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Poly High Internal Phase Emulsion for the Immobilization of Chemical Warfare Agents

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S Supporting Information

ABSTRACT: We report a facile method for the absorption (characterized by the weight/weight swelling degree, Q) of a variety of chemical warfare agents (CWAs); including sulfur mustard (HD) (Q = 40) and V-series (VM, VX, *i*-Bu-VX, *n*-Bu-VX) of nerve agents ($Q \geq 45$) and a simulant, methyl benzoate (Q = 55), through the use of a poly(styrene-*co*-vinyl benzyl chloride-*co*-divinylbenzene) lightly cross-linked poly high internal phase emulsion (polyHIPE). By varying the vinyl benzyl chloride (VBC) content and the volume of the internal phase of the precursor emulsion it is demonstrated that absorption is facilitated both by the swelling of the polymer and the uptake of liquid in the pores. In particular the sample prepared from a 95% internal emulsion water content showed rapid swelling (<5 min to total absorption) and the ability to swell both from a monolithic state and from a compressed state, making these systems ideal practical candidates for the rapid immobilization of CWAs.
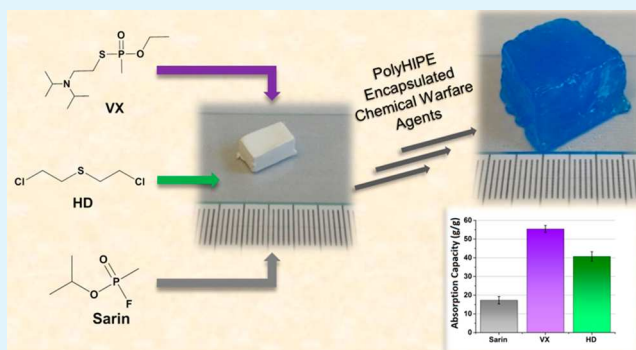
KEYWORDS: *polyHIPE, absorbent, polystyrene, chemical warfare agents, porosity, HD, VX*

Chemical warfare agents (CWAs) are a globally restricted item in accordance with the Chemical Weapons Convention implemented in 1997.[1] Regardless of this, there are still stockpiles of various agents across the globe,[2] and recent incidents have seen the suspected deployment of common CWAs; sulfur mustard (bis(2-chloroethyl) sulfide, HD) and VX (diisopropylaminoethyl O-ethyl methylphosphonothioate).[3] We believe an effective single system would ideally immobilize as many of the CWAs as possible, while not compromising the total swelling capacity, rate of uptake, or retention of any of the individual potential substrates. Superabsorbent materials for aqueous systems focus largely on the inclusion of ionic salt groups, which increase swelling through osmotic effects.[4] These same principles were then exploited with the introduction of ionic groups to form polyelectrolyte gels[5] and ionic polymers[6] for the absorption of organic solvents. For solvents such as oils which possess low dielectric constants, the swelling ability cannot be easily increased by adding an ionic moiety to the polymer. It is therefore becoming more commonplace that polymer morphologies are being modified to improve the swelling in low dielectric solvents, as shown in recent works that have included the electrospinning of porous fibers[7] and formation of nanocellulose floating aerogels, both for oil spill cleanup.[8] The most recent work on the development of absorbents specifically for CWAs has been based on utilizing hyper cross-linked toluene based polymer networks, which showed good swelling performance for HD, VX, and sarin (up to Q = 20),[9] where Q (swelling degree)

$$Q = \frac{(\text{mass swollen polymer} - \text{mass dry polymer})}{(\text{mass of dry polymer})}$$

The polymerization of a high internal phase emulsion (HIPE), and subsequent removal of the internal phase leads to the formation of a highly porous templated network known as a polyHIPE.[10] PolyHIPEs have been shown to possess very high surface areas exceeding 1200 m^2 g^{-1}.[11] With respect to their porosity, polyHIPEs have been shown to possess the ability to store active catalysts in the pores,[12] reversibly adsorb gases,[13] and importantly, show fast superabsorbent swelling ability.[14]

