

**School of Molecular Life Sciences**

**Hyper Crosslinked Polystyrene Based Materials for Carbon Dioxide  
Capture Applications.**

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**This thesis is presented for the Degree of  
Master of Research (Chemistry)  
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## Declaration

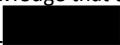
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## Attribution Statement

	Conception and Design	Acquisition of Data and Method	Data Conditioning and Manipulation	Analysis and Statistical Method	Interpretation and Discussion
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## Abstract

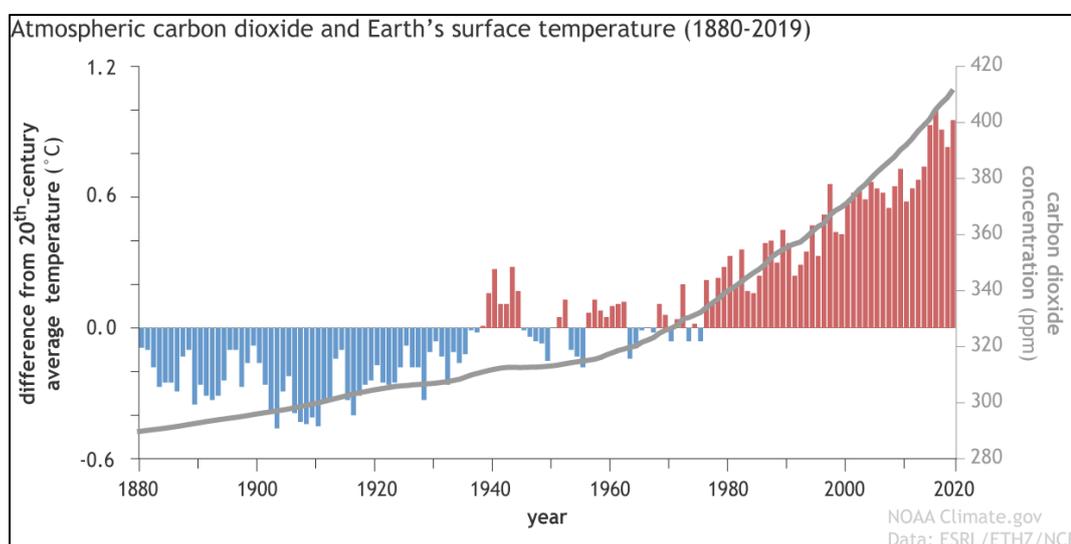
With the concentration of atmospheric carbon dioxide (CO<sub>2</sub>) continuing to rise and affect the climate it is imperative that measures be taken to avoid the direst consequences of global warming. CO<sub>2</sub> capture technologies provide a unique opportunity to do so, being able to affect CO<sub>2</sub> production and concentration in the atmosphere through flue gas and direct air capture. Hyper crosslinked polystyrene (HCP) is one such technology, with many qualities suited to CO<sub>2</sub> capture applications such as high CO<sub>2</sub> uptake, simple synthesis and good recyclability. In my earlier work HCP was combined with 100 wt % amines such as monoethanolamine (MEA) and diethanolamine (DEA) to achieve CO<sub>2</sub> uptakes of 23.89 and 12.03 % respectively, outperforming both previously reported HCP uptakes and 30 wt % aqueous amine solutions of DEA or MEA, the current industry standards for flue gas capture. Unfortunately, these systems were not recyclable, a quality which is key for effective CO<sub>2</sub> capture. As such this thesis looked to improve upon these HCP systems by: 1) optimisation of the crosslinking of the HCP, 2) changing of the sorbent liquid swollen into the HCP, and 3) functionalisation of the HCP by Reversible Addition–Fragmentation Chain-Transfer (RAFT) induced block copolymerisation, thus allowing for CO<sub>2</sub> capturing crosslinks to be implemented and CO<sub>2</sub> capturing nanogels to be formed. Herein this thesis reports the determination of a suitable solvent, cyclohexane, for low stoichiometric crosslinker ratio synthesis of HCP wherein the solvent does not participate in nor impede the Friedel-Crafts alkylation reaction required for HCP synthesis unlike similar syntheses found in the literature wherein the solvent, such as dichloromethane or dichloroethane, is also the crosslinker, as well as the synthesis and characterisation by IR spectroscopy of several HCPs from waste expanded polystyrene (WEPS) using various crosslinkers (dichloromethane, chloroform, dichloroethane, dichlorobutane, 1,3-dichloro-2-(chloromethyl)-2-methylpropane and dichlorohexane) at various crosslinker ratios of 1:0.5, 1:1 and 1:2 relative to the WEPS. These HCPs were then swollen with DEA at a 1:0.5 HCP to DEA mass ratio to achieve CO<sub>2</sub> uptakes of up to 4.63 wt %, achieving 90% of this uptake in as little time as 1800 s. Additionally, a higher crosslinked HCP was combined with amine blends of MEA/TEA, MEA/MDEA, DEA/TEA and DEA/MDEA at a 1:2 HCP to blend ratio, as done in the earlier work, in the hopes that the presence of the tertiary amines in the blends could increase recyclability while the primary/secondary amines would increase uptake. The highest

achieved CO<sub>2</sub> uptake of the blends was 6.52 wt % for the MEA/MDEA system, achieving 90% of this uptake in 600 s, outperforming the HCP/MDEA system from the earlier work. However, all blend systems were still unrecyclable. An alternative mechanism for crosslinking using difunctional alcohols was also investigated, wherein ethylene glycol was used as the crosslinker, which was ultimately unsuccessful. The synthesis of an amino acid ionic liquid comprised of betaine ([Bet]) and taurine ([Tau]) [Bet][Tau] that is theoretically capable of CO<sub>2</sub> capture was attempted, but ultimately unsuccessful. We believe that the synthesis provided in the literature for this ionic liquid is not valid, and thus provide evidence to support this. Finally, the synthesis and characterisation of various polystyrene macro chain transfer agents (PS-mCTAs) via RAFT polymerisation, and the successful synthesis and characterisation of the monomer 2-vinyl-4,4-dimethyl azlactone (VDMA) via a simplified method with an overall yield of 29.4% are also reported.

## 1 – Introduction and Literature Review

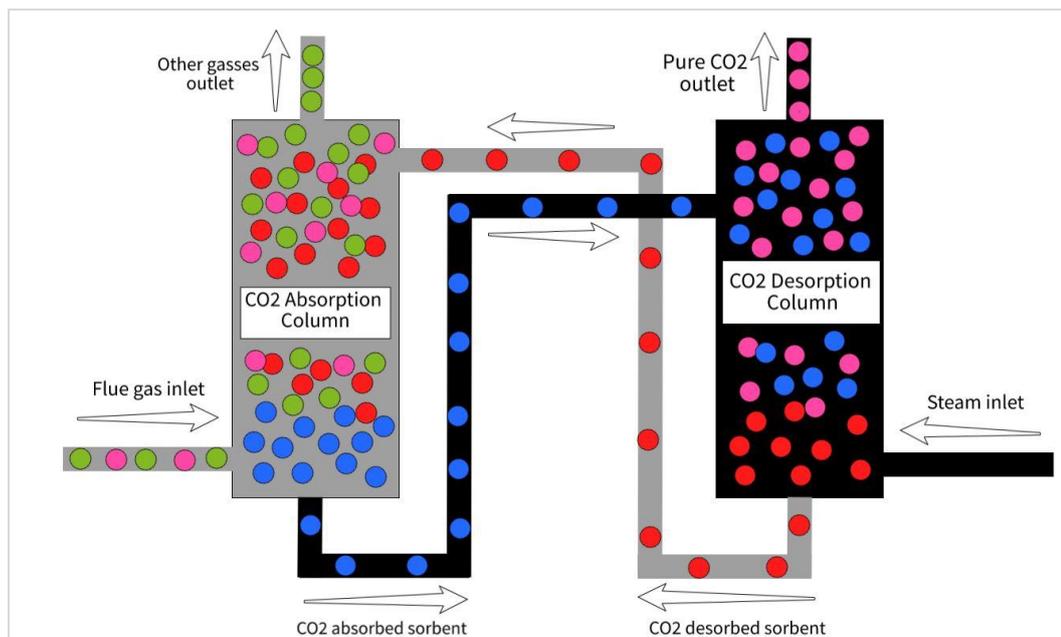
### 1.1 – General Overviews

The international panel for climate control recently published a report specifying many immediate and drastic changes that must be undertaken to combat the worsening effects of global warming.<sup>1, 2</sup> Alongside sweeping changes from fossil fuels to renewable energies, the report also recommended that carbon capture, specifically carbon dioxide (CO<sub>2</sub>) and methane, and storage technologies also be implemented at large scales.<sup>1, 2</sup> Though it is important to research and implement both carbon capture *and* storage technologies,<sup>1, 2</sup> for the purposes of this thesis only CO<sub>2</sub> capture will be discussed.



*Figure 1 – Graph of rise in concentration of atmospheric CO<sub>2</sub> over time and the average temperature difference compared to the 20<sup>th</sup> century over time. Reproduced and publicly available from climate.gov.<sup>126</sup>*

Currently there are two predominant forms of CO<sub>2</sub> capture, flue gas<sup>3-9</sup> and direct air capture (DAC).<sup>10-13</sup> For direct air capture, there is no current, widely implemented industry standard technology.<sup>10-13</sup> The industry standard for flue gas capture is 30 wt % aqueous amine (usually monoethanolamine (MEA) or diethanolamine (DEA)) columns,<sup>3-9</sup> through which the flue gas is bubbled allowing CO<sub>2</sub> capture to occur via a chemical reaction with the amine solution (Figure 2).<sup>3-9</sup> The CO<sub>2</sub> saturated amine is then transferred to another column which can be heated to release the CO<sub>2</sub> in a concentrated stream, regenerating the amine solution (Figure 2).<sup>3-9</sup>



*Figure 2 - Depiction of amine scrubbing process in which a 30 wt % aq. amine reacts with  $\text{CO}_2$  in the absorption column, and is regenerated by release of the  $\text{CO}_2$  in the desorption column. Blue =  $\text{CO}_2$  absorbed sorbent, red =  $\text{CO}_2$  desorbed sorbent, green = other gasses, pink = pure  $\text{CO}_2$ .*

Unfortunately, there are several drawbacks to these columns, including relatively low absorption capacity and mediocre recyclability with high desorption temperatures leading to amine degradation, water loss and corrosion of the column over time.<sup>3-13</sup> Furthermore, these columns cannot be used for direct air capture, as the ultra-low concentration of  $\text{CO}_2$  in air requires high flow rates of air through the material, which must in turn be more reactive with  $\text{CO}_2$  than 30 wt % amines to compensate.<sup>10-13</sup> An ideal  $\text{CO}_2$  capturing could be used for both flue gas and direct air capture. Such a material would therefore have to possess the following qualities: high absorption capacity and reactivity with  $\text{CO}_2$ , rapid  $\text{CO}_2$  uptake, high gas permeability, high gas to sorbent contact area, high recyclability, low desorption temperatures, high stability and no corrosive properties.<sup>10-13</sup>

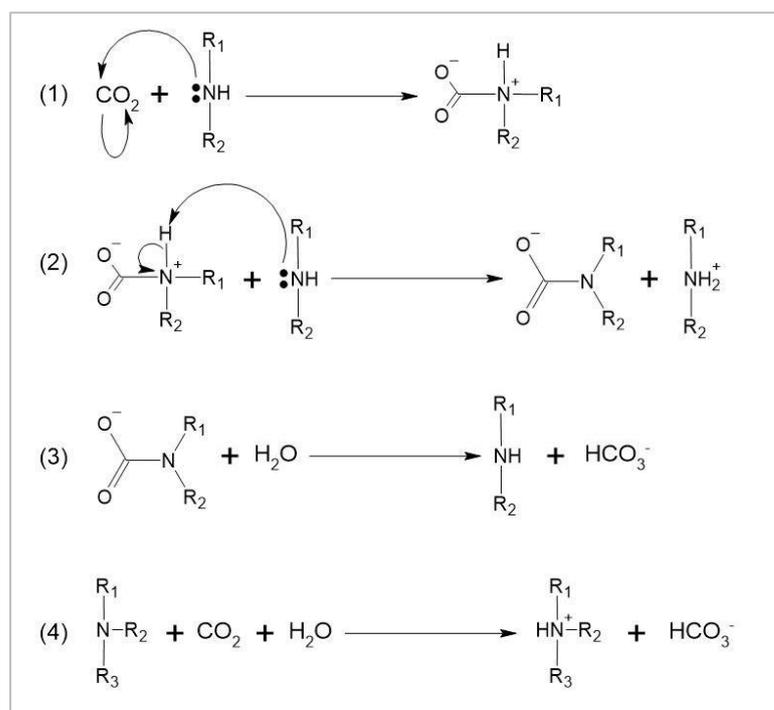
Though most papers focus exclusively on flue gas, pure  $\text{CO}_2$  or direct air capture, recent publications have increasingly featured materials useable for all 3 applications. Such materials fall under 3 broad categories, the general advantages and disadvantages, of which will be discussed below along with some specific examples relating directly to this thesis and the results generated from the earlier work.<sup>14</sup> These

categories are: liquid sorbents, solid sorbents and swollen sorbents (wherein a liquid sorbent is swollen into a solid material which may also be itself a sorbent). The disadvantages/advantages of other sorbents will be mentioned for comparison, but detailed analyses of their syntheses and sorption mechanisms will not be given. When discussing CO<sub>2</sub> uptake capabilities, the amount of CO<sub>2</sub> a material can absorb will be presented as a weight percentage of the material. Thus, for example, if 1 g of material absorbs 0.1 g of CO<sub>2</sub>, the CO<sub>2</sub> uptake of that material is 10 wt %.

