

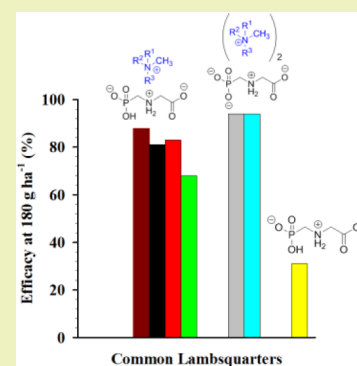
## Glyphosate-Based Herbicidal Ionic Liquids with Increased Efficacy

Juliusz Pernak,<sup>\*,†</sup> Michał Niemczak,<sup>†</sup> Rafał Giszter,<sup>†</sup> Julia L. Shamshina,<sup>‡,§</sup> Gabriela Gurau,<sup>‡,§</sup> O. Andreea Cojocaru,<sup>‡</sup> Tadeusz Praczyk,<sup>⊥</sup> Katarzyna Marcinkowska,<sup>⊥</sup> and Robin D. Rogers<sup>\*,‡</sup><sup>†</sup>Department of Chemical Technology, Poznan University of Technology, Poznan 60-965, Poland<sup>‡</sup>Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487, United States<sup>§</sup>S2S Solutions, Inc., 720 2nd Street, Tuscaloosa, Alabama 35401, United States<sup>⊥</sup>Institute of Plant Protection—National Research Institute, Poznan 60-318, Poland

## Supporting Information

**ABSTRACT:** Eight new glyphosate-based herbicidal ionic liquids (HILs), containing both mono- and dianions of glyphosate (benzalkonium glyphosate, bis(2-hydroxyethyl)-cocomethylammonium glyphosate, oleylmethylbis(2-hydroxyethyl)ammonium glyphosate, didecyltrimethylammonium glyphosate, di(hydrogenated tallow)dimethylammonium glyphosate, 4-decyl-4-ethylmorpholinium glyphosate, di(benzalkonium) glyphosate, and di(bis(2-hydroxyethyl)cocomethylammonium) glyphosate) were prepared via acid–base reaction between the corresponding ammonium hydroxides (some premade) and glyphosate free acid. The transformation of glyphosate free acid into ionic liquids led to an elimination of melting points in all but one compound and significant change in solubilities. All HILs exhibited higher thermal stability than glyphosate free acid. Greenhouse testing indicated that while at a higher application rate of 360 g/ha the efficacy of all the HILs was comparable to the commercial herbicide control, at a lower application rate of 180 g/ha, the efficacy of all HILs was as much as two and a half to three times higher when compared to the commercial formulation, and the dianionic glyphosates were the most effective. In field trials, all but one of the tested HILs demonstrated excellent efficacy. Laboratory regrowth tests established that the ionic liquids of glyphosate are efficiently translocated to rhizomes preventing the regrowth of plants.

**KEYWORDS:** Glyphosate, Roundup, Herbicidal ionic liquids, Efficacy, Greenhouse test, Field test, Regrowth



## INTRODUCTION

Glyphosate is a broad-spectrum, nonselective systemic herbicide widely used on all annual and perennial plants (e.g., grasses, sedges, broad-leaved weeds, woody plants).<sup>1</sup> The free acid is a phosphonomethyl derivative of the amino acid glycine and exists as a zwitterionic amphoteric substance (Figure 1)

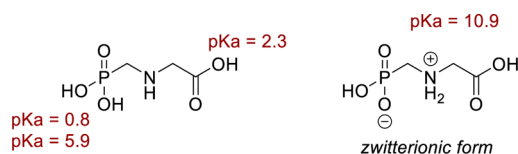


Figure 1. Glyphosate free acid and its zwitterionic form.

with three acidic sites available for deprotonation and one amino group that can be protonated.<sup>2</sup> To date, Monsanto Company is the major commercial supplier of this herbicide in the United States, selling several glyphosate formulations (e.g., Roundup,<sup>3</sup> Roundup Ultra, Roundup Pro, Landmaster, Fallow Master, Glypro); however, other companies also market glyphosate including Dow AgroSciences, DuPont, and Zeneca. These products may have variable concentrations of the active ingredient and may include various salt formulations with, for

example, cations such as dimethylammonium,<sup>4</sup> isopropylammonium,<sup>3</sup> monoammonium,<sup>5</sup> sodium,<sup>6</sup> or potassium<sup>7</sup> as the counterion. Some brands include glyphosate in its dianionic form paired with one protic cation (e.g., Touchdown iQ developed by Syngenta is the diammonium salt of glyphosate)<sup>8</sup> or more than one cation (e.g., the potassium/ammonium salt developed by Nufarm, Australia).<sup>9</sup>

Until recently, glyphosate was considered to be one of the safest herbicides. It has a high soil adsorption coefficient ( $K_d = 61$  g/mL), and therefore, it was hypothesized that glyphosate tightly binds to soil particles (and thus has a low mobility<sup>10</sup>) where it breaks down relatively quickly through biodegradation by soil microorganisms.<sup>11–15</sup> Recently, the proposed minimal environmental impact of glyphosate has been challenged,<sup>16</sup> as it has been shown that glyphosate is not entirely and immediately degraded in soils. Any environmental effects of glyphosate and its main metabolite, 2-amino-3-(5-methyl-3-oxo-1,2-oxazol-4-yl)propanoic acid (AMPA) are complex and multidirectional.<sup>16</sup> These can include off-target movement onto nontarget crops

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via both drift by physical movement of spray and lateral movement by groundwater.