We demonstrate the effectiveness of a copolymer of styrene, 4-vinylbenzyl chloride (VBC) and divinylbenzene polyHIPE for the encapsulation of a suitable physical HD simulant (methyl benzoate) and the subsequent absorption of the CWAs; GB (isopropyl methyl phosphonofluoridate; VM (diethylaminoethyl O-ethyl methylphosphonothioate); i-Bu-VX (diethylaminoethyl O-isobutyl methylphosphonthioate); *n*-Bu-

VX (diethylaminoethyl O-nbutyl methylphosphonothioate); VX (diisopropylaminoethyl O-ethyl methylphosphonothioate); and HD (bis (2-chloroethyl) sulfide) (Figure 1). The
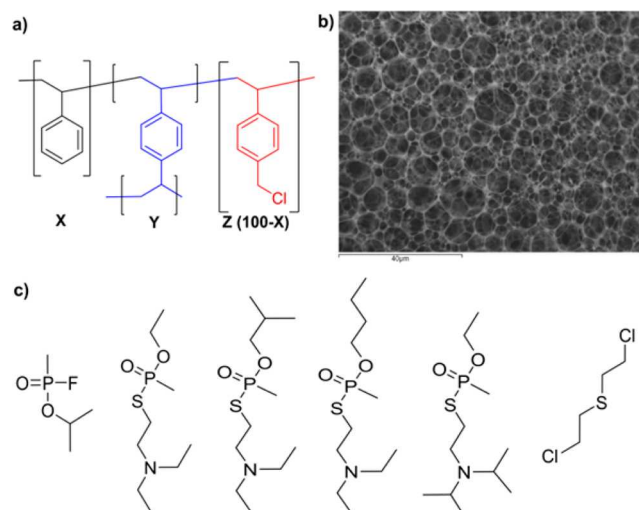
Figure 1. (a) General polyHIPE structure, (b) electron micrograph of the 5% VBC, 95% internal phase polyHIPE, (c) (from left to right) the chemical structures of the CWAs; sarin (GB), VM, *i*-Bu-VX, *n*-Bu-VX, VX, and sulfur mustard (HD).

polyHIPEs in this study were designed around a styrene (St) based polymer matrix, cross-linked with divinylbenzene (DVB). This copolymer system would provide good chemical resistance against any potential impurities or decomposition products associated with the CWAs ensuring the long-term stability of the swollen polymer. Any polyHIPE can be visualized as a sponge with good static uptake ability for liquids through capillary forces. However, the sponge will be rigid and unable to significantly expand if the cross-linking density is too high and/ or the solvent does not swell the polymer matrix. To allow the sponge to be dynamic and achieve higher swelling degrees, the polymer matrix must swell in the chosen solvent. Through this mechanism, the pore volume of the sponge can increase as both the pores and matrix absorb solvent. Polystyrene shows good compatibility with methyl benzoate, a physical simulant for HD (sulfur mustard). A simple cross-linked sample of polystyrene with 100:1 molar ratio of styrene:divinylbenzene (St_{100}) was observed to absorb 9.2 times its weight of methyl benzoate, $Q = 9.2 \pm 0.75$, (Figure 2a) after it had been immersed and allowed to fully equilibrate for a period of 72 h.