## 1.2 – Liquid Sorbents

### 1.2.1 – Amines and Amine Blends

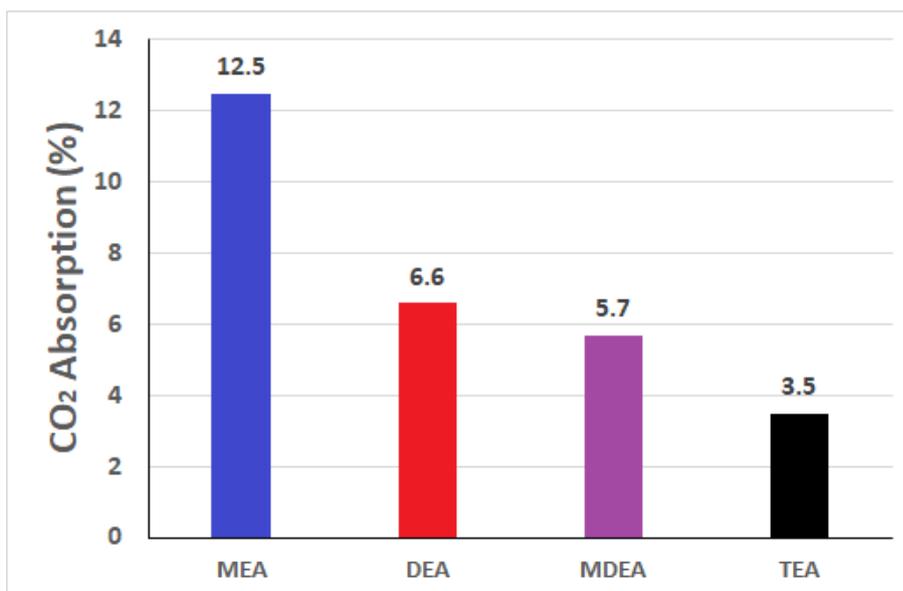
As mentioned above the current industry standard for flue gas CO<sub>2</sub> capture is a process called amine scrubbing, harnessing a chemical reaction between primary or secondary amines to capture CO<sub>2</sub> (Figure 3).<sup>3-9</sup> In this reaction (Equations 1-3) the amine reacts directly with CO<sub>2</sub> to form a zwitterion (Equation 1),<sup>15-17</sup> then transfers a proton to an unreacted amine forming a carbamate salt (Equation 2),<sup>15-17</sup> finally, the carbamate reacts with water to form a bicarbonate, regenerating the amine (Equation 3).<sup>15-17</sup> Tertiary amines react differently, catalysing the direct formation of bicarbonates (Equation 4).<sup>15-17</sup>



**Figure 3** – Aqueous amine reaction mechanisms for reactions of CO<sub>2</sub> and generic primary/secondary amines (Equations 1-3) or tertiary amines (Equation 4).

Generally, highly reactive primary amines, such as MEA, have rapid, high absorption capacities but similarly high volatility and degradation, and therefore lesser recyclability.<sup>15-17</sup> Tertiary amines, such as methyldiethanolamine (MDEA) or triethanolamine (TEA) however show lower reactivity, and therefore slower, reduced absorption capacities but increased stability and greater recyclability.<sup>15-17</sup> Secondary amines are somewhat of a compromise between the two, showing middling absorption capacities, absorption rates and recyclability.<sup>15-17</sup> Ultimately though, as discussed in section 1.1.1, aqueous amine solutions are undesirable for DAC purposes and are mediocre for flue gas capture purposes due to their high corrosivity, mediocre uptakes and recyclability issues.<sup>10-13</sup>

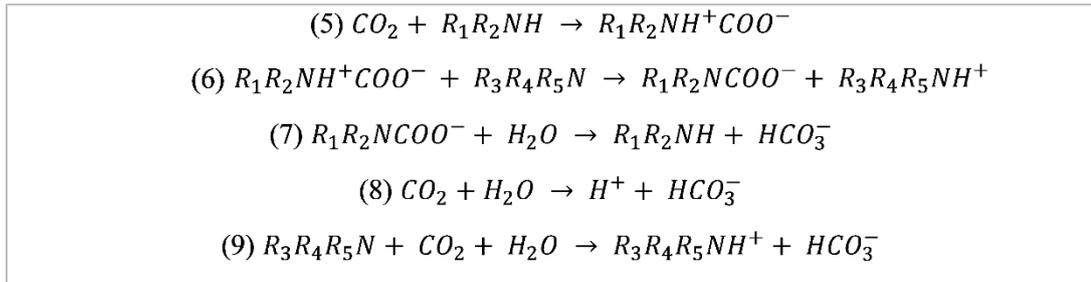
In 2017 El Hadri and co-workers found that under 15 % CO<sub>2</sub> streams, 30 wt % solutions of monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA) and triethanolamine (TEA) achieved CO<sub>2</sub> uptake capacities of 12.5, 6.6, 5.7 and 3.5 wt % (Figure 4).<sup>18</sup> These values will be used later in this thesis as benchmark comparisons for other materials, as they are conducted in conditions closest to real world flue gas capture conditions, along with the earlier work's results which will be discussed below.<sup>14, 18</sup> It should be noted however, that these values are likely less than would be expected of a 100 % CO<sub>2</sub> stream (as used in this thesis and the earlier work), simply due to the reduced amount of CO<sub>2</sub> present to react with the amines.<sup>12, 18</sup> This is conferred by Kim and co-workers' study in 2013 that found under 40 % CO<sub>2</sub> streams, 30 wt % aqueous MEA, DEA and TEA could achieve uptakes of 12.2, 8.6 and 4.3 wt %, albeit at a lower temperature than Hadri and co-workers' results.<sup>19</sup>



*Figure 4 - CO<sub>2</sub> absorption (%) comparison of various 30 wt % aq. amines under 15 % CO<sub>2</sub> stream as found by El Hadri and co-workers.<sup>18</sup>*

In an effort to improve upon the aqueous amines, amine blends have been proposed as a viable alternative.<sup>20-25</sup> Amine blends are simply a mixture of a primary or secondary amine with a tertiary amine in an aqueous solution. The goal of amine blends is to allow the rapid, high CO<sub>2</sub> uptake capacities of the primary/secondary amines to compensate for the slower, reduced CO<sub>2</sub> uptake capacities of the tertiary amines, while the higher stability of the tertiary amines compensates for the high volatility of the primary/secondary amine, increasing overall recyclability.<sup>20-25</sup>

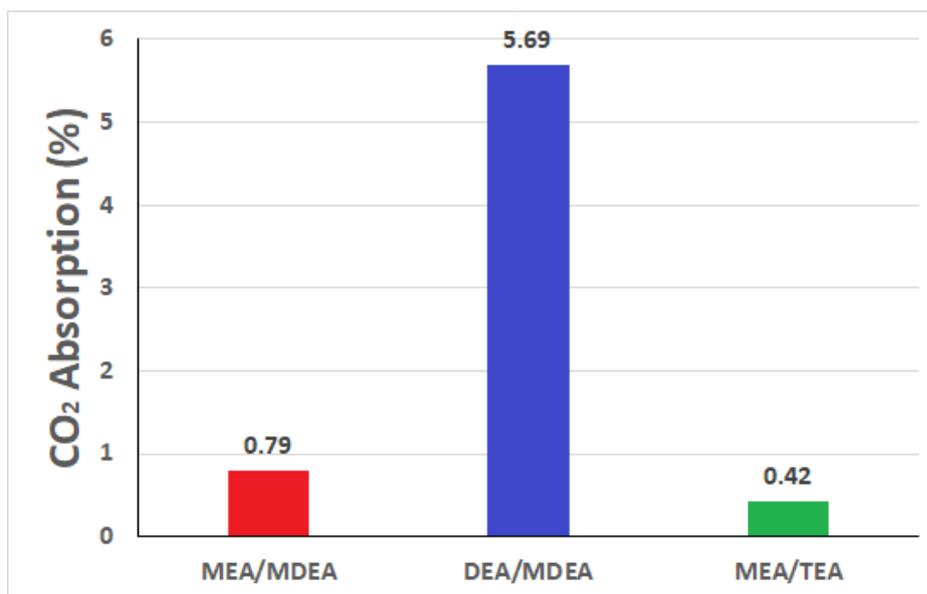
As a result of being mixtures of primary/secondary and tertiary amines, amine blends have a slightly different absorption reaction mechanism (Figure 5).<sup>23-25</sup> In this mechanism the primary/secondary amine reacts directly with CO<sub>2</sub> to form a carbamate (Equation 5) which then goes on to transfer a proton to the tertiary amine (Equation 6) before reacting with water, forming a carbonate and regenerating the primary/secondary amine (Equation 7).<sup>23-25</sup> It should be noted that this is the dominant mechanism, but other mechanisms including the dissolution of CO<sub>2</sub> into water and the reaction between tertiary amines and CO<sub>2</sub> also occur at the same time, albeit much slower (Equations 8 and 9).<sup>23-25</sup>



*Figure 5 - Amine blends CO<sub>2</sub> absorption mechanism as found in various literature sources.*

Many amine blends have been investigated in the literature,<sup>20-25</sup> so for the purposes of this thesis only blends of MEA, DEA, MDEA and TEA will be focussed on here.<sup>20-22</sup> It should however be noted that the majority of literature sources on this topic focus on the kinetics of absorption rather than absorption uptake.<sup>20-25</sup> Perhaps because of this focus on kinetics, there are no literature sources where absorption is conducted at ambient conditions.<sup>20-25</sup> Furthermore, studies including the recyclability of these systems are also rare.<sup>20-25</sup> Thus, a true representation and comparison of amine blends capabilities is difficult. Generally speaking, though, since amine blends are still comprised of amines, the same drawbacks apply to amine blends as they do to aqueous amine solutions, but to a lesser degree.<sup>20-25</sup>

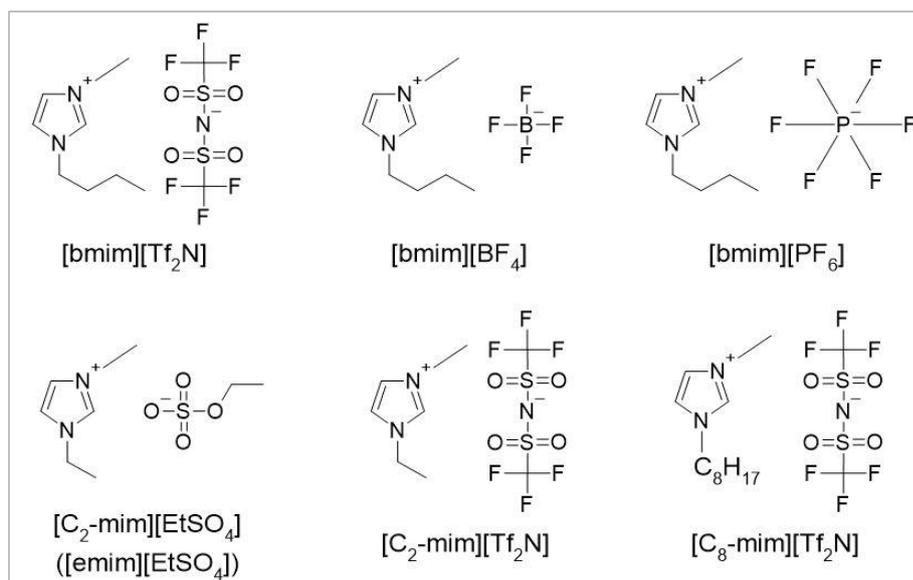
In 2002 Zhang and co-workers found that a 3/32 wt % DEA/MDEA aqueous blend could achieve CO<sub>2</sub> uptakes of 5.69 wt %.<sup>22</sup> However, this was done under 4.9 MPa (~48 atm) with a 100% CO<sub>2</sub> stream, which would have drastically increased CO<sub>2</sub> uptakes compared to ambient conditions and lower CO<sub>2</sub> concentrations.<sup>12, 22</sup> In Li and co-workers 2001/2002 works, 3/12 wt % MEA/MDEA and 2.5/7.5 wt % MEA/TEA amine blends achieved CO<sub>2</sub> uptakes of 0.79 and 0.42 wt % respectively.<sup>20, 21</sup> In this case the lower total wt % solutions and decreased pressure of CO<sub>2</sub> (0.3 atm for these works) would have led to drastically decreased CO<sub>2</sub> uptakes compared to Zhang and co-workers DEA/MDEA blend, and compared to experiments conducted at ambient conditions.<sup>12, 20, 21</sup> Interestingly, it appears that DEA/TEA has not been investigated in the literature, presumably because DEA is a less reactive amine than MEA, and TEA is a less reactive amine than MDEA (due to sterics),<sup>12</sup> thus the combination is undesirable for study.



