area is at a very preliminary stage and requires significantly more research focus.

Food sustainability also requires the control of biotic factors such as pests and diseases that limit crop productivity.<sup>112</sup> As we discussed above, the use of pesticides in combination with controlled delivery approaches can circumvent this issue; however, the long-term use of pesticides may still have adverse effects on human health and the environment. Recent studies



**Figure 7.** Structure of the functional polymers used as a gene carrier and artificial photosynthesis. Structures of cationic polymers as described in (a) ref 109 and (b) ref 113. (c) Illustration of the strategy for augmenting the light reaction of isolated chloroplasts with conjugated polymer nanoparticles (CPNs). Reproduced with permission from ref 119. Copyright 2017 John Wiley & Sons.

in the area of gene silencing revealed that polymeric nanoparticles could successfully reduce the risks of pests and diseases by delivering silencing agents to these organisms, hence minimizing environmental hazards from agrochemicals. An additional advantage of this technique is the high specificity for the target species, thereby sparing nontarget organisms. Research has shown promising results; for example, Liu et al.<sup>113</sup> reported the synthesis of a macromolecular nanocarrier and demonstrated its efficacy for transfection of *Helicoverpa armigera* nucleopolyhedrosis virus DNA (HaNPV) to specifically target the insect pest cotton bollworms.

Cationic guanidine-based polymers have often been investigated for gene delivery as a result of their inherent propensity to form stable polyplexes with nucleic acids. Parsons et al.<sup>114</sup> reported the synthesis of a poly[*N*-(3-guanidinopropyl)methacrylamide] (PGPMA) polymer and evaluated the potency of the resultant nanocarrier for dsRNA delivery. The polymer alone was found to be nontoxic in a number of cell lines, while the polymer–dsRNA complexes were efficiently taken up by cells and showed effective gene knockdown in the larvae of the insect *Spodoptera frugiperda*, resulting in enhanced larval mortality. In another report by Christiaens et al.,<sup>115</sup> a series of guanidine-containing random copolymers were synthesized through the copolymerization of *N*-(2-aminoethyl) methacrylate hydrochloride, 2-(dimethylamino) ethyl methacrylate, and guanylated-methacrylate as well as a control homopolymer of the corresponding monomers (Figure 7b). Guanidine-containing polymer–dsRNA polyplexes conferred improved stability as well as enhanced cellular uptake of dsRNA in lepidopteran CF203 midgut cells. Stability tests were performed at pH 11 to mimic conditions in the midgut, and the polymer–dsRNA complex was found to give strong protection against nucleolytic degradation for up to 30 h. In vivo experiments in *S. exigua* (beet army worm) resulted in a 53% increase in caterpillar mortality rate in comparison to a 16% mortality observed with the naked dsRNA.

**5.2. Augmented Photosynthesis.** A very different approach is bioprocess augmentation (nanobionics), and a prime example is research to enhance the photosynthetic efficiency of plants to improve crop productivity. Light absorption by chloroplasts is restricted to the visible spectrum, which greatly reduces the potential efficiency of solar energy. Some light-harvesting materials<sup>116</sup> can absorb UV light and then emit in the visible region of the spectrum, thus augmenting photosynthesis. Conjugated polymeric materials<sup>117,118</sup> appear to be compelling candidates for simulating this process. In order to demonstrate augmented photosynthesis in the presence of a light harvesting material, Wang et

al.<sup>119</sup> prepared conjugated polymer nanoparticles (CPNs) containing two different fluorene blocks, namely, poly[2,7-(9,9-dihexylfluorene)-*co-alt-p*-phenylene] (PFP) and poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(1,4-benzo-[2,1',3]-thiadiazole)] (PFBT). They found that the photosynthetic efficiency of the chloroplast/CPN complex was higher than for the natural chloroplast, as the former was able to capture a broader range of light including ultraviolet rays, thereby accelerating the electron transport rates in photosystem II (Figure 7c).

## 6. CONCLUSIONS AND PERSPECTIVE

Functional polymers have certainly been demonstrated to have many possibilities for agricultural related applications, but there is a long way to go before full implementation of these materials. The biggest limiting factor is always likely to be cost; although advanced polymeric materials show great promise for smart agriculture, the increased complexity of materials will naturally raise production prices and hamper their usage in field applications. This has led to significant research in the development of hybrid polymeric materials, which have the desirable chemical properties associated with synthetic polymers, while the inclusion of natural polymers lowers costs of production. Additionally, the lack of real-world field testing of these functional polymers also hinders their commercialization. The majority of research thus far has been conducted either in greenhouses or in growth chambers because of complex and often demanding legislative processes.

One of the most researched applications for polymeric materials has been agrochemical delivery. Despite the increased development of polymeric nanocarrier systems showing great potential for sustainable release as well as improved agrochemical stability, there are few products available on the market. One of the main factors influencing this low level of commercialization is that the great majority of studies are undertaken within universities and research institutes, which lack standard methods to validate agrochemical release profiles under field conditions. Another factor affecting the implementation of these materials is their high fabrication prices making them economically unviable. It is also possible that new nanobased products do not reach the market, as large companies are accumulating patents and waiting for opportunities for future exploitation following the development of more promising trading conditions. However, as with many other emerging technologies, it is expected that both societal priorities and national policies will change. In this case, it is likely that the pressure will increase for reducing the

environmental impact of agriculture and this may open the door for new, smart products.