Subsequently, a St:DVB polyHIPE (molar ratio St:DVB = 100:1) was synthesized using 92% internal water content ($St_{100}VBC_0IP_{92}$) in the emulsion mixture. A synthetic procedure (see the Supporting Information) was developed for these polymerizations, based upon previous work.[15] Despite the low level of cross-linking, the polyHIPE was stable to mechanical manipulation and could be readily compressed without mechanical failure. Upon immersion in methyl benzoate, it was observed to absorb 36.2 times its mass ($Q = 36.2 \pm 0.41$). This absorption capacity is one of the best organic liquid absorption capacities for a polyHIPE observed to date and comparable to the absorption capacity of other solvents in non-HIPE materials such as spongy graphene (Q ranging from 20 to 85) and carbon nanofiber aerogels (Q ranging from 40 to 115).[16,17] To further improve the absorption capacity, it was decided to copolymerize the styrene
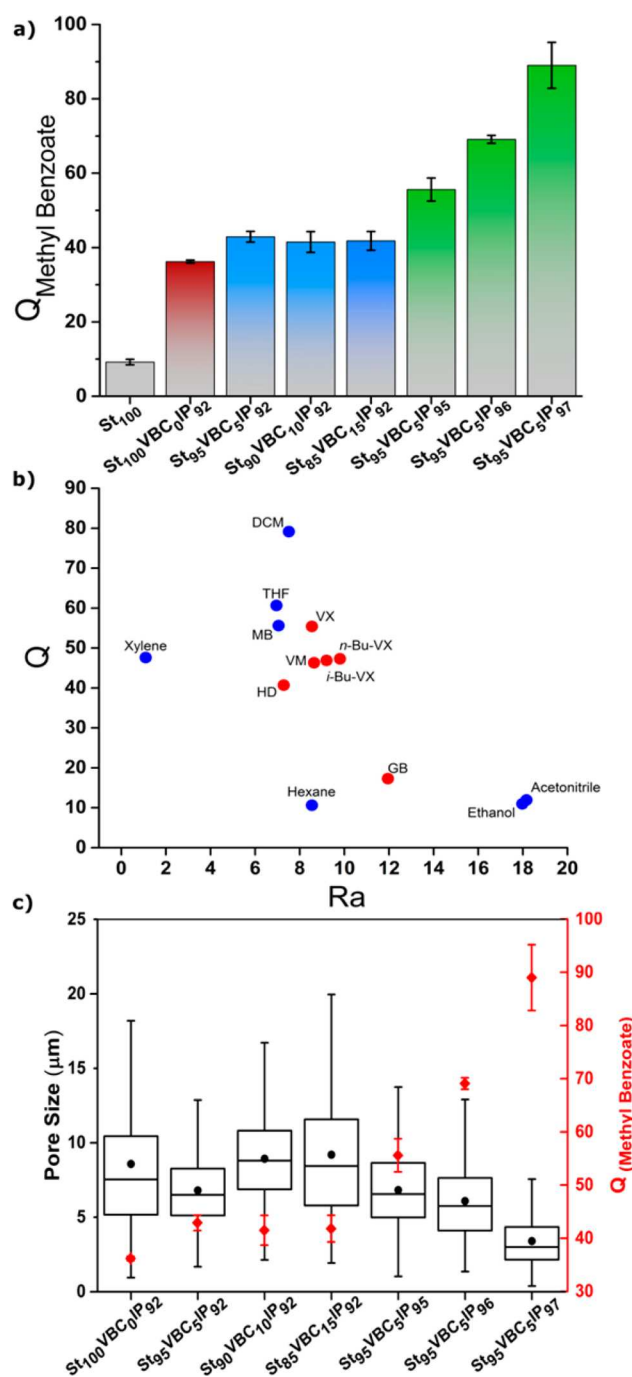
Figure 2. (a) Swelling degrees in methyl benzoate of a polystyrene gel (left) in contrast to polyHIPEs with 1% total monomers cross-linking, varying amounts of VBC doping and a variation in internal phase fraction. (b) Correlation of Ra (from Hansen solubility parameters) with degree of absorption in $St_{95}VBC_5IP_{95}$ for various solvents and the CWAs. (c) Absorption capacities Q of each of the polyHIPEs (red), contrasted with the respective pore size distributions (black), gathered from SEM images (Figure S2). The boxes represent the median and interquartile ranges and circles represents the mean pore size.