*Figure 6 - CO<sub>2</sub> absorption (%) comparison of various amine blends.<sup>20-22</sup>*

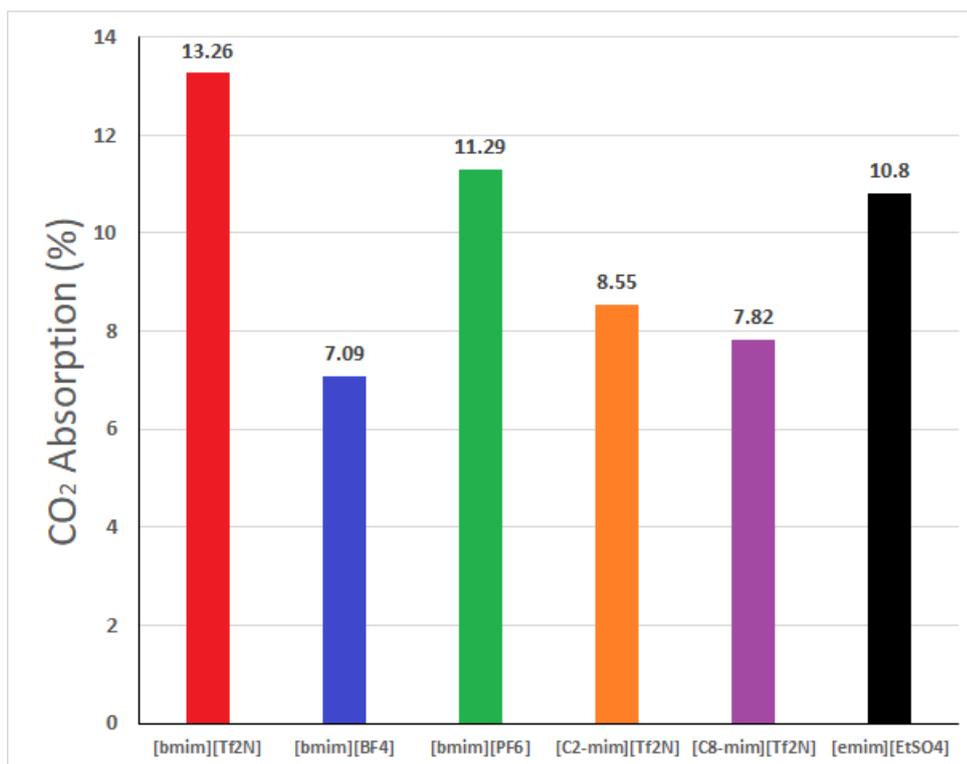
### 1.2.2 - Ionic Liquids

Ionic liquids have recently been the focus in many applicative fields of chemistry.<sup>26-</sup>  
<sup>32</sup> For CO<sub>2</sub> capture, their relatively easy synthesis, combined with high stability and potential for high CO<sub>2</sub> uptake makes them an attractive option.<sup>26-32</sup> Interestingly ionic liquids can absorb CO<sub>2</sub> via both chemical and physical means, whether by reaction between the ionic liquid and CO<sub>2</sub> or by dissolution of CO<sub>2</sub> into the ionic liquid.<sup>26-32</sup> Furthermore, by altering the ions comprising the liquid, ionic liquids can be tuned to produce differing absorption mechanisms, leading to variable CO<sub>2</sub> absorption uptake capacity, kinetics and recyclability.<sup>26-32</sup> Because of the high variability in mechanisms, only the CO<sub>2</sub> uptake capabilities of six ionic liquids (Figure 7) will be discussed here.<sup>27, 28, 30, 31</sup>



**Figure 7** - The ionic liquids discussed in this section:  $[bmim][Tf_2N]$ ,<sup>27</sup>  $[bmim][BF_4]$ ,<sup>28</sup>  $[bmim][PF_6]$ ,<sup>30</sup>  $[C_2\text{-mim}][EtSO_4]$  ( $[emim][EtSO_4]$ ),<sup>28</sup>  $[C_2\text{-mim}][Tf_2N]$ <sup>31</sup> and  $[C_8\text{-mim}][Tf_2N]$ <sup>31</sup> from multiple studies.

In their work Aki and co-workers found that the imidazolium based ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide  $[bmim][Tf_2N]$  displayed uptakes of 13.26 wt %, though this was achieved under 120 atm of pressure.<sup>27</sup> Using the 1-butyl-3-methylimidazolium  $[bmim]$  cation with other anions such as tetrafluoroborate  $[BF_4]$  and hexafluorophosphate  $[PF_6]$ , it was found by Shiflett et al. and Blanchard et al. that  $[bmim][BF_4]$  and  $[bmim][PF_6]$  could achieve uptakes of 7.09 and 11.29 wt %, at 20 and 92 atm, respectively.<sup>28, 30</sup> Blanchard and co-workers also demonstrated that 1-ethyl-3-methylimidazolium ethyl sulfate  $[emim][EtSO_4]$  could achieve uptakes of 10.8 wt % at 92 atm,<sup>28</sup> and finally Shin and co-workers demonstrated that 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids  $[C_2\text{-mim}][Tf_2N]$  and  $[C_8\text{-mim}][Tf_2N]$  (where  $C_n$  refers to the length of the alkyl group) could achieve uptakes of 8.55 and 7.82 wt % at 43 atm, respectively.<sup>31</sup> It should be noted that all of these ionic liquids displayed their respective  $CO_2$  uptakes under high pressure environments, and thus display higher  $CO_2$  uptakes than they would at ambient/low pressure.<sup>27, 28, 30, 31</sup> This makes direct comparisons difficult but still serves to demonstrate the possible  $CO_2$  uptakes achievable by ionic liquids, and can furthermore serve to highlight how impressive sorbents that can achieve higher uptakes at ambient/low pressures are.<sup>27, 28, 30, 31</sup>



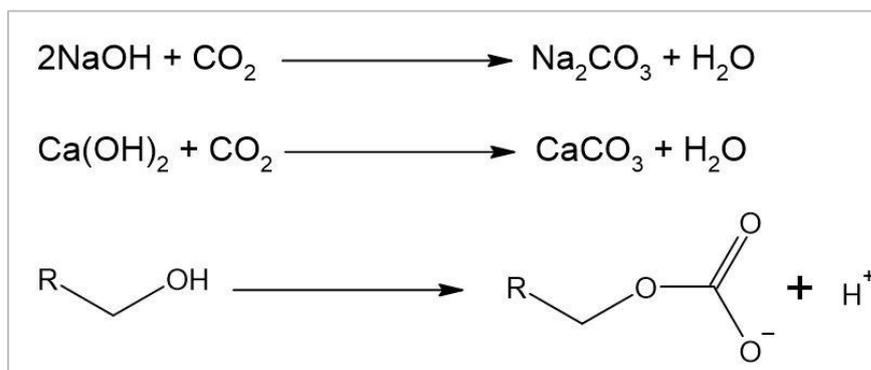
*Figure 8 - CO<sub>2</sub> absorption (%) comparison of various ionic liquids.<sup>27, 28, 30, 31</sup>*

Generally speaking, ionic liquids have 3 main drawbacks: water absorption, viscosity and synthetic accessibility.<sup>12, 26-32</sup> Water absorption in ionic liquids is very common, though in particular for CO<sub>2</sub> absorbing ionic liquids this can occur preferentially to the CO<sub>2</sub> absorption.<sup>12, 26-32</sup> Furthermore, the absorption of water can lead to decreased recyclability. The high viscosity observed in ionic liquids often means they must be used in solutions, leading to the aforementioned water related decreased recyclability for aqueous solutions, as well as potentially decreasing CO<sub>2</sub> uptake for other solutions.<sup>12, 26-32</sup> Finally, the synthesis of ionic liquids can be difficult and costly compared to other technologies, and often require high energetic costs to purify them.<sup>12, 26-32</sup>

### 1.2.3 - Other Liquids

Though technically a broad category in itself, “other liquids” really only features four main sorbent liquids: amino acid salt solutions,<sup>33-35</sup> imines,<sup>36</sup> hydroxides<sup>37-39</sup> and amine-ionic liquid blends.<sup>40</sup> Amino acid salt solutions,<sup>33-35</sup> imines<sup>36</sup> and amine-ionic liquid blends<sup>40</sup> functionally absorb CO<sub>2</sub> via similar, if not identical mechanisms as amines<sup>15-17</sup>, amine blends<sup>23-25</sup> (discussed section 1.2.1) and hydroxides<sup>37-39</sup> (discussed here). Hence, their specific mechanisms will not be explored here.

Hydroxides are generally used in aqueous solutions and absorb CO<sub>2</sub> via a direct reaction to form carbonates (Figure 9),<sup>37-39</sup> a mechanism that also applies to non-aqueous, non-liquid and non-hydroxide -OH groups found in other sorbent materials such as functionalised polymers, alcohols and glycols.<sup>37-39</sup>



*Figure 9 – Examples of reactions of CO<sub>2</sub> with aqueous sodium hydroxide, calcium hydroxide and a generic molecule containing a -OH group.*

Several aqueous hydroxides have been suggested for CO<sub>2</sub> capture purposes due to their high affinity for CO<sub>2</sub>.<sup>37-39</sup> Despite this, commercially proposed and used aqueous hydroxides such as calcium hydroxide, potassium hydroxide and sodium hydroxide are highly unviable, as their high affinity for CO<sub>2</sub> also requires significant upfront energetic costs to regenerate, making them difficult to recycle efficiently.<sup>12, 37-39</sup> Combined with factors such as the low solubility of calcium hydroxide and the higher cost of potassium hydroxide, aqueous hydroxides thus quickly become unattractive options for CO<sub>2</sub> capture applications.<sup>12, 37-39</sup>

Amino acid salt solutions are a relatively new technology, capable of useful CO<sub>2</sub> uptakes.<sup>33-35</sup> However, there are constraints on which amino acid salts can successfully be used, as some precipitate solid products upon reaction with CO<sub>2</sub>, while others can only absorb CO<sub>2</sub> at high pressures.<sup>33-35</sup> As with aqueous amines these amino acid salt solutions also suffer from water related recyclability and thermal degradation issues.<sup>33-35</sup> It is worth mentioning that theoretically any amino acid salt can absorb CO<sub>2</sub> so long as it possesses an amino group,<sup>33-35</sup> and when paired with the correct counterion (rather than K<sup>+</sup> or Na<sup>+</sup>), could exist as an ionic liquid at room temperature and thus overcome the thermal degradation issues, which is what inspired the exploration of [Bet][Tau] in this thesis.<sup>41</sup>

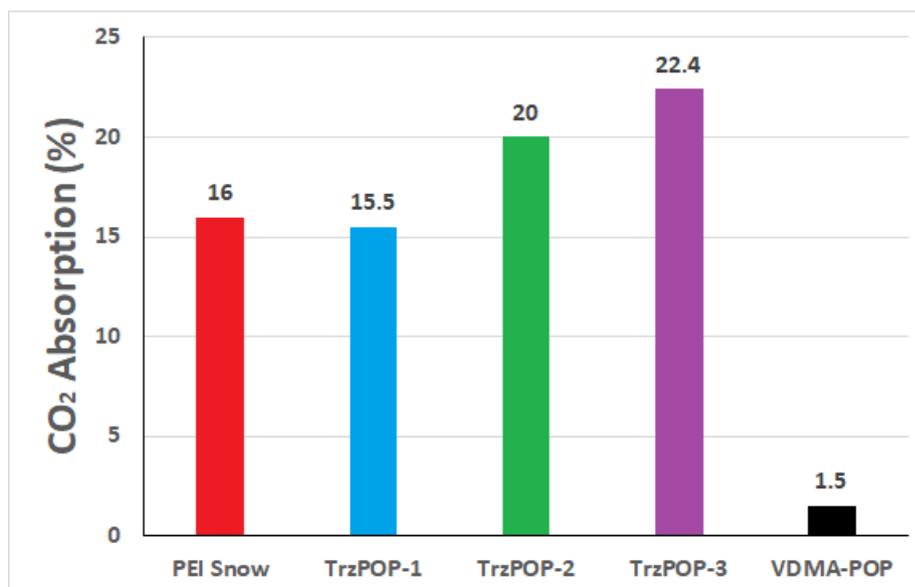
The most widely used example of an imine for CO<sub>2</sub> capture is polyethyleneimine (PEI).<sup>36</sup> However, as a highly viscous fluid, this means PEI is practically unusable as a liquid, only achieving meaningful CO<sub>2</sub> capture when combined with swellable materials (discussed section 1.4.3).<sup>36</sup> Besides this, imines predominantly exist as components for other sorbents such as ionic liquids, rather than being standard solvents, or as a component for other solid sorbents (discussed section 1.3.1).