It would be easy to make high-level comparisons between the fields of agriculture and biomedicine given their similarities in application requirements. However, biomedical applications focus on the treatment of humans as the final outcome, and usually, only two to three species of animal models are used for tests and trials, whereas for agricultural applications, the situation is far more complicated as this area deals with in excess of 7000 cultivated plant species<sup>120</sup> as well as countless pests and pathogens. During the last few decades, the number of studies related to agricultural science has strongly increased and numerous different nanoparticle delivery systems have been reported. As a result, researchers have been able to discern common factors for slowing agrochemical release rates, while retaining increased activity over the free compound, such as increasing nanoparticle hydrophobicity, size, and cross-linking density as well as reducing particle porosity. It is worth noting that many of these reported systems rely on physical encapsulation of agrochemicals, and there are only few reports of polymer–agrochemical conjugates, which may further affect release profiles. Ultimately, while factors affecting agrochemical release and activity have been identified across a range of plant species, the determination of the most effective nanocarrier system is more difficult, as results obtained on one type of plant species will not necessarily be valid for another.

There has also been significant research into using SAPs as a means to control water retention in soil. From the wide range of SAPs reported, it has been possible to determine which chemical functionalities (such as ionic groups, which increase water absorbance, or zwitterionic groups, which increase salt resistance) and synthetic factors (such as cross-linking density, temperature, monomer, and initiator concentration) affect both absorption capacity and mechanical properties.

While recent studies have mainly focused on agrochemical delivery and soil conditioning applications, which are likely to be used on a large scale, there are also emerging reports of niche, small-scale applications such as gene delivery and augmenting photosynthesis. We hope that continued research in these particular areas will yield greater understanding of the design parameters required to make these applications viable, as it has done for larger scale applications. With respect to agrochemical delivery and SAP, the progress that has been made toward synthesizing effective materials is promising; however, we believe the next key steps will include the identification of efficient cost-effective materials suitable for large-scale production. Additionally, the mitigation of any potential negative environmental impact from these materials will also be of the utmost importance for long-term sustainable agriculture.

## AUTHOR INFORMATION

### Corresponding Authors

**Rachel K. O'Reilly** – School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom; [orcid.org/0000-0002-1043-7172](https://orcid.org/0000-0002-1043-7172); Email: [r.oreilly@bham.ac.uk](mailto:r.oreilly@bham.ac.uk)

**Richard Napier** – School of Life Sciences, University of Warwick, Coventry CV4 7AL, United Kingdom; [orcid.org/0000-0002-0605-518X](https://orcid.org/0000-0002-0605-518X); Email: [Richard.Napier@warwick.ac.uk](mailto:Richard.Napier@warwick.ac.uk)

**Amrita Sikder** – School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom; Email: [A.Sikder.1@bham.ac.uk](mailto:A.Sikder.1@bham.ac.uk)

### Authors

**Amanda K. Pearce** – School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom; [orcid.org/0000-0003-3372-7380](https://orcid.org/0000-0003-3372-7380)

**Sam J. Parkinson** – School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsapm.0c00982>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

A.S. acknowledges funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 897666. R.K.O., R.N., A.K.P., and S.P. acknowledge financial support from the Leverhulme Trust for funding (Grant number RPG-2016-452).

## ABBREVIATIONS

AA, acrylic acid  
DPPE, 2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine  
2,4-D, 2,4-dichlorophenoxyacetic acid  
EGDMA, ethylene glycol-dimethacrylate  
GLA, glutaraldehyde  
NPK, nitrogen, phosphorus, and potassium  
MBA, *N,N'*-methylenebis(acrylamide)  
MCPA, 2-methyl-4-chlorophenoxyacetic acid  
PAH, poly(allylamine hydrochloride)  
PCA, poly(citric acid)  
PCL, poly(caprolactone)  
PDA, polydopamine  
PDI, perylene diimide  
PDopa, poly(L-3,4-dihydroxyphenylalanine)  
PEC, polyelectrolyte complex  
PEG, poly(ethylene glycol)  
PLGA, poly(lactic-*co*-glycolic acid)  
PHB, poly(hydroxybutyrate)  
PHBV, poly(hydroxybutyrate-valerate)  
PLA, polylactide  
PNIPAm, poly(*N*-isopropylacrylamide)  
PVA, poly(vinyl alcohol)

## REFERENCES

- (1) Byerlee, D.; Garcia, Andres, F.; Giertz, A.; Palmade, V. *Growing Africa: Unlocking the Potential of Agribusiness*; The World Bank: Washington, DC, 2013.
- (2) Damalas, C. A.; Eleftherohorinos, I. G. Pesticide Exposure, Safety Issues, and Risk Assessment Indicators. *Int. J. Environ. Res. Public Health* **2011**, *8*, 1402–1419.
- (3) Mishra, S.; Keswani, C.; Abhilash, P. C.; Fraceto, L. F.; Singh, H. B. Integrated Approach of Agri-Nanotechnology: Challenges and Future Trends. *Front. Plant Sci.* **2017**, *8*, 1–12.
- (4) Perlatti, B.; Bergo, P. L. S.; Fernandes, M. G. M. F.; Forim, M. R. *Insecticides-Development of Safer and More Effective Technologies*; Trdan, S., Ed.; InTech: Rijeka, 2013; pp 523–550.
- (5) Duran, N.; Marcató, P. D. Nanobiotechnology Perspectives. Role of Nanotechnology in the Food Industry: A Review. *Int. J. Food Sci. Technol.* **2013**, *48*, 1127–1134.