with a functional styrenic monomer that ostensibly would be more compatible with methyl benzoate. Vinyl benzyl chloride (VBC) was chosen for a number of reasons. The first was that of the various commercially available styrene monomers, it possessed Hansen solubility parameters for the homopolymer closest to those of methyl benzoate, indicating better solvent

compatibility (Table S1). It is also a relatively cheap monomer compared to most functional styrenes. It has been previously demonstrated that VBC is sufficiently hydrophobic not to interfere with the stability of the HIPE foam, which is a crucial factor in comonomer choice.[18] The introduction of the benzyl chloride function into the polyHIPE would allow for subsequent chemical modification via reactions with the chloromethyl group. Previous work has also reported reactivity ratios for the copolymerization of St and VBC of $r_1 = 0.72$ and $r_2 = 1.32$, respectively, with $r_1r_2 = 0.95$ which favors the formation of a statistically random copolymer, and minimal composition drift and segregation of the VBC in the copolymer chains.[19] The VBC comonomer was incorporated into polyHIPE emulsions at 5, 10, and 15 mol % with the styrene while maintaining the total internal phase at 92 wt % (samples $St_{95}VBC_5IP_{92}$, $St_{90}VBC_{10}IP_{92}$ and $St_{85}VBC_{15}IP_{92}$). In all cases monolithic mechanically stable polyHIPEs were obtained and their absorption capacities for methyl benzoate measured (Figure 2a). The swelling of the 5 mol % VBC polyHIPE, $St_{95}VBC_5IP_{92}$, gave a ∼ 20% increase in absorption capacity compared to the styrene only polyHIPE ($St_{100}VBC_0IP_{92}$) with $Q = 42.9 \pm 1.4$. However, there was no discernible improvement in absorption upon increasing the VBC content with $Q = 41.5 \pm 2.8$ for $St_{90}VBC_{10}IP_{92}$ and $Q = 41.8 \pm 2.5$ for $St_{85}VBC_{15}IP_{92}$.

The increase in swelling observed on incorporation of the VBC was originally thought to be due to the increased compatibility of the polymer matrix with the solvent, which was supported by examining the Hansen solubility parameters of the solvent against the polymer composition (Table S1). While the non-HIPE simple cross-linked equivalent polymers of St, VBC and DVB showed a slight decrease in swelling ability relative to the simple cross-linked styrene sample (St_{100}) (Table S5) chemical compatibility was necessary for high degrees of swelling. Six solvents (acetonitrile, dichloromethane, ethanol, hexane, tetrahydrofuran, and xylene) spanning a range of dielectric constants were tested in swelling $St_{95}VBC_5IP_{95}$ and correlated with their Hansen solubility parameters via the parameter Ra which can be seen as a measure of compatibility between the two substances. The lower the Ra, the more compatible the polymer and liquid. The results are shown in Figure 2b (blue circles) where a good correlation between relative degree of swelling and Ra is shown. Hexane, ethanol, and acetonitrile with Ra values greater than 8, do not swell $St_{95}VBC_5IP_{95}$ to the same degree as the other three solvents. The degree of absorption that was observed for ethanol, hexane and acetonitrile must be due to the spongelike nature of the polyHIPE, but for high degrees of swelling it is apparent that solvent polymer compatibility is needed.

SEM analysis of the $St_{100}VBC_0IP_{92}$ and $St_{95}VBC_5IP_{92}$ samples enabled measurement of pore sizes with the mean pore sizes equal to 8.6 and 6.8 μm respectively (Figure 2c, and Figures S1 and S2). Assuming capillary action can be taken as responsible for the absorption of the portion of solvent not involved in directly swelling the polymer matrix and that capillary pressure is inversely proportional to the pore radius, we attribute the increase in absorption to the decrease in pore radius according to the approximation.

$$\Delta P = \frac{2\gamma \cos \theta}{r}$$

Where ΔP = capillary pressure, γ = surface tension of liquid, θ = contact angle of liquid and solid, and r = pore radius.[20,21] It is possible that the increased absorption is a result of an increase in the contact angle for the methyl benzoate with the polymer surface but since the surface energies are very similar (38−39 mJ m² for polystyrene and 40−43 mJ m² for poly(vinylbenzyl chloride)) it is not likely that the contact angles should differ significantly.[15]

The pore sizes could be further reduced by increasing the internal phase of the emulsions. PolyHIPEs were synthesized from the 5% VBC content with 95, 96, and 97% water content in the emulsions. The absorption capacities of these polymers are shown in Figure 2a. The absorption of the polyHIPEs in methyl benzoate increased from $Q = 42$ for $St_{95}VBC_5IP_{92}$ to a remarkable $Q = 89$ for $St_{95}VBC_5IP_{97}$. The pore size distributions and the associated absorption capacities are shown in Figure 2c, and a clear correlation with the inverse of the average pore diameters in the structure is evident.