Finally, amine-ionic liquid blends seek to achieve similar results to amine blends, with the stability of the ionic liquid compensating for the amine volatility, and the amine reactivity bolstering the ionic liquids CO<sub>2</sub> uptake capabilities.<sup>40</sup> Despite this, amine-ionic liquid blends often display the same drawbacks as both amines and ionic liquids, being viscosity, water and recyclability related issues.<sup>40</sup>

### 1.3 – Solid Sorbents

#### 1.3.1 – Porous Organic Polymers (POPs)

As implied by the name Porous Organic Polymers (POPs) refers to porous materials that are made from a polymer or polymerisation process, and are often, if not always, crosslinked.<sup>42-48</sup> These are an attractive option for CO<sub>2</sub> capture applications, as they are often very effective and highly tailorable, meaning their structure and composition can be fine-tuned with relative ease.<sup>12, 42-48</sup> As solid materials POPs offer two methods of CO<sub>2</sub> absorption, physical and/or chemical.<sup>12, 42-48</sup> Chemical absorption usually relies on the same mechanisms as the liquid sorbents mentioned above, whereas physical absorption relies on the trapping of CO<sub>2</sub> within the porous 3D network of the material.<sup>12, 42-48</sup> In general, chemical absorption leads to higher CO<sub>2</sub> absorption capabilities, while the physical absorption leads to increased recyclability.<sup>12, 42-48</sup>



*Figure 10 - CO<sub>2</sub> Absorption (%) comparison of various POPs.<sup>42-48</sup>*

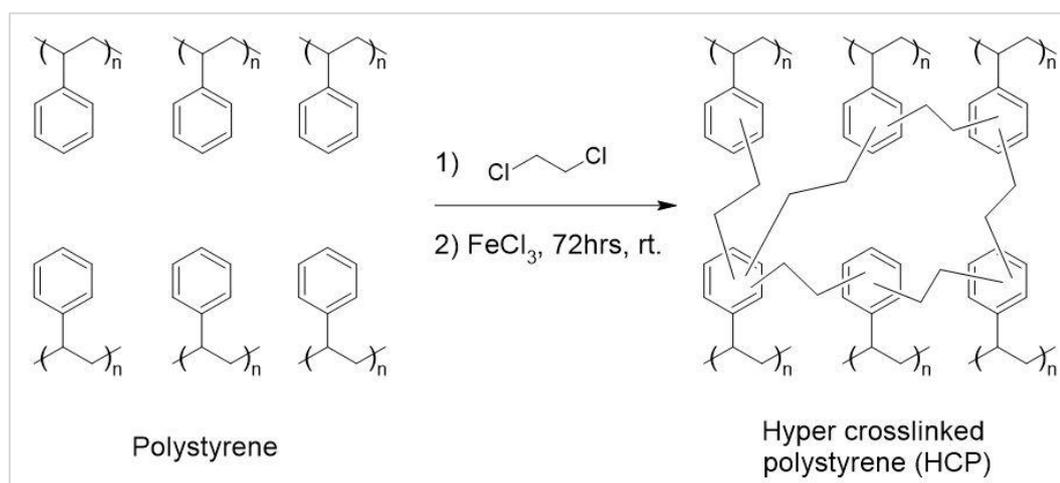
POPs cover a wide number of materials, of which a few will be discussed here for comparison, with their CO<sub>2</sub> uptakes summarised in Figure 10.<sup>42-48</sup> In their recent works Xu and co-workers have developed “PEI snow”, a crosslinked PEI based powder capable of CO<sub>2</sub> uptake up to 16 wt %.<sup>46-48</sup> Das and co-workers have also developed triazine based POPs called TrzPOPs(1/2/3), which display CO<sub>2</sub> uptakes of 15.5, 20 and 22.4 wt % for TrzPOP 1, 2 and 3 respectively.<sup>43</sup> Finally, Barkakaty and co-workers developed a VDMA based POP via functionalisation of the VDMA, achieving a CO<sub>2</sub> uptake of 1.5 wt %.<sup>42</sup> It should be noted, however, that all of the aforementioned POPs achieved these CO<sub>2</sub> uptakes under 100 vol % CO<sub>2</sub> streams, and thus would display lower CO<sub>2</sub> uptakes in DAC or flue gas capture scenarios.<sup>42-48</sup>

As with most materials that will be discussed in this section, the main drawbacks of POPs include long term stability, stability under humid conditions and recyclability issues.<sup>12, 44, 45</sup> Furthermore, POPs are seldom studied under DAC conditions, where they may display significantly lower CO<sub>2</sub> uptakes.<sup>12, 44, 45</sup> This is best demonstrated by the PEI snow mentioned above, which displayed a CO<sub>2</sub> uptake of only 5 wt % under DAC conditions.<sup>46</sup>

### 1.3.2 – Hyper-Crosslinked Polystyrene (HCP)

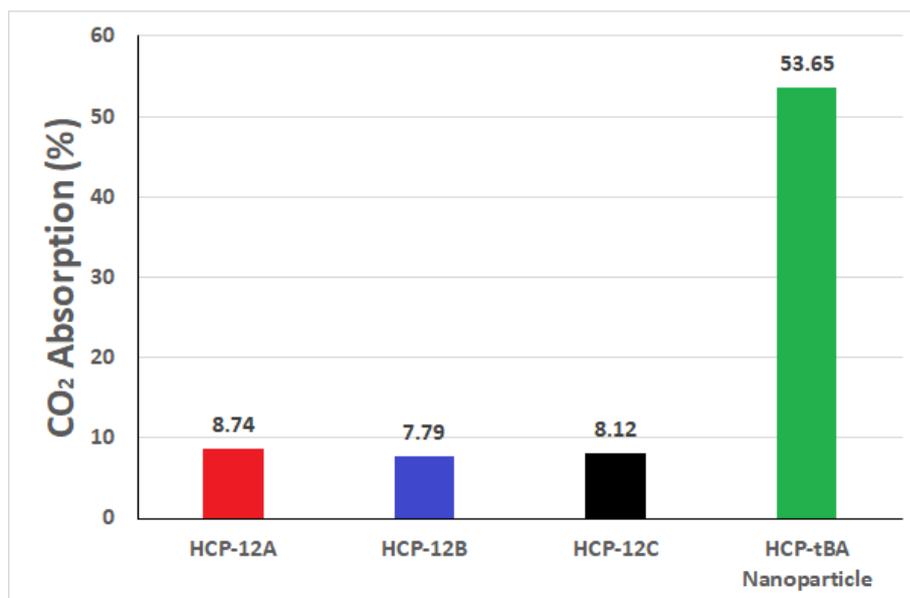
Though technically also a POP, hyper-crosslinked polystyrene (HCP) will be discussed here in specific detail as it is essentially the main focus of this thesis. First synthesised by Davankov in the 1970’s,<sup>49</sup> HCP has recently become a highly

attractive option for CO<sub>2</sub> capture applications due to its large internal surface area, relatively simple synthesis, good CO<sub>2</sub> capture ability and the ability to synthesise it from waste expanded polystyrene (WEPS), driving down cost of synthesis dramatically.<sup>50, 51</sup> This section will focus on the synthesis of HCP and its CO<sub>2</sub> capture capabilities by itself,<sup>50, 51</sup> but it should be noted that HCP can be swollen by other CO<sub>2</sub> absorbing materials (discussed in sections 1.4.2 and 1.5).



*Figure 11 - Synthesis of hyper crosslinked polystyrene as performed in this thesis.*

HCP was first synthesised from a variety of reactants, with a range of crosslinkers via a simple Friedel Crafts reaction.<sup>49</sup> This methodology has since been adapted by Fu and co-workers in order to synthesise HCP from waste expanded polystyrene (WEPS), and was also adapted further in this thesis (Figure 11).<sup>50, 51</sup> In these syntheses the polystyrene is dissolved in the crosslinker, primarily dichloroethane (though others have been used by Fu and co-workers<sup>51</sup>), to which the Lewis Acid catalyst is added, allowing electrophilic aromatic substitution to occur in order to produce HCP.<sup>50, 51</sup> The methods used by Fu and co-workers produced HCPs named HCP-12A, HCP-12B and HCP-12C, where 12 represents reaction time in hours and A/B/C represent the use of 3/1/0.33 g of starting WEPS material for the reaction, which displayed CO<sub>2</sub> uptakes of up to 8.74, 7.79 and 8.12 wt % respectively, as well as acceptable recyclability and CO<sub>2</sub> selectivity.<sup>50</sup> These uptakes were achieved under a 15 vol % simulated flue gas stream at 1 atm and 0 °C, and thus it should be noted that CO<sub>2</sub> uptakes may vary at higher temperatures or CO<sub>2</sub> vol % streams.<sup>50</sup>



*Figure 12 - CO<sub>2</sub> absorption (%) comparison of various HCP's synthesised by Fu et al.,<sup>50</sup> and the HCP-p(tBA) copolymer nanoparticle synthesised by Pan et al.<sup>52</sup>*

A benefit of HCP is the ability to functionalise the materials via direct pre/post-hyper crosslinking modification or by indirect modification via copolymerisation.<sup>52, 53</sup> Liao and co-workers, for example, modified HCP post hyper crosslinking to produce an ionic HCP that could be used for CO<sub>2</sub> conversion purposes (which is indirectly a form of CO<sub>2</sub> capture), converting CO<sub>2</sub> into cyclic carbonates.<sup>53</sup> Pan and co-workers developed a copolymer modified HCP by copolymerising polystyrene (PS) and poly(t-butyl acrylate) (p(tBA)), then hyper crosslinking the polystyrene and functionally crosslinking the p(tBA) via an aminolysis reaction with *para*-phenylenediamine, producing an HCP nanoparticle with a CO<sub>2</sub> uptake of 53.65 wt %.<sup>52</sup> This extremely high CO<sub>2</sub> uptake was however achieved under a 100 vol % CO<sub>2</sub> stream at 0°C, and thus is likely significantly higher than what would be achieved at ambient temperatures or under lower CO<sub>2</sub> vol % streams.<sup>52</sup>

Irrespective of the method of modification however, modified HCPs generally have lower Brunauer–Emmett–Teller (BET) surface areas than non-modified HCPs, as modification either inhibits hyper crosslinking due to sterics (copolymerisation/pre-hyper crosslinking modification) or destroys the crosslinks as modification proceeds (post-hyper crosslinking).<sup>50, 53, 54</sup> This is best demonstrated by Liao and co-workers work wherein their modified HCPs had a maximum BET surface area of 510 m<sup>2</sup>/g as opposed to their unmodified HCP which had a BET surface area of 1153 m<sup>2</sup>/g.<sup>53</sup>

Comparatively, the HCP produced by Fu and co-workers has a BET surface area of 572.6 m<sup>2</sup>/g.<sup>50</sup>

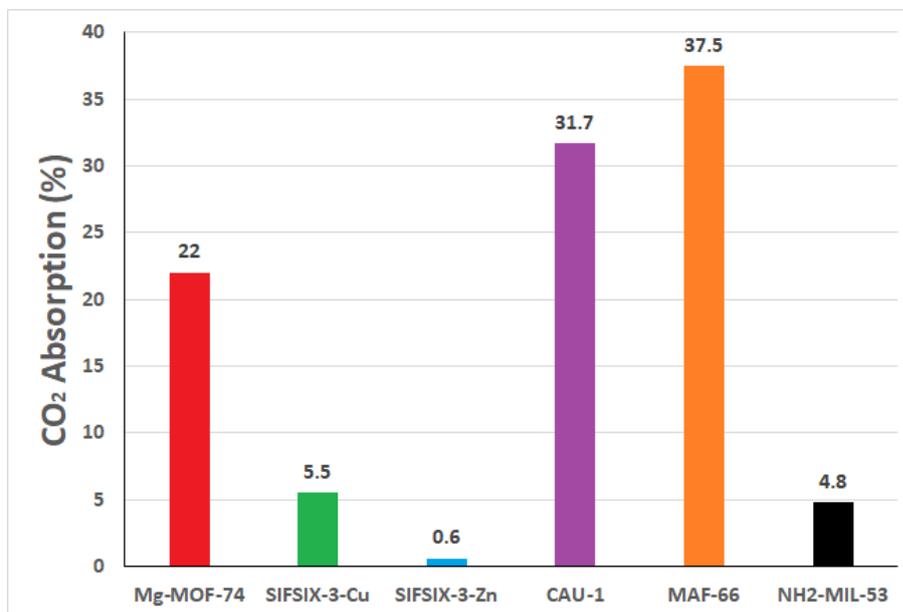
Despite the acceptable CO<sub>2</sub> uptake and recyclability, HCPs (functionalised and non-functionalised) display varying CO<sub>2</sub> selectivity depending on the degree of crosslinking, meaning that unless the required reaction conditions are met, high CO<sub>2</sub> selectivity is not guaranteed.<sup>50, 51</sup> Furthermore, most HCPs (functionalised and non-functionalised) are only capable of achieving such CO<sub>2</sub> uptakes under high pressure, dry environments.<sup>50, 51, 53</sup> Thus, consistent with other POPs, they are likely to display lower CO<sub>2</sub> uptakes and decreased recyclability under low pressure, humid conditions.<sup>50, 51, 53</sup> As discussed above, modified HCPs display less internal surface area than their unmodified counterparts, which may be undesirable, and also require more expensive/difficult syntheses to produce the modified HCPs.<sup>50-54</sup>

### 1.3.3 – Metal Organic Frameworks (MOFs)

MOFs have become another class of materials with a wide range of applications in various chemical fields thanks to their tuneability, high internal surface area and porosity.<sup>55-62</sup> For CO<sub>2</sub> capture applications their high surface area, porous structure allows for high gas flow rates to be achieved, and the tuneability of their composition and structure means they can be optimised for CO<sub>2</sub> capture with relative ease.<sup>55-62</sup> It is also due to this that MOFs have perhaps the largest variety of absorption mechanisms including physical adsorption due to swelling/contraction of pores during gas absorption, chemical/physical hybrid absorption due to exposed metal sites and gas-metal interactions, and chemical absorption via similar mechanisms to amines and hydroxides.<sup>55-62</sup>