- (6) Prasad, R.; Bhattacharyya, A.; Nguyen, Q. D. Nanotechnology in Sustainable Agriculture: Recent Developments, Challenges, and Perspectives. *Front. Microbiol.* **2017**, *8*, 1–13.
- (7) Campbell, B. M.; Thornton, P.; Zougmore, R.; Asten, P. V.; Lipper, L. Sustainable Intensification: What is its Role in Climate Smart Agriculture? *Curr. Opin. Environ. Sustain.* **2014**, *8*, 39–43.
- (8) Patterson, J. P.; Robin, M. P.; Chassenieux, C.; Colombani, O.; O'Reilly, R. K. The Analysis of Solution Self-Assembled Polymeric Nanomaterials. *Chem. Soc. Rev.* **2014**, *43*, 2412–2425.
- (9) Mai, Y.; Eisenberg, A. Self-Assembly of Block Copolymers. *Chem. Soc. Rev.* **2012**, *41*, 5969–5985.
- (10) Egli, S.; Schlaad, H.; Bruns, N.; Meier, W. Functionalization of Block Copolymer Vesicle Surfaces. *Polymers* **2011**, *3*, 252–280.
- (11) Stuart, M. A.; Huck, W. T.; Genzer, J.; Muller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. Emerging Applications of Stimuli-Responsive Polymer Materials. *Nat. Mater.* **2010**, *9*, 101–113.
- (12) Pascoli, M.; Lopes-Oliveira, P. J.; Fraceto, L. F.; Seabra, A. B.; Oliveira, H. C. State of the art of Polymeric Nanoparticles as Carrier Systems with Agricultural Applications: a Minireview. *Energy Ecol. Environ.* **2018**, *3*, 137–148.
- (13) Milani, P.; França, D.; Balieiro, A. G.; Faez, R. Polymers and its Applications in Agriculture. *Polim.: Cienc. Tecnol.* **2017**, *27*, 256–266.
- (14) Puoci, F.; Iemma, F.; Spizzirri, U. G.; Cirillo, G.; Curcio, M.; Picci, N. Polymer in Agriculture: A Review. *Am. J. Agric. Biol. Sci.* **2008**, *3*, 299–314.
- (15) Peteu, S. F.; Oancea, F.; Siciua, O. A.; Constantinescu, F.; Dinu, S. Responsive Polymers for Crop Protection. *Polymers* **2010**, *2*, 229–251.
- (16) Abobatta, W. F. Impact of Hydrogel Polymer in Agricultural Sector. *Adv. Agr. Environ. Sci.* **2018**, *1*, 59–64.
- (17) Wang, K.; Amin, K.; An, Z.; Cai, Z.; Chen, H.; Chen, H.; Dong, Y.; Feng, X.; Fu, W.; Gu, J.; Han, Y.; Hu, D.; Hu, R.; Huang, D.; Huang, F.; Huang, F.; Huang, Y.; Jin, J.; Jin, X.; Li, Q.; Li, T.; Li, Z.; Li, Z.; Liu, J.; Liu, J.; Liu, S.; Peng, H.; Qin, A.; Qing, X.; Shen, Y.; Shi, J.; Sun, X.; Tong, B.; Wang, B.; Wang, H.; Wang, L.; Wang, S.; Wei, Z.; Xie, T.; Xu, C.; Xu, H.; Xu, Z.-K.; Yang, B.; Yu, Y.; Zeng, X.; Zhan, X.; Zhang, G.; Zhang, J.; Zhang, M. Q.; Zhang, X.-Z.; Zhang, X.; Zhang, Y.; Zhang, Y.; Zhao, C.-S.; Zhao, W.; Zhou, Y.; Zhou, Z.; Zhu, J.; Zhu, X.; Tang, B. Z. Advanced Functional Polymer Materials. *Mater. Chem. Front.* **2020**, *4*, 1803–1915.
- (18) Du, J.; O'Reilly, R. K. Advances and challenges in smart and functional polymer vesicles. *Soft Matter* **2009**, *5*, 3544–3561.
- (19) Sikder, A.; Ghosh, S. Hydrogen-Bonding Regulated Assembly of Molecular and Macromolecular Amphiphiles. *Mater. Chem. Front.* **2019**, *3*, 2602–2616.
- (20) Jochum, F. D.; Theato, P. Temperature- and light-responsive smart polymer materials. *Chem. Soc. Rev.* **2013**, *42*, 7468–7483.
- (21) Theato, P.; Sumerlin, B. S.; O'Reilly, R. K.; Epps, E. H., III Stimuli responsive materials. *Chem. Soc. Rev.* **2013**, *42*, 7055–7056.
- (22) Hu, J.; Zhang, G.; Liu, S. Enzyme-responsive polymeric assemblies, nanoparticles and hydrogels. *Chem. Soc. Rev.* **2012**, *41*, 5933–5949.
- (23) Trease, G. E.; Evans, W. C. *Text Book of Pharmacognosy*, 15th ed.; Bailliere Tindall: London, 2002; pp 200–201.
- (24) Kaushik, K.; Sharma, R. B.; Agarwal, S. Natural polymers and their applications. *Int. J. Pharm. Sci. Rev. Res.* **2016**, *2*, 30–36.
- (25) Haug, A.; Larsen, B.; Smidsrod, O.; et al. Studies on the sequence of uronic acid residues in alginic acid. *Acta Chem. Scand.* **1967**, *21*, 691–704.
- (26) Muxika, A.; Etxabide, A.; Uranga, J.; Guerrero, P.; Caba, K. D. L. Chitosan as a bioactive polymer: Processing, properties and applications. *Int. J. Biol. Macromol.* **2017**, *105*, 1358–1368.
- (27) Shaghaleh, H.; Xu, X.; Wang, S. Current progress in production of biopolymeric materials based on cellulose, cellulose nanofibers, and cellulose derivatives. *RSC Adv.* **2018**, *8*, 825–842.