Despite the high absorption capacities of the 96 and 97% polyHIPEs, increasing volumes of the methyl benzoate would leak from the swollen polymer over 24 h on standing (losses of $16 \pm 3.4\%$ and $31 \pm 4.5\%$, respectively). This was an expected consequence of increasing the internal phase of the system to a point where polymer connectivity would be critically low and the chosen solvent was of low viscosity. In contrast the 95% polyHIPE ($St_{95}VBC_5IP_{95}$) with $Q = 55$ (5500 wt %) could be readily manipulated with minimal leaking of solvent (only $4 \pm 0.7\%$ loss on standing, Video S1). Furthermore, this sample showed rapid absorption of the solvent with a 100% loading capacity reached within 4 min (Figure 3a).
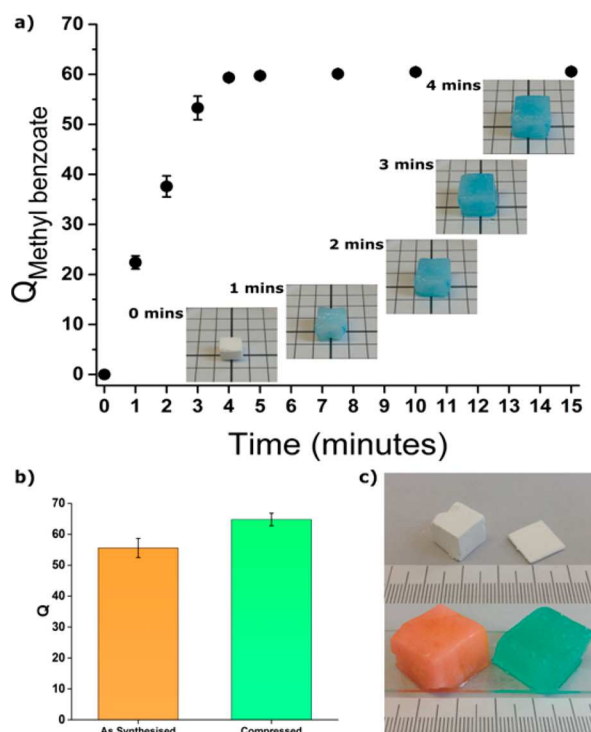
Figure 3. $St_{95}VBC_5IP_{95}$ polyHIPE; (a) the rate of swelling of a 8 × 8 × 10 mm cube submerged in dyed methyl benzoate. Pictures to the right demonstrate the volume increase in the first 4 min. (b) Swelling degree (Q) of cubes of the polymer both as synthesized and after having been compressed at 220N. (c) (above) Images of the two samples before swelling, (below) the swollen polyHIPEs after being exposed to dyed methyl benzoate.