Since glyphosate and its salts are highly soluble in water,<sup>17</sup> once in the aquatic environment, glyphosate rapidly dissipates.<sup>18–20</sup> However, the degree of reported dissipation varies with many studies reporting low concentrations of glyphosate,<sup>21,22</sup> but some studies reporting very high glyphosate concentrations up to 1700  $\mu\text{g}/\text{L}$ .<sup>23,24</sup> Dissipation of glyphosate increases through complexation with metal ions (e.g.,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in water ecosystems, sorption to sediment, and uptake by nontarget plants,<sup>25</sup> resulting in both direct effects on nontarget periphyton and phytoplankton in freshwater, and indirect effects via glyphosate degradation.

Minimization of off-target movement of glyphosate must be achieved to reduce environmental impact, diminish potential for human contamination, and lessen the potential economic losses due to movement onto nondesirable crops. We have recently suggested that converting known active herbicides into ionic liquids (ILs, currently defined as salts which melt below 100  $^{\circ}\text{C}$ <sup>26</sup>) might lead to a reduction in volatility and water solubility, reduced drift, and increased efficacy by more rapid sorption through the leaf and demonstrated this approach with 2,4-D, MCPA, triclopyr, cyhalofop, and dicamba.<sup>27–32</sup>

Glyphosate free acid can be easily converted into not only a monoanionic but also a dianionic form due to the presence of several acidic sites. Although glyphosate salts derived from protic ammonium cations (e.g.,  $\text{NH}_4^+$ ) and metal cations (e.g.,  $\text{K}^+$ ) are well investigated, glyphosate salts derived from monoanionic and dianionic glyphosate and aprotic cations have not yet been reported. Here we report the synthesis, characterization, and efficacy of monoanionic and dianionic glyphosate herbicidal ionic liquids (glyphosate HILs) containing cations with a second biological activity. The cations include those with additional herbicidal activity (e.g., morpholinium), those selected from “generally regarded as safe” lists (e.g., quarternary ammoniums), those with antimicrobial activity (e.g., quaternary tetraalkylammonium and morpholinium), and those with surfactant activity to improve absorption and membrane-transfer (e.g., coco-alkyl, hydrogenated tallow, and oleyl alkyl containing cations).

## EXPERIMENTAL SECTION

**Materials and Methods.** All materials were used as supplied unless otherwise noted. Deionized (DI) water was obtained from a commercial deionizer (Culligan, Northbrook, IL, USA) with specific resistivity of 16.82  $\text{M}\Omega\text{-cm}$  at 25  $^{\circ}\text{C}$ . Benzalkonium chloride (purity 95%), 4-ethylmorpholine (purity 97%), and 1-bromodecane (purity 98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Bis(2-hydroxyethyl)cocomethylammonium chloride (Ethoquad C/12, purity 75%), oylelmethylbis(2-hydroxyethyl)ammonium chloride (Ethoquad O/12, purity 75%), di(hydrogenated tallow)dimethylammonium chloride (Arquad 2HT-75, purity 75%), and didecyldimethylammonium chloride (Arquad 2.10–50, purity 50%) were purchased from Akzo Nobel (Amsterdam, The Netherlands). All solvents (methanol, DMSO, acetonitrile, acetone, isopropanol, ethyl acetate, chloroform, toluene, hexane) and KOH were purchased from Aldrich (European market, Poznan, Poland) and used without further purification. Roundup 360 SL was obtained from Monsanto Europe S.A. (Antwerpen, Belgium).

**Characterization Techniques.**  $^1\text{H}$  Nuclear magnetic resonance (NMR) spectra were recorded using a Mercury Gemini 300 spectrometer operating at 300 MHz with TMS as the internal standard.  $^{13}\text{C}$  NMR spectra were obtained with the same instrument at 75 MHz.

Elemental analyses (CHN) were performed at Adam Mickiewicz University, Poznan (Poland). The water content was determined by using an Aquastar volumetric Karl Fischer titrator EMD Millipore (Billerica, MA, USA) with Composite 5 solution as the titrant and anhydrous methanol as a solvent.

Thermal gravimetric analysis (TGA) was performed using a Mettler Toledo Star<sup>c</sup> TGA/DSC1 unit (Leicester, UK) under nitrogen. Samples between 2 and 10 mg were placed in aluminum pans and heated from 30 to 450  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . Thermal transition temperatures were determined by differential scanning calorimetry (DSC) using a Mettler Toledo Star<sup>c</sup> DSC1 (Leicester, UK) unit, under nitrogen. Samples between 5 and 15 mg were placed in aluminum pans and heated from 25 to 120  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  and cooled with an intracooler at a cooling rate of 10  $^{\circ}\text{C}/\text{min}$  to  $-100$   $^{\circ}\text{C}$  and then heated again to 120  $^{\circ}\text{C}$ .

**Syntheses. Synthesis of 4-Decyl-4-ethylmorpholinium Bromide.** 4-Decyl-4-ethylmorpholinium bromide was synthesized via the following quaternization reaction. In a 250 mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar, 4-ethylmorpholine (0.10 mol) was reacted with 1-bromodecane (0.11 mol) added at once into 100 mL of acetonitrile. The reactants were stirred in a round-bottom flask for 48 h at 60  $^{\circ}\text{C}$ , and then the solvent was evaporated using a vacuum evaporator. Next, 200 mL of ethyl acetate was added, and the product precipitated as a white solid. The product was carefully separated by vacuum filtration through a glass filter funnel, thoroughly washed with small portions of ethyl acetate (10  $\times$  3 mL), and dried under reduced pressure at 50  $^{\circ}\text{C}$  for 24 h. The spectral data were identical to those previously reported.<sup>33</sup>

**General Synthesis of HILs 1–6, 7, and 8.** First, the corresponding ammonium or morpholinium hydroxides were prepared. In a 100 mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar, 0.05 mol of the corresponding ammonium or morpholinium halide was dissolved in 25 mL of anhydrous methanol, followed by adding equimolar amount of methanolic potassium hydroxide in 25 mL of anhydrous methanol. The mixture was then stirred for 1 h at room temperature. The inorganic potassium halide byproduct precipitated as a white solid and was carefully separated by vacuum filtration through a glass filter funnel.