- (28) Anderson, B. C.; Andrews, G. D.; Arthur, P.; Jacobson, H. W.; Melby, L. R.; Playtis, A. J.; Sharkey, W. H. Anionic Polymerization of Methacrylates. Novel Functional Polymers and Copolymers. *Macromolecules* **1981**, *14*, 1599–1601.
- (29) Cabral, H.; Miyata, K.; Osada, K.; Kataoka, K. Block Copolymer Micelles in Nanomedicine Applications. *Chem. Rev.* **2018**, *118*, 6844–6892.
- (30) Alarcon, C. D. L. H.; Pennadam, S.; Alexander, C. Stimuli Responsive Polymers for Biomedical Applications. *Chem. Soc. Rev.* **2005**, *34*, 276–285.
- (31) Ma, Q.; Cheng, H.; Fane, A. G.; Wang, R.; Zhang, H. Recent Development of Advanced Materials with Special Wettability for Selective Oil/Water Separation. *Small* **2016**, *12*, 2186–2202.
- (32) Zhao, F.; Shi, Y.; Pan, L.; Yu, G. Multifunctional Nanostructured Conductive Polymer Gels: Synthesis, Properties, and Applications. *Acc. Chem. Res.* **2017**, *50*, 1734–1743.
- (33) Zhang, Y.; Feng, X.; Yuan, S.; Zhou, J.; Wang, B. Challenges and Recent Advances in MOF–Polymer Composite Membranes for Gas Separation. *Inorg. Chem. Front.* **2016**, *3*, 896–909.
- (34) Akelah, A. Applications of Functionalized Polymers in Agriculture. *Journal of Islamic Academy of Sciences* **1990**, *3*, 49–61.
- (35) Pillai, C. K. S. Challenges for Natural Monomers and Polymers: Novel Design Strategies and Engineering to Develop Advanced Polymers. *Des. Monomers Polym.* **2010**, *13*, 87–121.
- (36) Gauthier, M. A.; Gibson, M. I.; Klok, H.-A. Synthesis of Functional Polymers by Post-Polymerization Modification. *Angew. Chem., Int. Ed.* **2009**, *48*, 48–58.
- (37) Matyjaszewski, K.; Tsarevsky, N. V. Nanostructured functional materials prepared by atom transfer radical polymerization. *Nat. Chem.* **2009**, *1*, 276–288.
- (38) Grubbs, R. B. Nitroxide-Mediated Radical Polymerization: Limitations and Versatility. *Polym. Rev.* **2011**, *51*, 104–137.
- (39) Moad, G.; Rizzardo, E.; Thang, S. H. Radical Addition-Fragmentation Chemistry in Polymer Synthesis. *Polymer* **2008**, *49*, 1079–1131.
- (40) Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block Copolymers*; John Wiley & Sons, Inc., 2003; pp 383–408.
- (41) Tomalia, D. A.; Frechet, J. M. J. Discovery of dendrimers and dendritic polymers: a brief historical perspective. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719–2728.
- (42) Börner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Möller, M. Synthesis of Molecular Brushes with Block Copolymer Side Chains Using Atom Transfer Radical Polymerization. *Macromolecules* **2001**, *34*, 4375–4383.
- (43) Jikei, M.; Kakimoto, M.-a. Hyperbranched polymers: a promising new class of materials. *Prog. Polym. Sci.* **2001**, *26*, 1233–1285.
- (44) Vroman, I.; Tighzert, L. Biodegradable Polymers. *Materials* **2009**, *2*, 307–344.
- (45) Liang, W.; Yu, X.; Wang, G.; Zheng, F.; Jia, J.; Xu, H. Chitosan-based Nanoparticles of Avermectin to Control Pinewood Nematodes. *Int. J. Biol. Macromol.* **2018**, *112*, 258–263.
- (46) Liu, L. S.; Kost, J.; Yan, F.; Spiro, R. C. Hydrogels from Biopolymer Hybrid for Biomedical, Food, and Functional Food Applications. *Polymers* **2012**, *4*, 997–1011.
- (47) Mei, X. D.; Liang, Y. H.; Zhang, T.; Ning, J.; Wang, Z. Y. An Amphiphilic Chitosan-Polylactide Graft copolymer and its Nanoparticles as Fungicide Carriers. *Adv. Mater. Res.* **2014**, *1051*, 21–28.
- (48) Tong, Y.; Wu, Y.; Zhao, C.; Xu, Y.; Lu, J.; Xiang, S.; Zong, F.; Wu, X. Polymeric Nanoparticles as a Metolachlor Carrier: Water-Based Formulation for Hydrophobic Pesticides and Absorption by Plants. *J. Agric. Food Chem.* **2017**, *65*, 7371–7378.
- (49) Adak, T.; Kumar, J.; Shakil, N. A.; Walia, S. Development of Controlled Release Formulations of Imidacloprid Employing Novel Nano-Ranged Amphiphilic Polymers. *J. Environ. Sci. Health, Part B* **2012**, *47*, 217–225.
- (50) Meyer, W. L.; Gurman, P.; Stelinski, L. L.; Elman, N. M. Functional Nano-Dispensers (FNDs) for Delivery of Insecticides Against Phytopathogen Vectors. *Green Chem.* **2015**, *17*, 4173–4177.
- (51) Memarizadeh, N.; Ghadamyari, M.; Adeli, M.; Talebi, K. Preparation, Characterization and Efficiency of Nanoencapsulated