PolyHIPEs are intrinsically low density, high volume polymers and to be useful in a real world sense, the volume would ideally be reduced to aid in transport and deployment of a functioning product. The low cross-linking density of these polyHIPEs means that they are highly compressible and suffer no obvious mechanical damage (e.g., flaking or crumbling). Thus, we studied the ability of the $St_{95}VBC_5IP_{95}$ to absorb methyl benzoate after it had been compressed down to a significantly smaller volume. Samples of similar mases and dimensions were compressed under a pressure of 220 N and then swollen in the methyl benzoate. After compression at this force, the volume of the polymer was reduced to 17% of the original value (from 0.685 ± 0.032 cm^3 to 0.116 ± 0.004 cm^3) and the density was increased to 590% of the original value (from 0.064 ± 0.001 g cm^{-3} to 0.377 ± 0.004 g cm^{-3}). The compressed polymer showed the ability to regain its form and swell to even higher degrees than the uncompressed control with Q = 65 (Figure 3b, 3c). The increased performance is possibly due to slight fracturing of the polymer structure under compression; reducing its elastic potential and/or micro fractures improving the interconnectivity of pores in the polymer matrix. The higher absorption capacity of the 95% internal phase polyHIPE $St_{95}VBC_5IP_{95}$ in conjunction with its better handling properties and very fast rate of absorption made it the ideal candidate for testing on an array of CWAs. Samples of $St_{95}VBC_5IP_{95}$ were swollen in sarin, VM, i-Bu-VX, VX, n-Bu-VX, and HD (Figure 4) for 72 h.
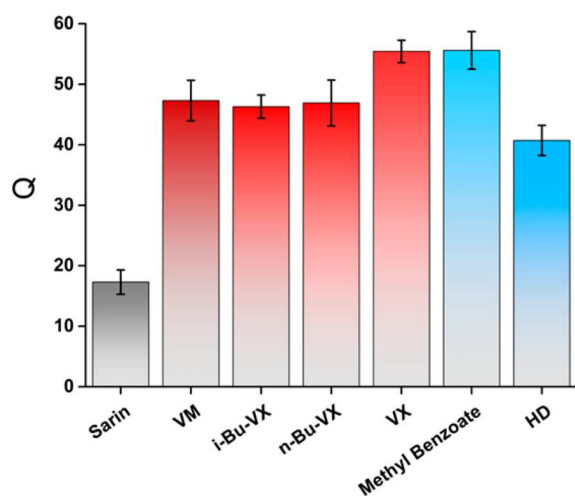
Figure 4. Swelling performance of the $St_{95}VBC_5IP_{95}$ polyHIPE in the CWAs: sarin (GB), VM, i-Bu-VX, n-Bu-VX, VX, and HD, shown alongside the original simulant result.

With the exception of sarin, the Q values for the agents exceeded 40, demonstrating the versatility of the absorbent and its ability to immobilize the V series of agents and sulfur mustard. While the absorption capacity for sarin was lower, it is still in line with other materials reported in the literature. The polyHIPE system described here was specifically designed to absorb HD (mustard agent) and thus the excellent absorption result for the V series of CWAs was particularly surprising given the dissimilarity in chemical structures between HD and the V series (Figure 1). Unfortunately, to the best of our knowledge, no simulants for solubility exist for the V series of CWAs and the Hansen solubility parameters have not been measured. Using predictive software (Y-MB method, HSiP, fourth edition, Table S2) solubility parameters were calculated for the CWAs

and the resultant Ra values versus degree of swelling are shown in Figure 2b (red circles). Although these are merely predicted values these results reinforce the general relationship between polymer–solvent compatibility and extensive absorption.

In conclusion, we have demonstrated that a 1 wt % cross-linked styrene-co-vinyl benzyl chloride based polyHIPE from a 95% internal phase emulsion can absorb unprecedented volumes of a broad spectrum of chemical warfare agents. The low cross-linking density and high internal phase applied does not appear to perturb the internal structure of the HIPE or the ability of the polymer to retain absorbed liquid. Additionally, the polymer is also able to swell in the simulant just as well after compression, which shows low fragility and makes it an ideal candidate for real world deployment, where high swelling degrees are required but at small transit volumes. The results indicate that solvent–polymer compatibility and "small" pore sizes are necessary for very high degrees of liquid absorption. The relative importance of these two properties (and others such as viscosity) are currently the subject of ongoing investigations. Furthermore, the polyHIPE swollen with the methyl benzoate simulant shows good resistance to leaking and fast absorption rates, which we expect to be translated to the absorption of the CWAs; these studies are also ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b09188.

Experimental data and micrographs (PDF)
Video S1 showing absorption (MPG)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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