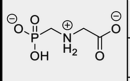
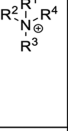

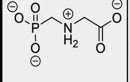
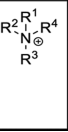
The filtrate (the ammonium or morpholinium hydroxide) was carefully transferred to a 100 mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar followed by addition of either a stoichiometric (HILs 1–6) or half-stoichiometric (HILs 7–8) amount of glyphosate (2-[(phosphonomethyl)amino]acetic acid), which was added all at once. Each mixture was then stirred for another 1 h at room temperature, and the solvent removed using a rotary evaporator followed by washing the residue with isopropanol. The products 1–6, 7, and 8 were dried under vacuum (10 mbar) at 60  $^{\circ}\text{C}$  for 48 h and stored over  $\text{P}_4\text{O}_{10}$ . The water contents of the dried salts were measured by the Karl Fischer method and found to be less than 500 ppm. All salts were stable in air and in contact with water and the tested organic solvents.

**Benzalkonium Glyphosate (1).** Yield 97%, colorless high viscosity liquid ( $T_g$   $-28$   $^{\circ}\text{C}$ ), refractive index 1.510.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz),  $\delta$  (ppm) 0.88 (t,  $J$  = 6.7 Hz, 3H), 1.26 (m, 20H), 1.65 (s, 2H), 1.99 (s, 1H), 2.83 (d,  $J$  = 10.8 Hz, 2H), 3.11 (s, 2H), 3.18 (s, 6H), 3.53 (s, 2H), 4.78 (s, 2H), 6.91 (s, 2H), 7.35 (m, 3H), 7.58 (t,  $J$  = 3.3 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K, 75 MHz),  $\delta$  (ppm) 169.4, 132.8, 129.7, 128.5, 127.8, 66.7, 61.8, 59.5, 49.8, 45.0, 40.1, 31.4, 29.2, 29.1, 29.0, 28.9, 28.8, 27.3, 27.1, 25.9, 22.2, 13.7.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 298 K, 121 MHz)  $\delta$  (ppm) 8.1 (s).

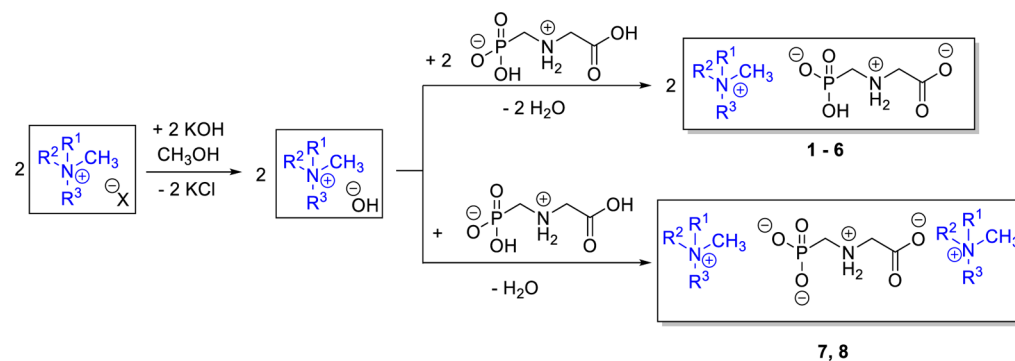
**Oylelmethylbis(2-hydroxyethyl)ammonium Glyphosate (2).** Yield 93%, yellowish wax ( $T_g$   $-45$   $^{\circ}\text{C}$ ), refractive index 1.493.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 300 MHz),  $\delta$  (ppm) 0.88 (t,  $J$  = 6.5 Hz, 3H), 1.27 (m, 22H), 1.68 (s, 2H), 2.01 (s, 4H), 3.25 (m, 5H), 3.39 (s, 3H), 3.63 (m, 6H), 4.02 (s, 4H), 5.34 (m, 2H), 7.07 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K, 75 MHz),  $\delta$  (ppm) 170.5, 129.9, 129.5, 64.3, 62.9, 55.5, 50.2, 50.0, 32.6, 31.8, 31.7, 29.7, 29.6, 29.5, 29.2, 28.9, 27.2, 26.5, 25.3, 22.6, 14.0.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 298 K, 121 MHz)  $\delta$  (ppm) 8.5 (s).