This wide variety of absorption mechanisms and MOF compositions also results in a diverse range of CO<sub>2</sub> absorption capabilities.<sup>55-62</sup> MOFs that utilise physical adsorption such as Mg-MOF-74, for example, display often highly varying uptake values, with Mg-MOF-74 displaying a CO<sub>2</sub> uptake of 22 wt % under a 100 vol % CO<sub>2</sub> stream at ambient conditions.<sup>58</sup> Meanwhile, under ambient conditions and a 400ppm CO<sub>2</sub>/N<sub>2</sub> stream, SIFSIX-3-Cu and SIFSIX-3-Zn display uptakes of 5.5 and 0.6 wt % respectively,<sup>59,60</sup> demonstrating how simply changing the metal within the same MOF structure can affect CO<sub>2</sub> capture.<sup>59,60</sup> This is similarly the case with chemisorbing, amine functionalised MOFs such as CAU-1, MAF-66 and NH<sub>2</sub>-MIL-

53 which display uptakes of 31.7, 37.5 and 4.8 wt % respectively under 100 vol% CO<sub>2</sub> streams at 0°C and 1 atm of pressure.<sup>57,61,62</sup>



*Figure 13 - CO<sub>2</sub> absorption (%) comparison of various MOFs.*<sup>55-62</sup>

Unfortunately, MOFs reported in the literature face considerable drawbacks with many properties yet to be tested.<sup>12</sup> Firstly, MOFs are often tested for 100 vol % CO<sub>2</sub> gas capture or simulated flue gas/DAC conditions (wherein only CO<sub>2</sub> and N<sub>2</sub> are present in the gas stream), meaning their performance under actual DAC or flue gas conditions is unknown.<sup>12, 55-62</sup> This is especially concerning given that most MOFs face selectivity issues, often preferentially absorbing other gasses and water over CO<sub>2</sub>.<sup>12</sup> Secondly, relative to other technologies, their syntheses are difficult and costly to perform on a large scale (especially for functionalised MOFs). And finally, MOFs are renowned for their water related issues such as the preferential absorption of water over CO<sub>2</sub> and degradation under humid conditions, leading to decreases in absorption capacity and recyclability.<sup>12, 55-62</sup>

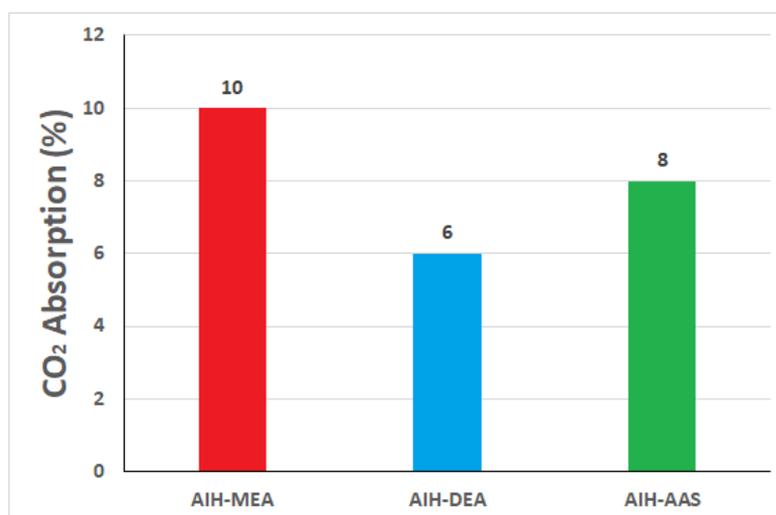
## 1.4 – Swollen Sorbents

### 1.4.1 – Amine Infused Hydrogels (AIHs)

Amine Infused Hydrogels (AIHs) are a specific type of swollen sorbent developed by Xu and co-workers wherein a poly(acrylamide-co-acrylic acid) hydrogel was swollen with 30 wt % aqueous MEA or DEA.<sup>63-65</sup> This was done in excess, with an amine to hydrogel ratio of five, to overcome acid-base neutralisation of the amines

caused by the acrylic acid component.<sup>63-65</sup> In doing so this increased the gas to sorbent contact surface area afforded to the amine, increasing the rate of CO<sub>2</sub> uptake without affecting recyclability.<sup>63-65</sup> This did however come at the cost of a slight decrease in CO<sub>2</sub> uptake compared to the non-AIH aqueous amines, with AIH-MEA and AIH-DEA achieving uptakes of 10 and 6 wt % under a 100 vol % CO<sub>2</sub> stream respectively.<sup>63</sup>

This concept was further expanded to 30 wt % aqueous amino acid salt (AAS) solutions,<sup>35</sup> specifically potassium sarcosinate (SarK), potassium lysinate (LysK) and potassium 2-methylalaninate (MetK) and their sodium-amino acid counterparts (these won't be discussed as they displayed worse CO<sub>2</sub> uptakes than the potassium-based materials).<sup>35</sup> These systems achieved uptakes ranging from 7-8 wt % (exact measurements are not stated in the paper and can only be approximated from graphs), with sarcosinate systems displaying slightly higher uptakes as stated in the paper.<sup>35</sup> Again this was performed under a 100 vol % CO<sub>2</sub> stream.<sup>35</sup>



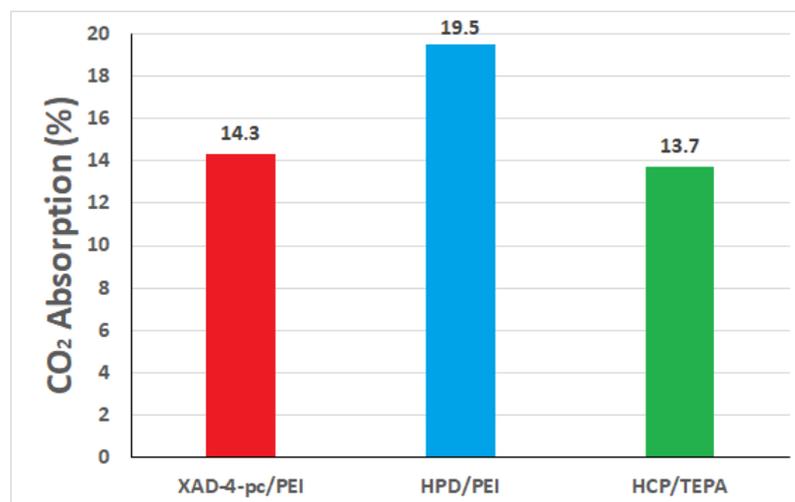
*Figure 14 - CO<sub>2</sub> absorption (%) comparison of various AIH systems.*<sup>35, 63</sup>

As stated above the aqueous amine based AIHs displayed worse CO<sub>2</sub> uptakes than the solutions upon which they are based, and unfortunately do not solve the water related recyclability nor the amine degradation related issues featured in aqueous amines.<sup>63-65</sup> Though they do not suffer degradation related drawbacks, amino acid salt based AIHs similarly suffer from water related recyclability issues.<sup>35</sup> As found in the earlier work, the hydrogels can also degrade over time, decreasing uptake and recyclability beyond that point, but this usually takes many cycles for aqueous

AIHs.<sup>14</sup> Furthermore, it is likely the case that these AIHs would display worse CO<sub>2</sub> uptakes under flue gas or DAC conditions. These issues (except hydrogel degradation) were solved by moving to non-aqueous solutions and is discussed in Section 1.5.<sup>14, 66</sup>

#### 1.4.2 – Sorbents Swollen into HCP

In recent works HCP has been swollen with various CO<sub>2</sub> absorbing liquids such as tetraethylenepentamine (TEPA),<sup>67</sup> PEI<sup>68, 69</sup> and 100 wt % amines<sup>14</sup> (discussed section 1.5). Usually, these liquids cannot be utilised by themselves due to issues with viscosity, but the large internal surface area of HCP grants these liquids a higher gas to sorbent contact area as they occupy this surface area, effectively rendering viscosity issues moot.<sup>67-69</sup> This is demonstrated in two separate studies by Liu et al.<sup>69</sup> and Bai et al.<sup>68</sup> wherein HCP/PEI systems named XAD-4-pc/PEI and HPD/PEI were able to achieve CO<sub>2</sub> uptakes of 14.3 and 19.5 wt % respectively.<sup>68, 69</sup> Liu and co-workers also demonstrate this in another work wherein HCP/TEPA systems were capable of CO<sub>2</sub> uptakes of 13.7 wt %.<sup>67</sup> Furthermore, all of these systems displayed good recyclability over many regeneration cycles.<sup>67-69</sup> All of these uptakes were achieved under 100 vol % CO<sub>2</sub> streams and thus are likely higher than would be expected of lower CO<sub>2</sub> vol % streams.<sup>67-69</sup>



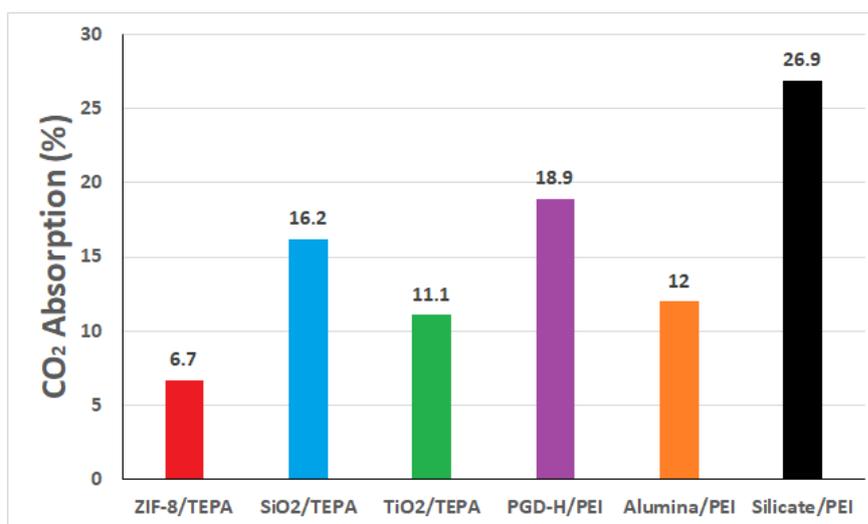
*Figure 15 - CO<sub>2</sub> absorption (%) comparison of various sorbent swollen HCP systems.<sup>67-69</sup>*

As with the majority of absorbents discussed so far, swollen HCP sorbents generally display the same drawbacks as either HCP or the sorbent liquid.<sup>67-69</sup> Namely, CO<sub>2</sub>

capture can usually only occur at high pressures, and that long term recyclability in humid conditions is often an issue due to water related degradation or absorption.<sup>67-69</sup>

### 1.4.3 – Other Swollen Sorbents

Similar to “other liquids”, “other swollen sorbents” is a very broad category given that any form of porous solid structure can technically be swollen by any liquid sorbent mentioned thus far.<sup>70-75</sup> TEPA based examples include TEPA swollen into MOF ZIF-8,<sup>71</sup> SiO<sub>2</sub> nanowires<sup>72</sup> and mesoporous TiO<sub>2</sub>,<sup>73</sup> displaying CO<sub>2</sub> uptakes of 6.7, 16.2 and 11.1 wt % respectively,<sup>71-73</sup> which were achieved under simulated flue gas (ZIF-8 and TiO<sub>2</sub>)<sup>71,73</sup> and 100 vol % CO<sub>2</sub> streams (SiO<sub>2</sub>)<sup>72</sup>. PEI based examples include PEI swollen into MOF PGD-H,<sup>75</sup> mesoporous alumina<sup>70</sup> and layered silicate<sup>74</sup> displaying CO<sub>2</sub> uptakes of 18.9, 12 and 26.9 wt % respectively under 100 vol % CO<sub>2</sub> streams.<sup>70, 74, 75</sup> Regardless, similar to swollen HCP systems, issues with high pressure restricted uptake and long-term stability issues are also issues for these swollen sorbents.<sup>70-75</sup>