Imidacloprid Under Laboratory Conditions. *Ecotoxicol. Environ. Saf.* **2014**, *107*, 77–83.

(52) Rychter, P.; Lewicka, K.; Pastusiak, M.; Domański, M.; Dobrzynski, P. PLGA-PEG Terpolymers as a Carrier of Bioactive Agents, Influence of PEG Blocks Content on Degradation and Release of Herbicides into Soil. *Polym. Degrad. Stab.* **2019**, *161*, 95–107.

(53) Dabbaghi, A.; Rahmani, S. Synthesis and Characterization of Biodegradable Multicomponent Amphiphilic Conetworks with Tunable Swelling through Combination of Ring-Opening Polymerization and “Click” Chemistry Method as a Controlled Release formulation for 2,4-Dichlorophenoxyacetic Acid Herbicide. *Polym. Adv. Technol.* **2019**, *30*, 368–380.

(54) Urbano-Juan, M. M.; Socías-Viciano, M. M.; Ureña-Amate, M. D. Evaluation of Nitrate Controlled Release Systems based on (Acrylamide-co-Itaconic acid) Hydrogels. *React. Funct. Polym.* **2019**, *141*, 82–90.

(55) Liu, X.; He, B.; Xu, Z.; Yin, M.; Yang, W.; Zhang, H.; Cao, J.; Shen, J. A Functionalized Fluorescent Dendrimer as a Pesticide Nanocarrier: Application in Pest Control. *Nanoscale* **2015**, *7*, 445–449.

(56) Grillo, R.; Pereira, A. E. S.; Melo, N. F. S.; Porto, R. M.; Feitosa, L. O.; Tonello, P. S.; Filho, N. L. D.; Rosa, A. H.; Lima, R.; Fraceto, L. F. Controlled Release System for Ametryn using Polymer Microspheres: Preparation, Characterization and Release Kinetics in Water. *J. Hazard. Mater.* **2011**, *186*, 1645–1651.

(57) Pereira, A. E. S.; Grillo, R.; Mello, N. F. S.; Rosa, A. H.; Fraceto, L. F. Application of Poly(Epsilon-Caprolactone) Nanoparticles Containing Atrazine Herbicide as an Alternative Technique to Control Weeds and Reduce Damage to the Environment. *J. Hazard. Mater.* **2014**, *268*, 207–215.

(58) Liu, B.; Wang, Y.; Yang, F.; Wang, X.; Shen, H.; Cui, H.; Wu, D. Construction of a Controlled-Release Delivery System for Pesticides using Biodegradable PLA-based Microcapsules. *Colloids Surf., B* **2016**, *144*, 38–45.

(59) Boyandin, A. N.; Volova, T. G. Application of Polyhydroxyalkanoates for Development of Targeted forms of Pesticides. In *Proc. of the Second Int. Conf. on Advances in Applied Science and Environmental Engineering*, December 20–21, 2014; pp 92–96.

(60) Kwicien, I.; Adamus, G.; Jiang, G.; Radecka, I.; Baldwin, T. C.; Khan, H. R.; Johnston, B.; Pennetta, V.; Hill, D.; Bretz, I.; Kowalczyk, M. Biodegradable PBAT/PLA Blend with Bioactive MCPA-PHBV Conjugate Suppresses Weed Growth. *Biomacromolecules* **2018**, *19*, 511–520.

(61) Khan, H.; Kaur, S.; Baldwin, T. C.; Radecka, I.; Jiang, G.; Bretz, I.; Duale, K.; Grażyna, A.; Marek, K. Effective Control against Broadleaf Weed Species Provided by Biodegradable PBAT/PLA Mulch Film Embedded with the Herbicide 2-Methyl-4-Chlorophenoxyacetic Acid (MCPA). *ACS Sustainable Chem. Eng.* **2020**, *8*, 5360–5370.

(62) Shang, Q.; Shi, Y.; Zhang, Y.; Zheng, T.; Shi, H. Pesticide-Conjugated Polyacrylate Nanoparticles: Novel Opportunities for Improving the Photostability of Emamectin Benzoate: Pesticide-Conjugated Polyacrylate Nanoparticles. *Polym. Adv. Technol.* **2013**, *24*, 137–143.

(63) Li, M.; Huang, Q.; Wu, Y. A Novel Chitosan-poly(lactide) Copolymer and its Submicron Particles as Imidacloprid Carriers. *Pest Manage. Sci.* **2011**, *67*, 831–836.

(64) Zhang, J.; Li, M.; Fan, T.; Xu, Q.; Wu, Y.; Chen, C.; Huang, Q. Construction of Novel Amphiphilic Chitosan Copolymer Nanoparticles for Chlorpyrifos Delivery. *J. Polym. Res.* **2013**, *20*, 1–11.