**Bis(2-hydroxyethyl)cocomethylammonium Glyphosate (3).** Yield 98%, yellowish wax ( $T_g$   $-17$   $^{\circ}\text{C}$ ), refractive index 1.496.  $^1\text{H}$  NMR

Table 1. Glyphosate Herbicidal Ionic Liquids

	HIL	Cation	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	State at 25 °C	T <sub>g</sub> <sup>a</sup> (°C)	T <sub>dec</sub> <sup>b</sup> (°C)	T <sub>5% onset</sub> <sup>c</sup> (°C)
 Monoanion	1	 R <sup>2</sup> R <sup>1</sup> N <sup>⊕</sup> R <sup>3</sup>	CH <sub>3</sub>	Benzyl	Alkyl <sup>d</sup>	CH <sub>3</sub>	Liquid <sup>h</sup>	-28	310	159
	2		(CH <sub>2</sub> ) <sub>2</sub> OH	(CH <sub>2</sub> ) <sub>2</sub> OH	Alkyl <sup>f</sup>	CH <sub>3</sub>	Wax	-17	342	208
	3		(CH <sub>2</sub> ) <sub>2</sub> OH	(CH <sub>2</sub> ) <sub>2</sub> OH	Alkyl <sup>f</sup>	CH <sub>3</sub>	Wax	-45	305	170
	4		CH <sub>3</sub>	C <sub>10</sub> H <sub>21</sub>	C <sub>10</sub> H <sub>21</sub>	CH <sub>3</sub>	Wax	-11	218	161
	5		CH <sub>3</sub>	Alkyl <sup>d</sup>	Alkyl <sup>e</sup>	CH <sub>3</sub>	Solid	(38, <sup>i</sup> 45 <sup>i</sup> )	353	196
	6	 C <sub>10</sub> H <sub>21</sub>	C <sub>10</sub> H <sub>21</sub>	C <sub>2</sub> H <sub>5</sub>	-	-	Wax	-26	249	140
 Dianion	7	 R <sup>2</sup> R <sup>1</sup> N <sup>⊕</sup> R <sup>3</sup>	CH <sub>3</sub>	Benzyl	Alkyl <sup>d</sup>	CH <sub>3</sub>	Liquid	-15	265	148
	8		(CH <sub>2</sub> ) <sub>2</sub> OH	(CH <sub>2</sub> ) <sub>2</sub> OH	Alkyl <sup>f</sup>	CH <sub>3</sub>	Wax	-37	290	155

<sup>a</sup>T<sub>g</sub>—glass transition temperature. <sup>b</sup>T<sub>dec</sub>—decomposition temperature. <sup>c</sup>T<sub>5% onset</sub>—decomposition temperature of 5% of the sample. <sup>d</sup>Mixture of saturated alkyl substituents C<sub>12</sub>–60%, C<sub>14</sub>–40%. <sup>e</sup>Oleoyl—mixture of unsaturated alkyl substituents C<sub>12</sub>–5%, C<sub>14</sub>–1%, C<sub>16</sub>–14%, C<sub>18</sub>–80%. <sup>f</sup>Coco—mixture of saturated alkyl substituents C<sub>8</sub>–5%, C<sub>10</sub>–6%, C<sub>12</sub>–50%, C<sub>14</sub>–19%, C<sub>16</sub>–14%, C<sub>18</sub>–10%. <sup>g</sup>Hydrogenated tallow—mixture of saturated alkyl substituents C<sub>12</sub>–1%, C<sub>14</sub>–4%, C<sub>16</sub>–31%, C<sub>18</sub>–64%. <sup>h</sup>High viscosity. <sup>i</sup>Crystallization on cooling. <sup>j</sup>Melting on heating.

Scheme 1. Synthesis of Monoanionic (1–6) and Dianionic (7 and 8) Glyphosate HILs<sup>a</sup>

<sup>a</sup>R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are defined in Table 1.

(CDCl<sub>3</sub>, 298 K, 300 MHz),  $\delta$  (ppm) 0.88 (t,  $J$  = 6.6 Hz, 3H), 1.26 (m, 20H), 1.68 (s, 2H), 2.01 (s, 1H), 3.23 (m, 5H), 3.38 (s, 2H), 3.58 (m, 6H), 4.00 (quint,  $J$  = 6.2 Hz, 4H), 6.67 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K, 75 MHz),  $\delta$  (ppm) 170.6, 64.2, 63.9, 62.8, 55.5, 50.2, 49.9, 31.9, 29.7, 29.6, 29.3, 27.2, 26.5, 25.3, 22.6, 14.0. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K, 121 MHz)  $\delta$  (ppm) 9.4 (s).

*Didecylidimethylammonium Glyphosate (4)*. Yield 93%, colorless wax (T<sub>g</sub> -11 °C), refractive index 1.485. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  ppm 0.85 (t,  $J$  = 6.7 Hz, 6H), 1.24 (m, 28H), 1.61 (q,  $J$  = 7.3 Hz, 4H), 2.83 (d,  $J$  = 12.4 Hz, 2H), 2.99 (s, 6H), 3.21 (t,  $J$  = 8.3 Hz, 4H), 3.28 (s, 2H), 4.02 (m, 3H). <sup>13</sup>C NMR  $\delta$  ppm = 168.1, 62.9, 50.3, 46.2, 44.4, 31.5, 29.1, 29.0, 28.9, 28.7, 25.9, 22.3, 21.8, 14.1. Anal. Calcd for C<sub>25</sub>H<sub>55</sub>O<sub>5</sub>N<sub>2</sub>P: C 60.68, H 11.23, N 5.66. Found: C 60.99, H 11.02, N 5.86.

*Di(hydrogenated tallow)dimethylammonium Glyphosate (5)*. Yield 97%, white solid (T<sub>m</sub> = 45 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 400 MHz),  $\delta$  (ppm) 0.88 (t,  $J$  = 6.8 Hz, 6H), 1.26 (m, 60H), 1.63 (s, 4H), 3.05 (d,  $J$  = 11.5 Hz, 2H), 3.29 (s, 6H), 3.36 (m, 4H), 3.52 (s, 2H), 6.24 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K, 100 MHz),  $\delta$  (ppm) 169.5, 63.5, 62.5, 53.0, 51.7, 49.5, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 25.2, 22.5, 22.4, 13.9. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K, 121 MHz)  $\delta$  (ppm) 8.3 (s).