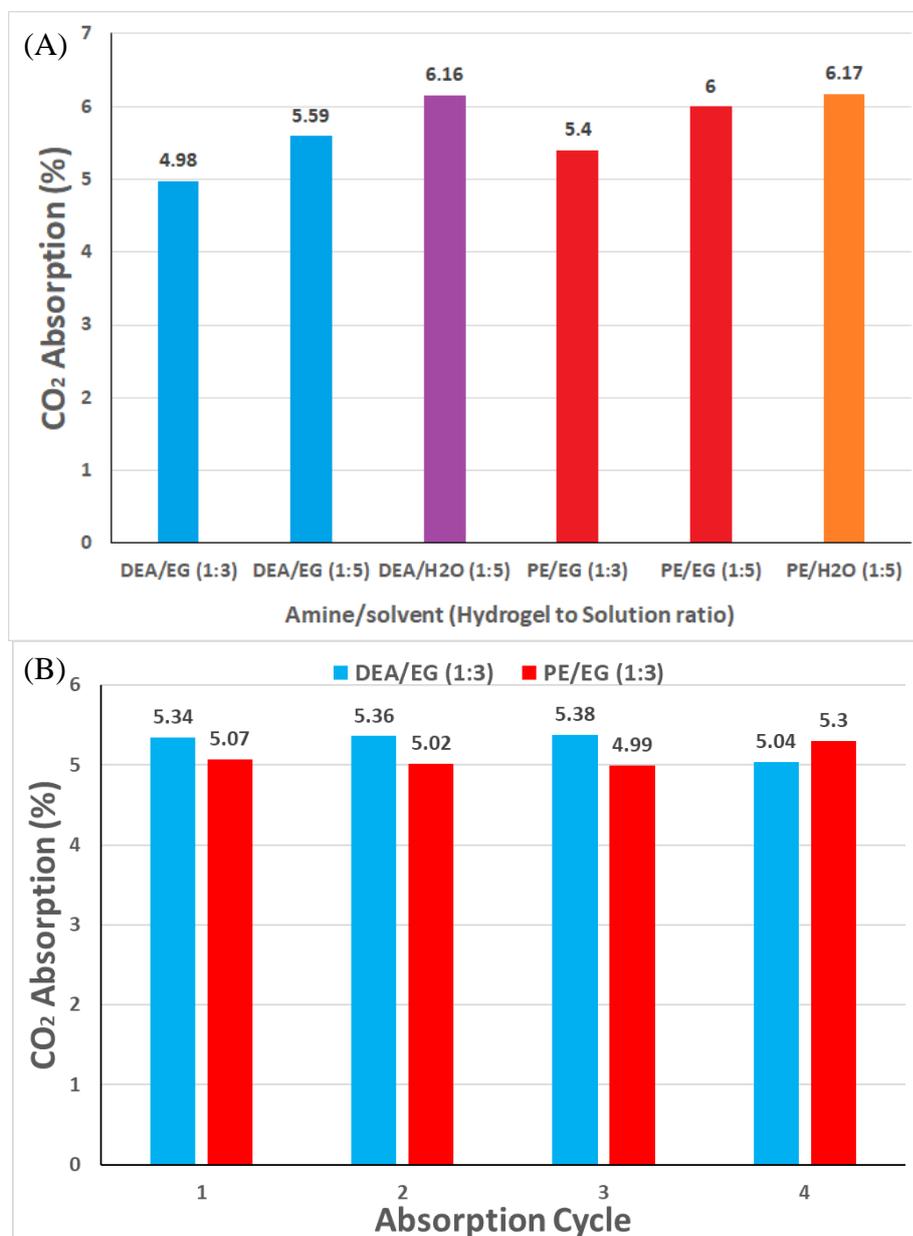


*Figure 16 - CO<sub>2</sub> absorption (%) comparison of various other swollen TEPA/PEI systems.<sup>70-75</sup>*

### 1.5 – Earlier Work

The earlier work component of this thesis (abbreviated to EW in some figures) was mainly focused on improving the AIH work done by Xu and co-workers.<sup>35, 63-65</sup> This was primarily achieved by increasing the recyclability and CO<sub>2</sub> capture capabilities of the AIH systems by moving from aqueous solutions of amines to non-aqueous solutions and swelling them into various polymeric materials to increase gas-sorbent

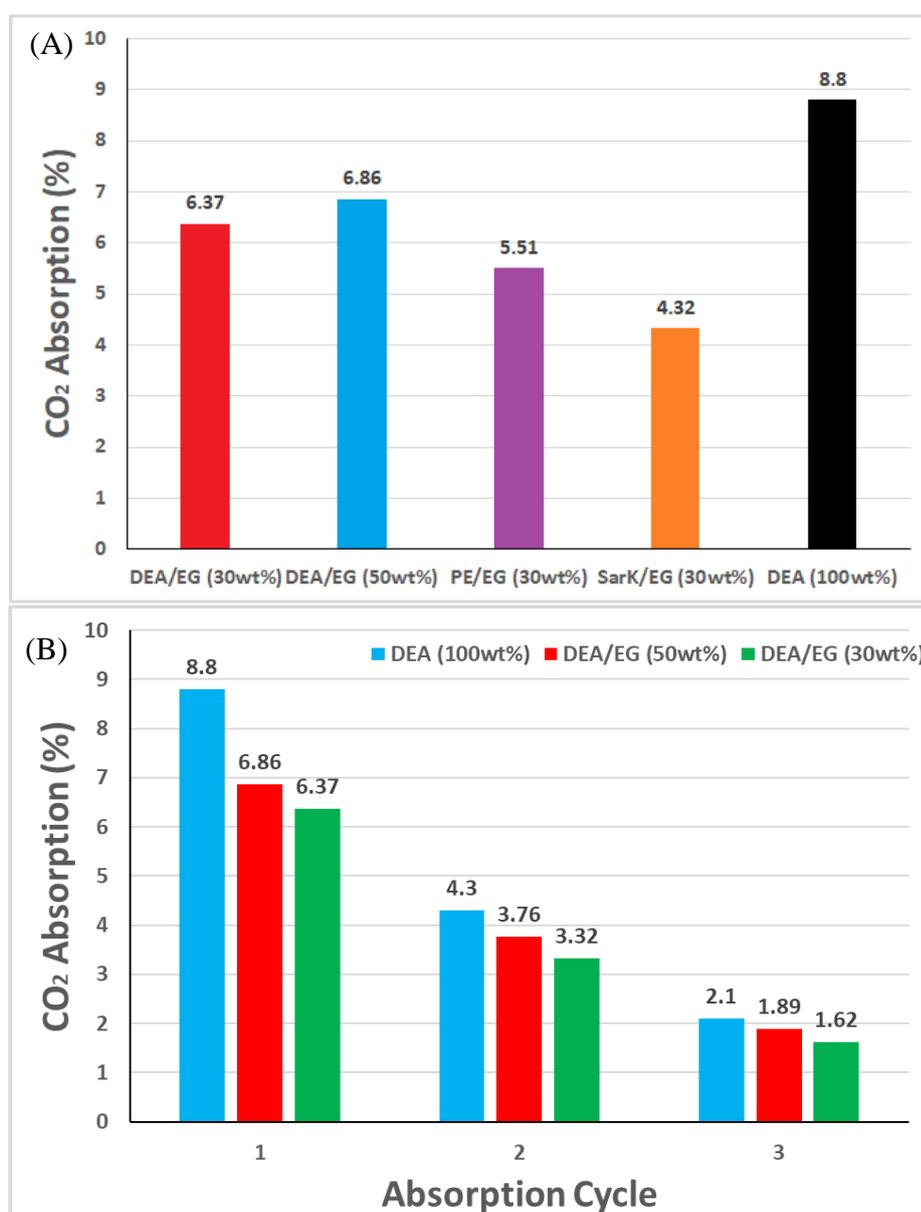
contact surface area.<sup>14, 66</sup> Eventually it was found that, with certain materials, 100 wt % amines could be used without need for a solvent, leading to drastic improvements in CO<sub>2</sub> uptake and/or recyclability (depending on the material being swelled).<sup>14, 66</sup>



**Figure 17** – (A) CO<sub>2</sub> absorption (%) of various 30 wt % amine in ethylene glycol hydrogel systems at different (hydrogel to sorbent) ratios. (B) Recyclability of the DEA/EG (1:3) and PE/EG (1:3) hydrogel systems.<sup>14</sup>

Experiments initially employed the poly(acrylamide-*co*-acrylic acid) hydrogel used by Xu and co-workers,<sup>63-65</sup> but using DEA and 2-piperidine ethanol (PE) in ethylene glycol (EG) solutions instead of the aqueous MEA/DEA solutions to swell the hydrogel.<sup>14, 66</sup> These experiments were also conducted at 1:3 and 1:5 hydrogel to

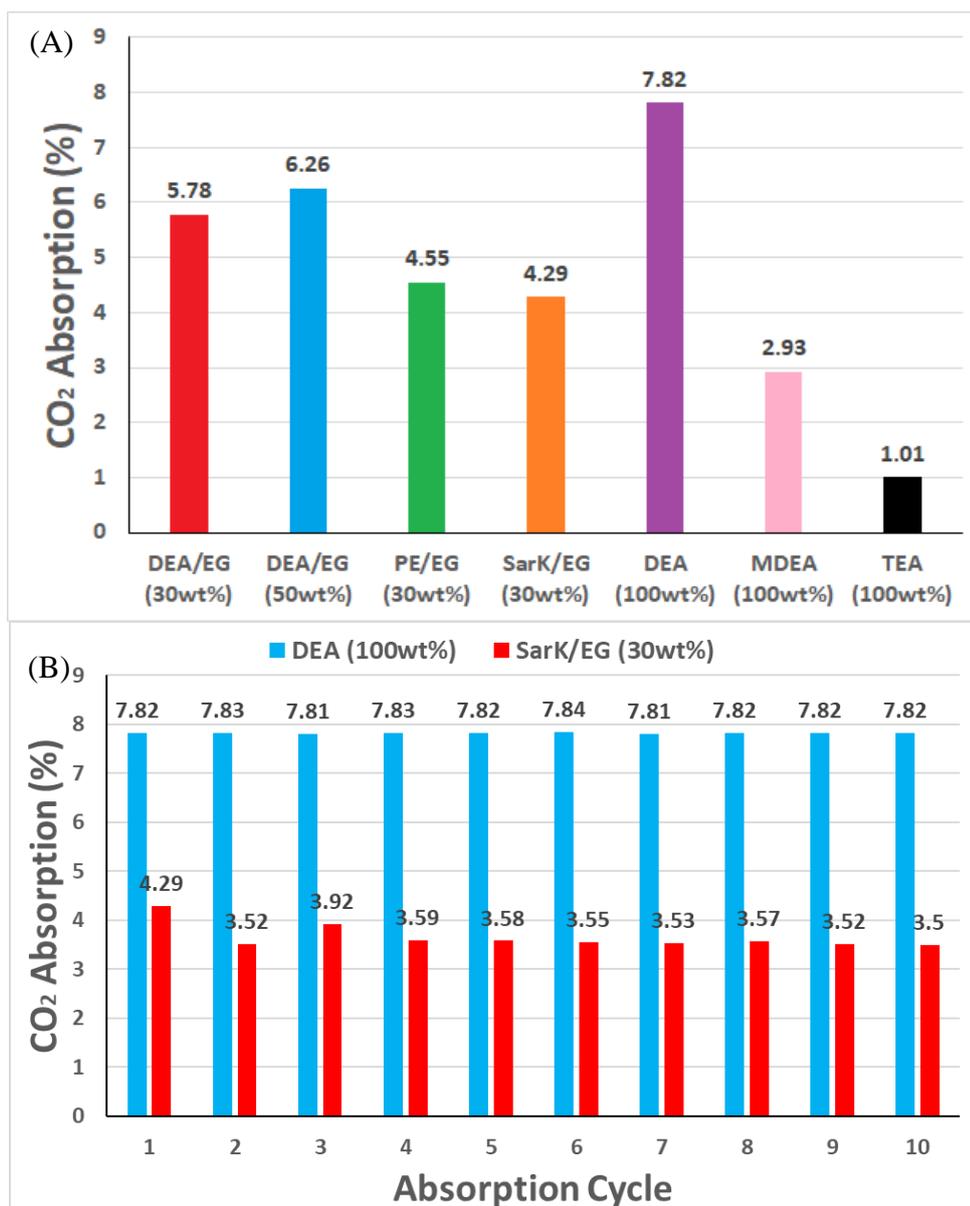
EG/amine solution ratios, an excess which again overcame acid-base neutralisation caused by interactions between the amine and co-acrylic acid components.<sup>14</sup> Though this resulted in improved recyclability (Figure 17B), a slight decrease in CO<sub>2</sub> capture capabilities compared to the aqueous AIH counterparts occurred (Figure 17A).<sup>14</sup> This was overcome by swelling sorbent liquids into a synthesised crosslinked polyacrylamide (PAM) material of greater surface area instead, increasing CO<sub>2</sub> capture capabilities (Figure 18A) and allowing for a larger variety of amines/amine solutions, solvents and amino acid salts to be used, but this came at the cost of recyclability (Figure 18B).<sup>14, 66</sup>



*Figure 18 - (A) CO<sub>2</sub> absorption (%) of various sorbent systems swollen into PAM.*