(65) Chen, C.; Gao, Z.; Qiu, X.; Hu, S. Enhancement of the Controlled-Release Properties of Chitosan Membranes by Cross-linking with Suberoyl Chloride. *Molecules* **2013**, *18*, 7239–7252.

(66) Gabriel Paulraj, M.; Ignacimuthu, S.; Gandhi, M. R.; Shajahan, A.; Ganesan, P.; Packiam, S. M.; Al-Dhabi, N. A. Comparative Studies of Tripolyphosphate and Glutaraldehyde Cross-linked Chitosan-Botanical Pesticide Nanoparticles and their Agricultural Applications. *Int. J. Biol. Macromol.* **2017**, *104*, 1813–1819.

(67) Sun, C.; Shu, K.; Wang, W.; Ye, Z.; Liu, T.; Gao, Y.; et al. Encapsulation and Controlled Release of Hydrophilic Pesticide in Shell Cross-linked Nanocapsules Containing Aqueous Core. *Int. J. Pharm.* **2014**, *463*, 108–114.

(68) Ye, Z.; Guo, J.; Wu, D.; Tan, M.; Xiong, X.; Yin, Y.; He, G. Photo-responsive Shell Cross-linked Micelles based on Carboxymethyl Chitosan and their Application in Controlled Release of Pesticide. *Carbohydr. Polym.* **2015**, *132*, 520–528.

(69) Gao, Y.; Zhang, Y.; He, S.; Xiao, Y.; Qin, X.; Zhang, Y.; et al. Fabrication of a Hollow Mesoporous Silica Hybrid to Improve the Targeting of a Pesticide. *Chem. Eng. J.* **2019**, *364*, 361–369.

(70) Xu, X.; Bai, B.; Wang, H.; Suo, Y. A Near-Infrared and Temperature-Responsive Pesticide Release Platform through Core-Shell Polydopamine@PNIPAm Nanocomposites. *ACS Appl. Mater. Interfaces* **2017**, *9*, 6424–6432.

(71) Ding, K.; Shi, L.; Zhang, L.; Zeng, T.; Yin, Y.; Yi, Y. Synthesis of Photoresponsive Polymeric Propesticide Micelles based on PEG for the Controlled Release of a Herbicide. *Polym. Chem.* **2016**, *7*, 899–904.

(72) Atta, S.; Paul, A.; Banerjee, R.; Bera, M.; Ikbali, M.; Dhara, D.; Singh, N. D. P. Photoresponsive Polymers based on a Coumarin Moiety for the Controlled Release of Pesticide 2,4-D. *RSC Adv.* **2015**, *5*, 99968–99975.

(73) Ullah, F.; Othman, M. B. H.; Javed, F.; Ahmad, Z.; Akil, H. M. Classification, Processing and Application of Hydrogels: A Review. *Mater. Sci. Eng., C* **2015**, *57*, 414–433.

(74) Zohuriaan-Mehr, M. J.; Kabiri, K. Superabsorbent Polymer Materials: A Review. *Iran. Polym. J.* **2008**, *17*, 451–477.

(75) Montesano, F. F.; Parente, A.; Santamaria, P.; Sannino, A.; Serio, F. Biodegradable Superabsorbent Hydrogel Increases Water Retention Properties of Growing Media and Plant Growth. *Agriculture and Agricultural Science Procedia*. **2015**, *4*, 451–458.

(76) Bakass, M.; Mokhlisse, A.; Lallemand, M. Absorption and Desorption of Liquid Water by a Superabsorbent Polymer: Effect of Polymer in the Drying of the Soil and the Quality of Certain Plants. *J. Appl. Polym. Sci.* **2002**, *83*, 234–243.

(77) Guilherme, M. R.; Aouada, F. A.; Fajardo, A. R.; Martins, A. F.; Paulino, A. T.; Davi, M. F. T.; Rubira, A. F.; Muniz, E. C. Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil conditioner and nutrient carrier: A review. *Eur. Polym. J.* **2015**, *72*, 365–385.

(78) Kim, Y. J.; Hong, S. J.; Shin, W. S.; Kwon, Y. R.; Lim, S. H.; Kim, H. C.; Kim, J. S.; Kim, J. W.; Kim, D. H. Preparation of a biodegradable superabsorbent polymer and measurements of changes in absorption properties depending on the type of surface-crosslinker. *Polym. Adv. Technol.* **2020**, *31*, 273–283.

(79) Li, A.; Zhang, J.; Wang, A. Utilization of starch and clay for the preparation of superabsorbent composite. *Bioresour. Technol.* **2007**, *98*, 327–32.

(80) Erickson, R. E. (1984), US Patent No. 4.424.247, Washington: U.S. Patent and Trademark Office.

(81) Xu, S.; Yin, Y.; Wang, Y.; Li, X.; Hu, Z.; Wang, R. Amphoteric Superabsorbent Polymer based on Waste Collagen as Loading Media and Safer Release Systems for Herbicide 2, 4-D. *J. Appl. Polym. Sci.* **2020**, *137*, 48480.

(82) Ovalsha, M. A.; Yadav, B.; Rai, P. K. Effects of Polymer Seed Coating and Seed Treatment on Plant Growth, Seed Yield and Quality of Cowpea (*Vigna unguiculata*). *Journal of Pharmacognosy and Phytochemistry* **2017**, *6*, 106–109.