*4-Decyl-4-ethylmorpholinium Glyphosate (6)*. Yield 95%, colorless wax (T<sub>g</sub> -26 °C), refractive index 1.490. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 400 MHz)  $\delta$  (ppm) 0.88 (t,  $J$  = 6.7 Hz, 3H), 1.26 (m, 9H), 1.37 (m, 8H), 1.66 (s, 2H), 2.76 (d,  $J$  = 12.4 Hz, 2H), 3.30 (d,  $J$  = 11.5 Hz, 2H), 3.40 (m, 2H), 3.57 (m, 2H), 3.76 (m, 4H), 3.96 (m, 2H), 4.15 (m,

2H), 5.88 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K, 100 MHz)  $\delta$  (ppm) 172.2, 62.9, 60.2, 57.5, 57.0, 54.6, 53.3, 49.0, 48.5, 47.2, 31.5, 29.2, 29.0, 28.9, 26.1, 25.1, 22.3, 21.1, 13.8, 7.0. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K, 121 MHz)  $\delta$  (ppm) 8.9 (s). Elemental analysis calcd (%) for C<sub>19</sub>H<sub>41</sub>N<sub>2</sub>O<sub>6</sub>P (424.51) C 53.76, H 9.73, N 6.60. Found C 53.62, H 9.89, N 6.49.

*Di(benzalkonium) Glyphosate (7)*. Yield 90%, colorless liquid (T<sub>g</sub> -15 °C), refractive index 1.508. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 300 MHz),  $\delta$  (ppm) 0.88 (t,  $J$  = 6.8 Hz, 6H), 1.26 (m, 40H), 1.63 (s, 4H), 2.86 (d,  $J$  = 11.1 Hz, 2H), 3.04 (m, 4H), 3.16 (s, 12H), 3.60 (s, 2H), 4.71 (s, 4H), 6.05 (s, 1H), 7.34 (m, 6H), 7.54 (t,  $J$  = 3.3 Hz, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K, 75 MHz),  $\delta$  (ppm) 167.0, 133.0, 129.9, 128.8, 128.0, 67.0, 61.9, 59.8, 50.3, 45.3, 40.4, 31.7, 29.4, 29.3, 29.1, 29.0, 27.6, 27.3, 26.1, 22.5, 13.9. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K, 121 MHz)  $\delta$  (ppm) 8.3 (s).

*Di(bis(2-hydroxyethyl)cocomethylammonium) Glyphosate (8)*. Yield 93%, yellowish wax (T<sub>g</sub> -37 °C), refractive index 1.494. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K, 400 MHz),  $\delta$  (ppm) 0.88 (t,  $J$  = 6.8 Hz, 6H), 1.26 (m, 40H), 1.68 (s, 4H), 2.01 (s, 1H), 2.93 (s, 2H), 3.26 (s, 6H), 3.37 (m, 4H), 3.59 (m, 2H), 3.65 (s, 8H), 4.00 (s, 8H), 6.22 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K, 100 MHz),  $\delta$  (ppm) 171.5, 70.5, 64.2, 63.8, 62.7, 55.3, 50.2, 49.7, 31.8, 31.7, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 27.1, 26.5, 25.3, 22.6, 22.5, 14.0. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 298 K, 121 MHz)  $\delta$  (ppm) 9.4 (s).

**Greenhouse and Field Trials.** The environmental conditions used in the experiments were a temperature of 20 ± 2 °C, a humidity of 60%, and a photoperiod of 16/8 h day/night. All plants

Table 2. Solubilities of Glyphosate Herbicidal Ionic Liquids<sup>a</sup>

	HIL	solvent									
		water	methanol	DMSO	acetonitrile	acetone	isopropanol	ethyl acetate	chloroform	toluene	hexane
monoanionic glyphosate HILs	1	S <sup>a</sup>	S	L	N	N	L	N	S	N	N
	2	S	S	N	N	N	L	N	L	N	N
	3	S	S	N	N	N	N	N	N	N	N
	4	L	S	L	S	L	L	L	S	S	N
	5	N	S	N	N	N	S	N	S	S	N
	6	S	S	S	S	S	S	N	L	N	N
dianionic glyphosate HILs	7	L	S	S	S	S	L	N	S	N	N
	8	L	S	N	N	N	L	N	L	N	N

<sup>a</sup>S: soluble. L: limited solubility. N: not soluble.

(couchgrass) and seeds were collected from fields at the Experimental Station in Winna Gora and were grown in 0.5 L plastic pots filled with potting material. The plants were thinned to four per pot 14 days after emergence, and watered as needed. The HILs and the commercial Roundup 360 SL were sprayed using a moving sprayer (APORO, Poznan, Poland) equipped with a TeeJet VP 110/02 flat-fan nozzle (TeeJet Technologies, Wheaton, IL, USA) delivering 200 L/ha of spray, at 0.2 MPa operating pressure. The distance between the nozzle and the target plants was 40 cm.

For field trials, a knapsack sprayer (APORO, Poznan, Poland) equipped with TeeJet AI/XR 110/03 (TeeJet Technologies, USA) flat-fan nozzles was used to deliver 200 L/ha of spray solution at 0.3 MPa pressure. Weed control was evaluated visually 4 weeks after herbicide applications by using a scale of 0 (no action of the applied compound) to 100% (complete weed destruction).