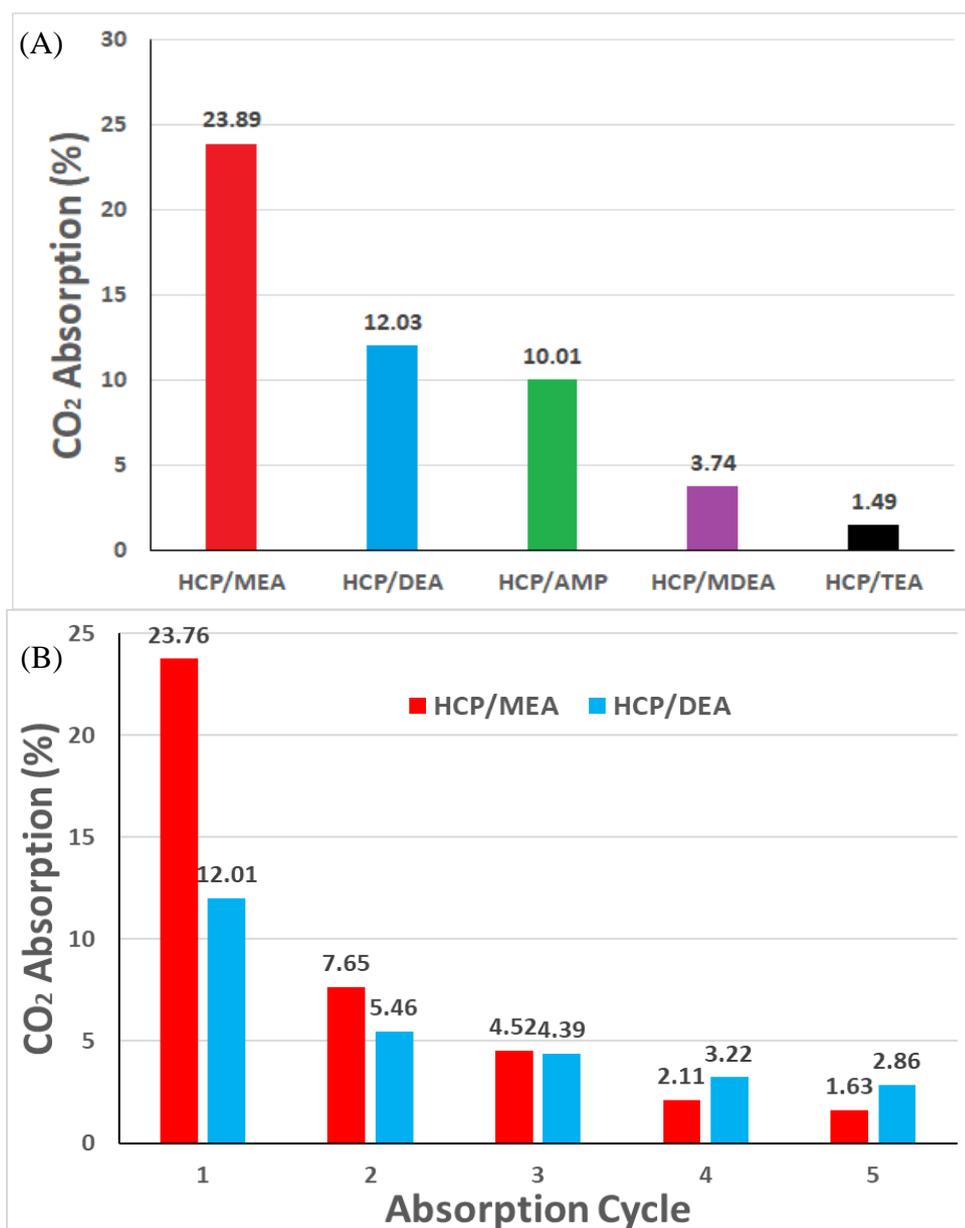
*(B) Recyclability of DEA sorbent systems swollen into PAM.<sup>14, 66</sup>*

Given the recyclability issues with PAM systems, a poly(*N*-2-hydroxyethyl) acrylamide (PHEAA) material was swollen with sorbent liquids instead, resulting in slightly decreased CO<sub>2</sub> uptakes compared to the PAM (Figure 19A), but greatly increased recyclability for the 100 wt % DEA and 30 wt % SarK (an amino acid salt) systems over 10 regeneration cycles (Figure 19B).<sup>14, 35, 66</sup> At this point tertiary amines also became viable, though they displayed reduced CO<sub>2</sub> uptakes compared to the primary/secondary amines and amino acid salt solutions (Figure 19A).<sup>14</sup>



**Figure 19** - (A) CO<sub>2</sub> absorption (%) comparison of various sorbent systems swollen into PHEAA. (B) Recyclability of the DEA (100wt%) and SarK/EG (30wt%) swollen PHEAA.<sup>14, 35, 66</sup>

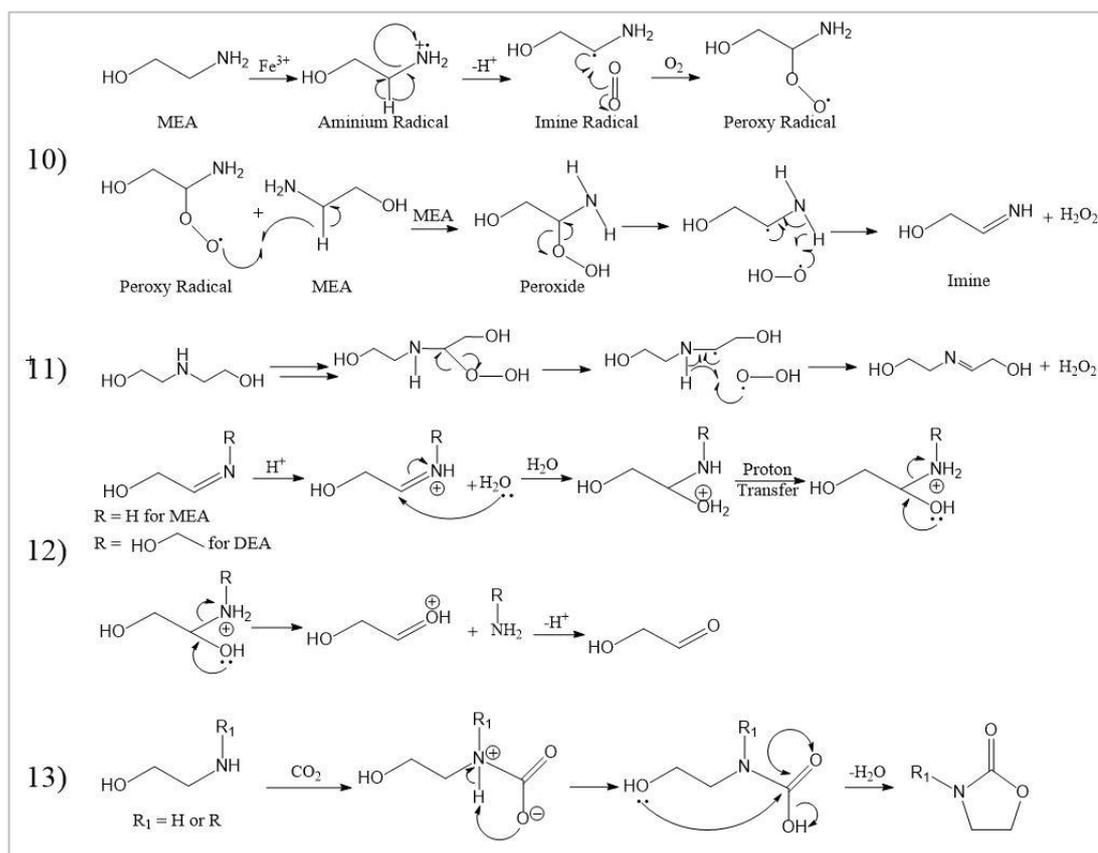
Finally, HCP was swollen with various 100 wt % amines, resulting in the best CO<sub>2</sub> capture results, even under direct air capture conditions (Figure 20A).<sup>14</sup> This is presumed to be because of the considerably higher internal surface area of the HCP compared to the other materials, granting the amines drastically higher gas to sorbent contact areas, thus increasing uptake.<sup>14</sup> Unfortunately, this came at the cost of recyclability (Figure 20B), due to degradation of the amines (discussed below).<sup>14</sup>



*Figure 20 - (A) CO<sub>2</sub> absorption (%) comparison of various 100 wt % amines swollen into HCP. (B) Recyclability of the HCP/MEA and HCP/DEA systems.<sup>14</sup>*

Ordinarily amines such as MEA and DEA cannot be used in 100 wt % solutions due to their high viscosity, resulting from hydrogen bonding via the -OH groups present

in ethanolamines and  $\text{-NH}_2$  or  $\text{-NH}$  groups present in all amines, which heavily impacts  $\text{CO}_2$  migration through the liquid, decreasing absorption.<sup>14, 66</sup> This is overcome when swelling the amine into a high internal surface area material as the amine is granted a greater surface area to spread over, effectively increasing the gas to sorbent contact area of the amine, increasing uptake and uptake kinetics.<sup>14, 66</sup>



**Figure 21** – Examples of possible degradation pathways of primary/secondary ethanolamines via iron catalysed oxidation (Equations 10 and 11),<sup>76-78</sup> or  $\text{CO}_2$  (Equation 13) related degradation.<sup>79,80</sup> Also described is the degradation pathway from imines to aldehydes (Equation 12).<sup>76-80</sup>

The volatility of most primary/secondary amines also usually prevents them being used in 100 wt % solutions, due to oxidation<sup>76-78</sup> (Figure 21, equations 10 and 11) and  $\text{CO}_2$  (Figure 21, equation 13) related degradation,<sup>79, 80</sup> the former of which can be iron catalysed,<sup>76, 77</sup> hence why the amines used with HCP (due to residual iron from the synthesis) and for DAC experiments showed reduced recyclability.<sup>14</sup> Equation 12 also describes the further degradation of the degradation produced imines, which can absorb  $\text{CO}_2$ , to aldehydes, which cannot absorb  $\text{CO}_2$ .<sup>76-80</sup> It should also be noted that direct oxidation of the nitrogen in amines to form N-oxides is

possible, but not detailed in Figure 21.<sup>76-78</sup> Additionally, it must be considered that hydrogen abstraction as detailed in equations 10 and 11 can occur at the OH-CH<sub>2</sub> carbon, but is also not detailed in Figure 21.<sup>76-80</sup> In the case of the swollen PAM materials, the amines likely also degraded due to transamidation reactions.<sup>81, 82</sup> PHEAA, having no residual iron in its structure, thus displayed the greatest recyclability of the swollen materials used in the earlier work.<sup>14</sup>

### 1.6 – Aims for this Work

The primary goal of this project/thesis was to improve upon the HCP systems previously examined by either increasing CO<sub>2</sub> uptake capabilities or recyclability.<sup>14</sup> In the process from monomer to swelled HCP there are four ways HCP systems can be improved: 1) altering of the hyper crosslinking itself, 2) altering the sorbent liquid swollen into the HCP, 3) indirect functionalisation via copolymerisation prior to crosslinking, and; 4) direct functionalisation of the HCP. Of these 4 options, the former 3 were chosen as they presented more opportunities for the preparation of new materials. Thus, the aims for this thesis/project were:

- 1) Investigate how changing the crosslinkers and crosslinker ratios in a traditional Friedel Crafts synthesis of HCP affected the end product HCP, and how this in turn affected CO<sub>2</sub> uptake capabilities once swelled with DEA.
- 2) Investigate the CO<sub>2</sub> capture capabilities of novel 100 wt % amine blends of MEA, DEA, MDEA and TEA swollen into HCP, wherein 30 wt % of the blend is MEA or DEA and the remaining 70 wt % is MDEA or TEA. Theoretically the MEA/DEA should increase the absorption capacity of the tertiary amines, while the MDEA/TEA should increase the recyclability of the primary/secondary amines.<sup>23-25</sup>
- 3) Attempt to synthesise a novel HCP via an alternative hyper crosslinking mechanism found in the literature,<sup>83-89</sup> and thus investigate how the HCP and amine swelled HCP produced by this mechanism compared to HCP's synthesised by the "traditional"<sup>49-51</sup> method.
- 4) Synthesise and investigate the CO<sub>2</sub> uptake capabilities of a [betaine][taurine] ionic liquid found in literature, which had previously only been used for protein delivery applications,<sup>41</sup> but is theoretically capable of CO<sub>2</sub> capture due to the -NH<sub>2</sub> of the taurine.

5) Synthesise a RAFT prepared copolymer crosslinked nanogel by copolymerising a block copolymer of polystyrene and poly(VDMA), which could then be hyper crosslinked via the polystyrene block, and functionally cross linked by a reaction between the VDMA block and TEPA. This would then produce a novel copolymer nanogel capable theoretically capable of CO<sub>2</sub> capture, which would also be investigated.

## 2 – Materials and Analytical Methodologies

### 2.1 – Materials and Preparations

All gasses were supplied by BOC. All materials were purchased from Sigma Aldrich at their highest available purity and used without further purification, with the exceptions of the azobisisobutyronitrile (AIBN), styrene and WEPS.

The WEPS was sourced from laboratory equipment packaging, and was used without further purification.

AIBN (12 wt % in acetone) was purified by first removing the acetone, then recrystallising the crude AIBN from methanol (MeOH) twice.

Styrene was purified by passing through a basic alumina column to remove the polymerisation inhibitor.

### 2.2 – Analytical Methodologies

#### 2.2.1 – ATR-FTIR Spectroscopy

FTIR Spectroscopy was performed on the Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific) using a diamond ATR accessory. Scans were performed with a resolution of 4 cm<sup>-1</sup> over the 4000-400 cm<sup>-1</sup> range, with 64 scans per sample. Spectra were recorded and ATR corrected using the OPUS data acquisition program (Bruker). In some cases, figures in this thesis show spectra directly imported from OPUS, while others show spectra that have been processed with Excel. The diamond was cleaned with ethanol between samples, and a background collection was performed before each sample. All scans were conducted at ambient conditions.

#### 2.2.2 – <sup>1</sup>H NMR Spectroscopy

<sup>1</sup>H NMR Spectroscopy was performed using a Bruker Avance 400 spectrometer at ambient conditions, with the data processed using TopSpin 4.1.