(83) Callaghan, T. V.; Abdelnour, H.; Lindley, D. K. The Environmental Crisis in the Sudan: the Effect of Water-Absorbing Synthetic Polymers on Tree Germination and Early Survival. *Journal of Arid Environments* **1988**, *14*, 301–317.

(84) Woodhouse, J.; Johnson, M. S. Effect of Superabsorbent Polymers on Survival and Growth of Crop Seedlings. *Agricultural Water Management* **1991**, *20*, 63–70.

(85) Bai, W.; Zhang, H.; Liu, B.; Wu, Y.; Song, J. Q. Effects of Superabsorbent Polymers on the Physical and Chemical Properties of Soil

following Different Wetting and Drying Cycles. *Soil Use Manage.* **2010**, *26*, 253–260.

(86) Dabbaghi, A.; Kabiri, K.; Ramazani, A.; Zohuriaan-Mehr, M. J.; Jahandideh, A. Synthesis of Bio-Based Internal and External Cross-linkers based on Tannic Acid for Preparation of Antibacterial Superabsorbents. *Polym. Adv. Technol.* **2019**, *30*, 2894–2905.

(87) Cheng, D.; Liu, Y.; Yang, G.; Zhang, A. Water- and Fertilizer-Integrated Hydrogel Derived from the Polymerization of Acrylic Acid and Urea as a Slow-Release N Fertilizer and Water Retention in Agriculture. *J. Agric. Food Chem.* **2018**, *66*, 5762–5769.

(88) Stahl, J. D.; Cameron, M. D.; Haselbach, J.; Aust, S. D. Biodegradation of Superabsorbent Polymers in Soil. *Environ. Sci. Pollut. Res.* **2000**, *7*, 83–88.

(89) Sharma, S.; Dua, A.; Malik, A. Polyaspartic acid based superabsorbent polymers. *Eur. Polym. J.* **2014**, *59*, 363–376.

(90) Galal Ibrahim, A.; Sayed, A. Z.; El-Wahab, H. A.; Sayah, M. M. Synthesis of Poly(Acrylamide-Graft-Chitosan) Hydrogel: Optimization of The Grafting Parameters and Swelling Studies. *American Journal of Polymer Science and Technology* **2019**, *5*, 55–62.

(91) Mukerabigwi, J. F.; Lei, S.; Wang, H.; Luo, S.; Ma, X.; Qin, J.; Huang, X.; Cao, Y. Synthesis and properties of a novel ecofriendly superabsorbent hydrogel nanocomposite based on xyloglucan-graft-poly(acrylic acid)/diatomite. *RSC Adv.* **2015**, *5*, 83732–83742.

(92) Ahmed, E. M.; Zahran, M. A. H.; Aggor, F. S.; Elhady, S. A. A.; Nada, S. S. Synthesis and Swelling Characterization of Carboxymethyl Cellulose-g-Poly (Acrylic acid-co-Acrylamide) Hydrogel and their Application in Agricultural Field. *Int. J. Chem. Tech Res.* **2016**, *9*, 270–281.

(93) Gharekhani, H.; Olad, A.; Mirmohseni, A.; Bybordi, A. Superabsorbent Hydrogel made of NaAlg-g-poly(AA-co-AAm) and Ricehusk Ash: Synthesis, Characterization, and Swelling Kinetic Studies. *Carbohydr. Polym.* **2017**, *168*, 1–13.

(94) Zhou, M.; Zhao, J.; Zhou, L. Utilization of Starch and Montmorillonite for the Preparation of Superabsorbent Nanocomposite. *J. Appl. Polym. Sci.* **2011**, *121*, 2406–2412.

(95) Kazeminejadfard, F.; Hojjati, M. R. Preparation of Superabsorbent Composite based on Acrylic acid-Hydroxypropyl Distarch Phosphate and Clinoptilolite for Agricultural Applications. *J. Appl. Polym. Sci.* **2019**, *136*, 47365.

(96) Zhan, F.; Liu, M.; Guo, M.; Wu, L. Preparation of Superabsorbent Polymer with Slow Release Phosphate Fertilizer. *J. Appl. Polym. Sci.* **2004**, *92*, 3417–3421.

(97) Xu, S.; Li, X.; Wang, Y.; Hu, Z.; Wang, R. Characterization of Slow-release Collagen-g-Poly(Acrylic Acid-co-2-Acrylamido-2-Methyl-1-Propane Sulfonic Acid)-iron(III) Superabsorbentpolymer Containing Fertilizer. *J. Appl. Polym. Sci.* **2019**, *136*, 47178.

(98) Thombare, N.; Mishra, S.; Siddiqui, M. Z.; Jha, U.; Singh, D.; Mahajan, G. R. Design and development of guar gum based novel, superabsorbent and moisture retaining hydrogels for agricultural applications. *Carbohydr. Polym.* **2018**, *185*, 169–178.

(99) Kizilkaya, R.; Aşkın, T.; Bayraklı, B.; Sağlamc, M. Microbiological Characteristics of Soils Contaminated with Heavy Metals. *Eur. J. Soil Biol.* **2004**, *40*, 95–102.

(100) Teodorescu, M.; Lungu, A.; Stanescu, P. O.; Neamtu, C. Preparation and properties of novel slow-release NPK agrochemical formulations based on poly(acrylic acid) hydrogels and liquid-fertilizers. *Ind. Eng. Chem. Res.* **2009**, *48*, 6527–6534.