**Regrowth of Couchgrass.** Laboratory regrowth tests were performed on Petri dishes using couchgrass rhizomes picked from the field trials 8 weeks after application. The rhizomes were cut into sections that each had four buds and placed in Petri dishes on a filter paper moistened with DI water (5 rhizomes/Petri dish). The Petri dishes were kept under controlled environmental conditions in a greenhouse (temperature  $20 \pm 2$  °C, relative humidity 60%, photoperiod 16/8 day/night) for three weeks. The evaluation of couchgrass regrowth was performed visually as the average of four replicates, and the results were reported in percent regrowth, where 100% means regrowth from all buds and 0% means no regrowth symptoms.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** Six monoanionic glyphosate HILs (compounds 1–6, Table 1) and two dianionic glyphosate HILs (compounds 7 and 8, Table 1) were synthesized by using a two-step approach (Scheme 1). The first step involved utilizing a KOH ion-exchange reaction to convert the cation halide to the hydroxide form of the cation. The second step involved a direct acid–base reaction between the cation hydroxide and glyphosate free acid in either 1:1 (HILs 1–6) or 2:1 (HILs 7 and 8) stoichiometries. All of the HILs (Table 1) were obtained in high yields (>93%) and with high purities (>95%) as determined by NMR analysis.

Five of the HILs (2, 3, 4, 6, 8) are waxes, two (1, 7) are liquids, and one (5) is a low melting crystalline solid. Details of the synthesis of the compounds and their full characterization are provided in the Experimental Section.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) data for the HILs are presented in Table 1. While glyphosate itself is a high-melting solid with  $T_m = 184.5$  °C, among the glyphosate HILs we prepared, only one, di(hydrogenated tallow)dimethylammonium glyphosate 5 was solid (albeit low melting) with  $T_m = 45$  °C and a crystallization event on cooling at 38 °C. This behavior might

be attributable to the presence of two saturated high molecular weight alkyl chain substituents on the ammonium cation, since both mono- and dianionic benzalkonium glyphosates 1 and 7 were liquids.

All the other compounds were waxes exhibiting only glass transitions. Among these, the lowest glass transitions were observed for those possessing the bis(2-hydroxyethyl)-cocomethylammonium cation 3 and 8, with both monoanionic (3,  $T_g = -45$  °C) and dianionic (8,  $T_g = -37$  °C) glyphosate anions. A slightly higher glass transition ( $T_g = -17$  °C) was observed for bis(2-hydroxyethyl)oleylmethylammonium glyphosate 2, where the cation differs in containing an unsaturated and higher molecular weight oleyl-alkyl side chain instead of a saturated and lower molecular weight coco-alkyl. An even higher glass transition ( $T_g = -11$  °C) was observed for didecylmethylammonium glyphosate 4 where there are no hydroxyethyl- substituents present on the cation. The depression of melting or glass transitions when hydroxyethyl groups are present in an IL cation is in line with trends reported in the literature.<sup>34</sup>

The glyphosate HILs exhibited higher thermal stability (Table 1) than glyphosate free acid's first decomposition step. The lowest decomposition temperature ( $T_{dec} = 218$  °C) was observed for didecylmethylammonium glyphosate 4, and the highest ( $T_{dec} = 353$  °C) was observed for the crystalline solid di(hydrogenated tallow)dimethylammonium glyphosate 5. The thermal stabilities of the HILs appear to be related to factors such as the length of the substituent, R, the extent of saturation, and the fraction of higher molecular weight substituents on the cation.<sup>35</sup> Among the two dianionic glyphosate HILs, the higher thermal stability was obtained for di(bis(2-hydroxyethyl)-cocomethylammonium) glyphosate 8 where two hydroxyethyl groups are present on both cations (following trends reported in the literature<sup>34</sup>).

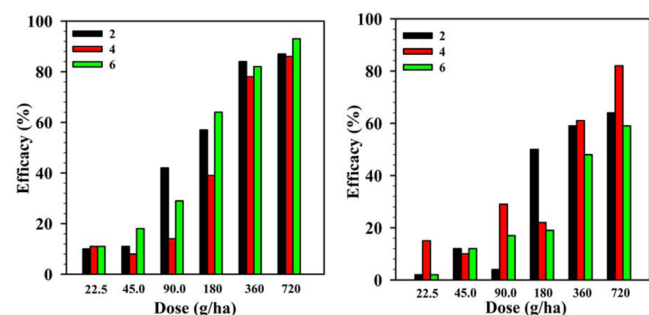
**Solubilities.** The solubilities of the prepared HILs in ten representative solvents were determined according to the protocols in Vogel's Textbook of Practical Organic Chemistry<sup>36</sup> (Table 2). The solvents chosen for study were selected in descending order of the value of their Snyder polarity index: water 9.0, methanol 6.6, DMSO 6.5, acetonitrile 6.2, acetone 5.1, ethyl acetate 4.3, isopropanol 4.3, chloroform 4.1, toluene 2.3, and hexane 0.0. A 0.1 g sample of each HIL was added to a certain volume of solvent and the samples were thermostated (MEMMERT Water Bath, Model WNB 7, Germany) at 25 °C. Based on the volume of solvent used, 3 types of behaviors were recorded: "soluble" applies to compounds which dissolved in 1 mL of solvent, "limited solubility" applies to compounds that dissolved in 3 mL of solvent, and "not soluble" applies to the compounds which did not dissolve in 3 mL of solvent.

As expected, all the tested compounds were soluble in methanol and insoluble in hexane. Among the monoanionic glyphosate HILs, the benzalkonium glyphosate 1, oleylmethylbis(2-hydroxyethyl)ammonium glyphosate 2, and bis(2-hydroxyethyl)cocomethylammonium glyphosate 3 were soluble in the most polar solvents (water and methanol) and in chloroform but had limited or no solubility in all the other solvents tested. The HIL didecylmethylammonium glyphosate 4 was soluble in polar methanol, acetonitrile, much less polar chloroform and toluene and insoluble in low polar hexane and had limited solubility in all other solvents. The HIL di(hydrogenated tallow)dimethylammonium glyphosate 5 was soluble in methanol, isopropanol, chloroform, and toluene and not soluble in any other solvents. The 4-decyl-4-ethylmorpholinium glyphosate 6 exhibited the best solubility and was soluble in water, alcohols, DMSO, acetonitrile, and acetone and not soluble or had limited solubility in ethyl acetate, chloroform, toluene, and hexane. Both the dianionic glyphosate HILs di(benzalkonium) glyphosate 7 and di(bis(2-hydroxyethyl)cocomethylammonium) glyphosate 8 were soluble in methanol, showed a limited solubility in water and were insoluble in the less polar solvents toluene and hexane.

**Efficacy.** Greenhouse tests were conducted using glyphosate HILs 1–8 and field trials were conducted with HILs 2–6. Both types of trials were compared to the use of a commercial formulation of Roundup 360 SL (Monsanto).

**Greenhouse Trials (HILs 1–8).** Greenhouse tests were conducted under controlled conditions with a temperature of  $20 \pm 2$  °C, relative humidity of 60%, and a photoperiod of 16/8 h day/night. The plants were separated into three groups (1) those sprayed with the glyphosate HILs as aqueous solutions, (2) those sprayed with commercially available Roundup 360 SL, and (3) those not sprayed (the control group). Three weeks after treatment (WAT), four plants were randomly selected from each group and their fresh weight was determined. The efficacy data is expressed as percent fresh weight reduction compared to the control group (see the Experimental Section for additional details).

To select the best application rate, the monoanionic glyphosate HILs 2, 4, and 6 were tested on cornflower (*Centaurea cyanus*) and winter wheat (*Triticum aestivum*) with different application rates varying from 22.5 to 720 g/ha. It was observed (Figure 2) that the efficacy greatly depended on application rate, increasing with increasing application rate. All tested HILs were more effective at rates higher than 180 g/ha of active ingredient. Since good efficacies were obtained for

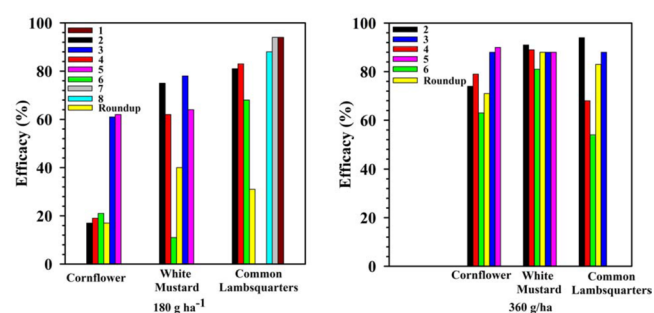


**Figure 2.** Efficacy (measured as fresh weight reduction 3 weeks after treatment) of glyphosate HILs 2 (black), 4 (red), and 6 (green) on cornflower (left) and winter wheat (right) at different application rates.

application rates of 180 and 360 g/ha and these two rates are commonly used for Roundup applications, these rates were chosen for further study.

The efficacies of monoanionic glyphosate HILs 2–6 were further tested on cornflower, white mustard, and common lambsquarters at application rates of 180 and 360 g/ha of active ingredient and compared to that of the commercial Roundup 360 SL. The efficacies of dianionic glyphosate HILs 7 and 8 were tested using a rate of 180 g/ha of active ingredient only. In general, the efficacies of 2–6 and the commercial formulation were similar for the application rate 360 g/ha; however, there was a minor dependence on plant species. For cornflower, 2–5 showed a slightly higher activity compared to Roundup 360 SL, while 6 was comparable to that of the commercial formulation. On white mustard, 2–6 showed results similar to Roundup 360 SL. In the case of common lambsquarters, 4 and 6 showed a lower efficacy when compared to the commercial product.

The differences were much more striking for the lower application rate of 180 g/ha. On cornflower, 2, 4, and 6 did not show any improvements over Roundup 360 SL, while 3 and 5 exhibited considerably higher activity. On white mustard, all HILs but 6 were much more effective than the commercial herbicide. Interestingly, on common lambsquarters, at the application rate of 180 g/ha, efficacies of all the monoanionic glyphosate HILs (1, 2, 4, and 6) and the two dianionic glyphosate HILs 7 and 8 were as much as 2.5–3 times higher when compared to the commercial formulation. Of these, the dianionic 7 and 8 were the most effective (Figure 3).



**Figure 3.** Greenhouse efficacy (measured as fresh weight reduction 4 weeks after treatment) of glyphosate HILs 1 (brown), 2 (black), 3 (blue), 4 (red), 5 (fuschia), 6 (green), 7 (gray), and 8 (aqua) compared to Roundup 360 SL (yellow) on cornflower, white mustard, and common lambsquarters at different application rates of 180 (left) and 360 g/ha (right).

**Field Trials.** Field trials were conducted with monoanionic glyphosate HILs 2–6 (7 and 8 were not yet available) in 2011, 2012, and 2013 at the Experimental Station in Winna Gora, Poland, on stubble, strongly infested by couchgrass (*Elymus repens* (L.) Gould). All herbicidal treatments were conducted at the end of couchgrass tillering with an application rate of 1180 g/ha. Weed control was evaluated visually 2 (2 WAT) and 4 (4 WAT) weeks after herbicide applications using a scale of 0 (no control) to 100% (complete weed destruction). Four of the HILs tested (2–5) gave excellent results, with near complete eradication of the couchgrass comparable to that of the commercial formulation, Roundup 360 SL. On the other hand, the morpholinium HIL 6, only slightly damaged couchgrass plants (Table 4).