(101) Al-Sagheer, F. A.; Khalil, K. D.; Ibrahim, E. I. Synthesis and characterization of chitosan-g-poly(2-(furan-2-carbonyl)-acrylonitrile): Grafting of chitosan using a novel monomer prepared by a BaylisHillman reaction. *Eur. Polym. J.* **2013**, *49*, 1662–1672.

(102) Xiang, T.; Lu, T.; Zhao, W.-F.; Zhao, C.-S. Ionic-Strength Responsive Zwitterionic Copolymer Hydrogels with Tunable Swelling and Adsorption Behaviors. *Langmuir* **2019**, *35*, 1146–1155.

(103) Yoo, S.-D.; Cho, Y.-H.; Sheen, J. Arabidopsis Mesophyll Protoplasts: a Versatile Cell System for Transient Gene Expression Analysis. *Nat. Protoc.* **2007**, *2*, 1565–1572.

(104) Beyene, A. G.; Demirer, G. S.; Landry, M. P. Nanoparticle-Templated Molecular Recognition Platforms for Detection of

Biological Analytes. *Current protocols in chemical biology* **2016**, *8*, 197–223.

(105) Sadanandom, A.; Napier, R. M. Biosensors in Plants. *Curr. Opin. Plant Biol.* **2010**, *13*, 736–743.

(106) Koo, Y.; Wang, J.; Zhang, O.; Zhu, H.; Chehab, E. W.; Colvin, V. L.; Alvarez, P. J. J.; Braam, J. Fluorescence Reports Intact Quantum Dot Uptake into Roots and Translocation to Leaves of Arabidopsis thaliana and Subsequent Ingestion by Insect Herbivores. *Environ. Sci. Technol.* **2015**, *49*, 626–632.

(107) van Kooten, O.; Snel, J. F. H. The Use of Chlorophyll Fluorescence Nomenclature in Plant Stress Physiology. *Photosynth. Res.* **1990**, *25*, 147–150.

(108) Kakizawa, Y.; Kataoka, K. Block Copolymer Micelles for Delivery of Gene and Related Compounds. *Adv. Drug Delivery Rev.* **2002**, *54*, 203–222.

(109) Silva, A. T.; Nguyen, A.; Ye, C.; Verchot, J.; Moon, J. H. Conjugated Polymer Nanoparticles for Effective siRNA Delivery to Tobacco BY-2 Protoplasts. *BMC Plant Biol.* **2010**, *10*, 291.

(110) Jiang, L.; Ding, L.; He, B.; Shen, J.; Xu, Z.; Yin, M.; Zhang, X. Systemic Gene Silencing in Plants Triggered by Fluorescent Nanoparticle-Delivered Double Stranded RNA. *Nanoscale* **2014**, *6*, 9965–9969.

(111) Finiuk, N.; Buziashvili, A.; Burlaka, O.; Zaichenko, A.; Mitina, N.; Miagkota, O.; Lobachevska, O.; Stoika, R.; Blume, Y.; Yemets, A. Investigation of Novel Oligoelectrolyte Polymer Carriers for their Capacity of DNA Delivery into Plant Cells. *Plant Cell, Tissue Organ Cult.* **2017**, *131*, 27–39.

(112) Oerke, E. C. Crop Losses to Pests. *J. Agric. Sci.* **2006**, *144*, 31–43.

(113) Liu, X.; Zheng, Y.; Zhang, S.; Liu, K.; Zhang, S.; Yin, M.; Zhang, L.; Shen, J. Peryleneimide-cored Cationic Nanocarriers Deliver virus DNA to Kill Insect Pests. *Polym. Chem.* **2016**, *7*, 3740–3746.

(114) Parsons, K. H.; Mondal, M. H.; McCormick, C. L.; Flynt, A. S. Guanidinium-Functionalized Interpolyelectrolyte Complexes Enabling RNAi in Resistant Insect Pests. *Biomacromolecules* **2018**, *19*, 1111–1117.

(115) Christiaens, O.; Tardajos, M. G.; Reyna, Z. L. M.; Dash, M.; Dubruel, P.; Smagghe, G. Increased RNAi Efficacy in Spodoptera exigua via the Formulation of dsRNA With Guanylated Polymers. *Front. Physiol.* **2018**, *9*, 1–13.

(116) Hedley, G. J.; Ruseckas, A.; Samuel, I. D. W. Light Harvesting for Organic Photovoltaics. *Chem. Rev.* **2017**, *117*, 796–837.

(117) Ooms, M. D.; Dinh, C. T.; Sargent, E. H.; Sinton, D. Photon Management for Augmented Photosynthesis. *Nat. Commun.* **2016**, *7*, 12699.

(118) Zhu, C.; Liu, L.; Yang, Q.; Lv, F.; Wang, S. Water-Soluble Conjugated Polymers for Imaging, Diagnosis, and Therapy. *Chem. Rev.* **2012**, *112*, 4687–4735.

(119) Wang, Y.; Li, S.; Liu, L.; Lv, F.; Wang, S. Conjugated Polymer Nanoparticles to Augment Photosynthesis of Chloroplasts. *Angew. Chem., Int. Ed.* **2017**, *56*, 5308–5311.

(120) Kumar, V.; Arora, K. Trends in Nano-inspired Biosensors for Plants. *Materials Science for Energy Technologies* **2020**, *3*, 255–273.