**Regrowth of Couchgrass.** The most persistent perennials (such as couchgrass) spread by underground creeping rhizomes

**Table 3. Greenhouse Efficacy of Glyphosate Herbicidal Ionic Liquids**

compound	cornflower ( <i>Centaurea cyanus</i> )		white mustard ( <i>Sinapis alba</i> )		common lambsquarters ( <i>Chenopodium album</i> )		
	180 g/ha	360 g/ha	180 g/ha	360 g/ha	180 g/ha	360 g/ha	
Fresh Weight Reduction (%)							
monoanionic glyphosate HILs	1	NT <sup>b</sup>	NT	NT	NT	84	NT
	2	17	74	75	91	81	94
	3	61	88	78	88	NT	88
	4	19	79	62	89	83	68
	5	62	90	64	88	NT	NT
	6	21	63	11	81	68	54
dianionic glyphosate HILs	7	NT	NT	NT	NT	94	NT
	8	NT	NT	NT	NT	94	NT
Roundup 360 SL <sup>a</sup>	17	71	40	88	31	83	

<sup>a</sup>Composition: isopropylamine salt of glyphosate (41.5 wt %); ethoxylated tallowamine (15.5 wt %); water (43 wt %). <sup>b</sup>Not tested.

**Table 4. Couchgrass Control by of Glyphosate Herbicidal Ionic Liquids 4 WAT**

compound <sup>a</sup>	couchgrass destruction (%)			
	year	2011	2012	2013
monoanionic glyphosate HILs	2	99	NT	99
	3	NT	NT	100
	4	94	100	100
	5	100	100	100
	6	99	20	50
	Roundup 360 SL <sup>b</sup>	99	100	100

<sup>a</sup>All herbicides were applied at a rate of 1180 g/ha. <sup>b</sup>Composition: isopropylamine salt of glyphosate (41.5 wt %); ethoxylated tallowamine (15.5 wt %); water (43 wt %).

that can “regrow” from a small residual portion. Thus, laboratory regrowth tests were performed on Petri dishes using the couchgrass rhizomes picked from the field trials (2013) noted above. The couchgrass rhizomes were picked up after the herbicidal treatments with glyphosate HILs 4, 5, and 6 and Roundup 360 SL 8 weeks after application. They were then cut into sections with four buds each, placed in Petri dishes, and kept under controlled environmental conditions (temperature 20 ± 2 °C, relative humidity 60%, photoperiod 16/8 day/night) in a greenhouse for 3 weeks before visual evaluated. The results (the average of four replicates) are presented on a percent scale of regrowth, where 100% means regrowth from all buds and 0% means no regrowth.

The regrowth results (Table 5) demonstrated that all glyphosate HILs tested can prevent regrowth, even the least effective 6, albeit not as well as the other HILs or Roundup 360 SL. Glyphosate HIL 5 gave the highest regrowth inhibition after foliar application, comparable to that of Roundup. These results indicate that HIL formulations of glyphosate are efficiently translocated to rhizomes preventing the regrowth of plants.

## CONCLUSIONS

Eight new glyphosate-based herbicidal ionic liquids (HILs), containing both mono- and dianions of glyphosate free acid were prepared via acid–base reaction between the corresponding ammonium hydroxides and glyphosate free acid. To test the

**Table 5. Regrowth of Couchgrass from Rhizome Buds**

compound	couchgrass regrowth (%)
none applied	75
4	16
5	7
6	26
Roundup 360 SL <sup>a</sup>	3

<sup>a</sup>Composition: isopropylamine salt of glyphosate (41.5 wt %); ethoxylated tallowamine (15.5 wt %); water (43 wt %).

efficacy of these glyphosate HILs, both greenhouse and field trials were conducted and compared to the efficacy of the commercial herbicide formulation Roundup 360 SL. In greenhouse testing, at the lower application rate of 180 g/ha, the efficacy of all HILs was as much as two and a half to three times higher when compared to the commercial formulation, and dianionic glyphosates were found to be the most effective. Only the monoanionic glyphosate HILs were tested in the field, and all but one demonstrated excellent efficacy comparable to that of the commercial formulation. Laboratory regrowth tests established that the new HILs of glyphosate are efficiently translocated to rhizomes preventing the regrowth of plants. While more field trials have to be conducted in order to screen a wider variety of glyphosate HILs (e.g., dianionic glyphosate HILs) and more types of plants, the work presented here indicates that not only the water solubility but also the biological activity of glyphosate can be modified by proper choice of cations in the synthesis of HILs.

## ASSOCIATED CONTENT

### Supporting Information

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P spectra of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Authors

\*Tel.: 00148-61-6653682. E-mail: [juliusz.bernak@put.poznan.pl](mailto:juliusz.bernak@put.poznan.pl) (J.P.).

\*Tel.: +1-205-348-4323. E-mail: [RDRogers@ua.edu](mailto:RDRogers@ua.edu) (R.D.R.).

### Author Contributions

The manuscript was written through contributions of all authors.

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### Notes

The authors declare the following competing financial interest(s): Dr. Robin D. Rogers has partial ownership of 525 Solutions. Bernak, J.; Shamshina, J.; Praczyk, T.; Gurau, G.; Cojocaru, O. A.; and Rogers, R. D. are named inventors on related patent applications. Dr. Julia Shamshina and Dr. Gabriela Gurau are employees of 525 Solutions. The University of Alabama maintains approved Conflict Of Interest Management Plans.

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