### 2.2.3 – Size Exclusion Chromatography (SEC)

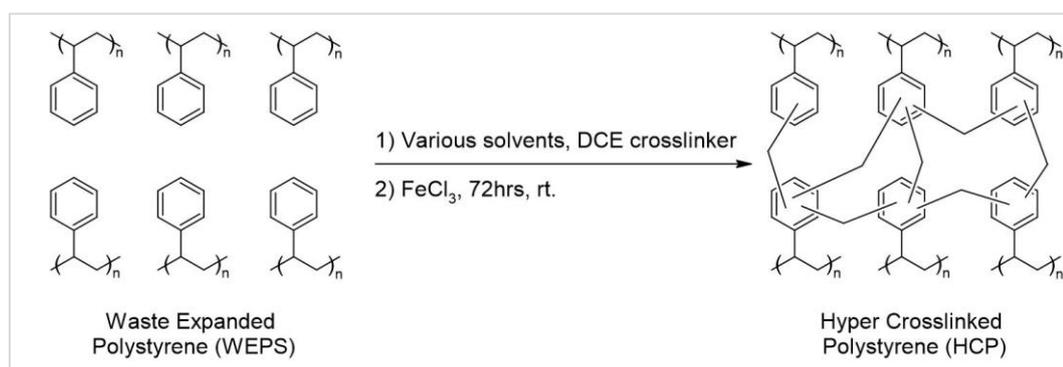
To determine the molecular weight (number average molecular weight,  $M_n$ , and weight average molecular weight,  $M_w$ ) and dispersity of the polymers synthesised in section 3.1, SEC was performed on a Shimadzu modular system equipped with Phenomenex Security Cartridge Guard (4mm x 3mm), two linear phenogel columns ( $10^3$  and  $10^4$  Å pore size), an RID-20A refractive index detector, an SPD-M20A prominence diode detector and a miniDAWN TREOS multiangle static light scattering detector. Dimethylacetamide containing 30mM LiBr was used as a solvent, with a flow rate of 1.0 ml/min at 40°C. Chromatograms were processed with Lab Solutions' SEC software.

## 3 – New Hyper Crosslinked Polystyrenes

### 3.1 – HCP from traditional Friedel Crafts Reactions

#### 3.1.1 – Solvent Selection Results and Discussion

Since HCP is traditionally synthesised using the crosslinker as the solvent,<sup>50, 51</sup> as reported in the earlier work,<sup>14</sup> to investigate the effect of different crosslinkers and amount of crosslinkers had on the HCP, this required a solvent that was not a crosslinker. As such, a suitable solvent was required to; 1) not participate in Friedel Crafts Alkylation (FCA) reaction, 2) not inhibit the FCA reaction, 3) be capable of dissolving one or both of the WEPS and  $FeCl_3$  and 4) have formed HCP upon completion of the reaction detailed below (Figure 22).



**Figure 22** - Synthesis of hyper crosslinked polystyrene (HCP) from waste expanded polystyrene (WEPS) using dichloroethane (DCE) as the crosslinker,  $FeCl_3$  as the Lewis Acid catalyst and various solvents to conduct the reaction in.

WEPS (1 g, 9.6 mmol based on repeating styrene units) and  $\text{FeCl}_3$  (1 g, 6.17 mmol) were combined separately with the chosen solvent (15 ml) and left overnight to dissolve. If dissolution of either the WEPS or the  $\text{FeCl}_3$  was successful, then WEPS (1 g, 9.6 mmol based on repeating styrene units) and  $\text{FeCl}_3$  (4.67 g, 28.8 mmol) was dissolved in the chosen solvent (30 ml), to which DCE (2.85 g, 28.8 mmol, except in the 50/50 wt % acetone/DCE trial) was added as a crosslinker. The reaction was sealed and left to proceed with vigorous stirring for 72 hours. Had a solid formed it was then isolated via vacuum filtration and washed with HCl (30%, 3 x 30 ml), methanol (3 x 30 ml), acetone (3 x 30 ml), methanol (3 x 30 ml) and DCM (3 x 30 ml) at which point the filtrate was clear/colourless. The solid was then left to dry overnight in a 60 °C vacuum oven. Following this the solids were submerged in 100 ml of DCM for 1 hr (this is explained below), and were subsequently dried in the vacuum oven again for further usage.

*Table 1 - Summary of results for investigating suitable solvent for HCP synthesis.*

Solvent	Dissolved WEPS?	Dissolved $\text{FeCl}_3$ ?	Description of Reaction Product.	DCM Soluble Product?	Suitable Solvent?
Acetone	Yes	Yes	White, glue-like solid.	Yes	No
Acetone/DCE (1:1)	Yes	Yes	White, glue-like solid.	Yes	No
Tetrahydrofuran	Yes	No	No product formed.	-	No
Dimethylformamide	Yes	Yes	White, glue-like solid.	Yes	No
Acetonitrile	Yes	Yes	White, glue-like solid.	Yes	No
Methanol	Yes	No	No product formed.	-	No
Ethanol	No	No	-	-	No
Pentane	No	No	-	-	No
Octane	No	No	-	-	No
Decane	No	No	-	-	No
Dodecane	No	No	-	-	No
Pet. Spirits	Yes	No	No product formed.	-	No
Cyclohexane	Yes	Yes	Brown, powdery solid.	No	Yes

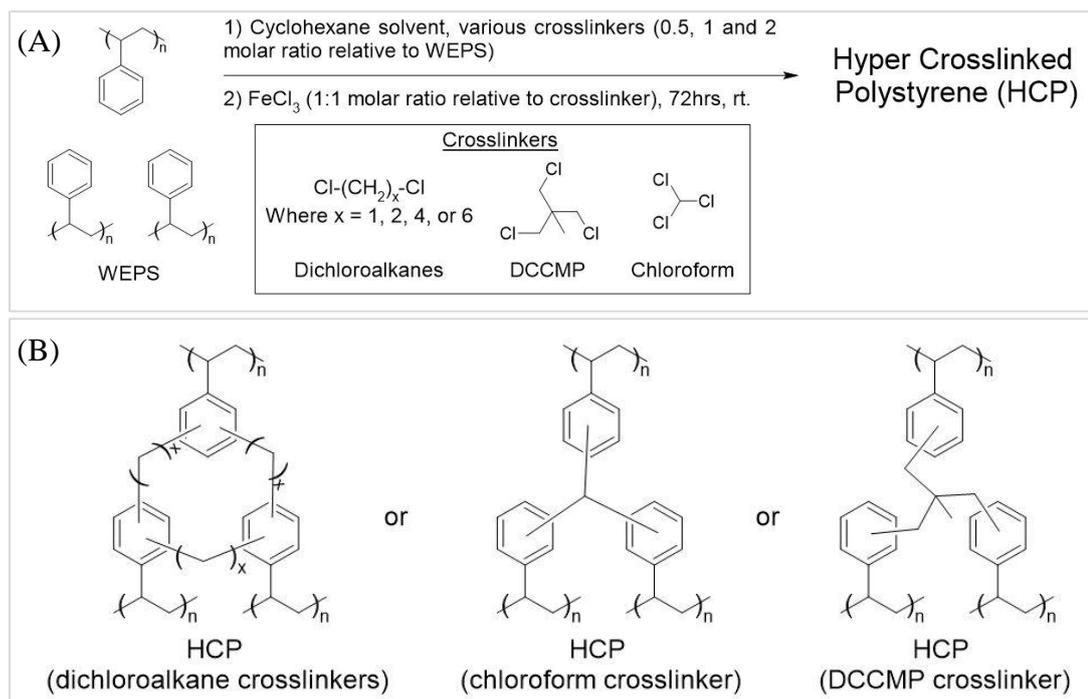
As seen in Table 2, several solvents, namely ethanol, pentane, octane, decane and dodecane were deemed unsuitable for the synthesis of HCP due to the fact they were incapable of dissolving the WEPS or  $\text{FeCl}_3$ . Despite THF, acetone (neat and 1:1 with DCE), methanol, acetonitrile and dimethylformamide being capable of dissolving one or both reactants, all of these solvents were deemed unsuitable as they either produced no product, or a product that was not HCP (discussed below). This is likely because these solvents are a mixture of bases and Lewis bases, thus inhibiting the FCA reaction from proceeding by effectively neutralising the  $\text{FeCl}_3$  catalyst. It is unclear as to why the petroleum spirits were unable to facilitate the reaction, but this

result in particular suggests that it is necessary to have a homogenous reaction in which both the WEPS *and* the FeCl<sub>3</sub> must be dissolved.

Several solvents, namely acetone, 50% acetone / 50% DCE, *N,N*-dimethylformamide and acetonitrile formed solids after the syntheses were completed. However, given that HCP, regardless of the synthesis methodology, is a brown, powdery solid<sup>50,51</sup> an additional experiment was conducted in which the solids formed were submerged in DCM (100 ml). In all of these cases the solid dissolved, indicating the solid was unreacted polystyrene rather than HCP. It is unclear why the unreacted polystyrene was only present after allowing the reactions to proceed for 72 hours, but it is evident that in all of these cases the FCA reaction failed to proceed due to the solvents neutralising the FeCl<sub>3</sub> catalyst, as discussed above. In contrast to this, the cyclohexane trial formed the expected brown, powdery solid<sup>50,51</sup> which was insoluble in DCM, indicating successful HCP synthesis, thus cyclohexane was deemed a suitable solvent. Interestingly many of these results disagree with the suggested solvents from the literature, though the reason for this is unknown.<sup>90</sup>

### 3.1.2 – HCP Synthesis Results and Discussion

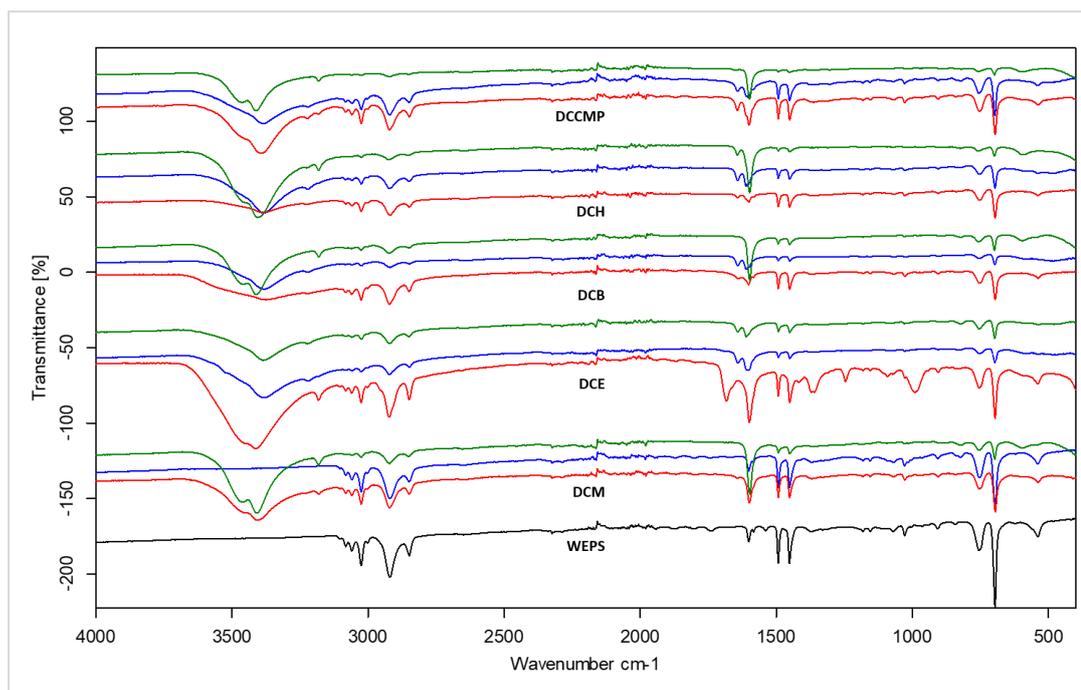
In contrast to the earlier work where we prepared HCP with very high crosslinking densities,<sup>14</sup> for the first part of this study we decided to examine much lower ratios of WEPS/haloalkanes in an effort to observe potential significant differences in CO<sub>2</sub> uptake as a function of crosslinking agent structure. Thus, having identified an appropriate solvent, HCP was synthesised using varying ratios of different crosslinkers via an adapted version of the procedure used in the earlier work,<sup>14</sup> which was in turn adapted from Fu and co-workers' procedure for synthesis of HCP from WEPS.<sup>50, 51</sup> In all procedures the molar ratio of FeCl<sub>3</sub> to crosslinker was kept 1:1 i.e. if the reaction had a 1:2 WEPS to crosslinker (CL) molar ratio, it would also therefore have a 1:2 WEPS to FeCl<sub>3</sub> molar ratio. A generic procedure for this synthesis is as follows:



**Figure 23** – (A) Synthesis of HCP from WEPS using cyclohexane as a solvent and various crosslinkers (dichloro-meth/eth/but/hex-ane, chloroform and 1,3-dichloro-2-(chloromethyl)-2-methylpropane (DCCMP)) at 1:0.5, 1:1 and 1:2 WEPS to crosslinker molar ratios. (B) Possible HCP structures produced from the synthesis of HCP with various crosslinkers detailed in (A).

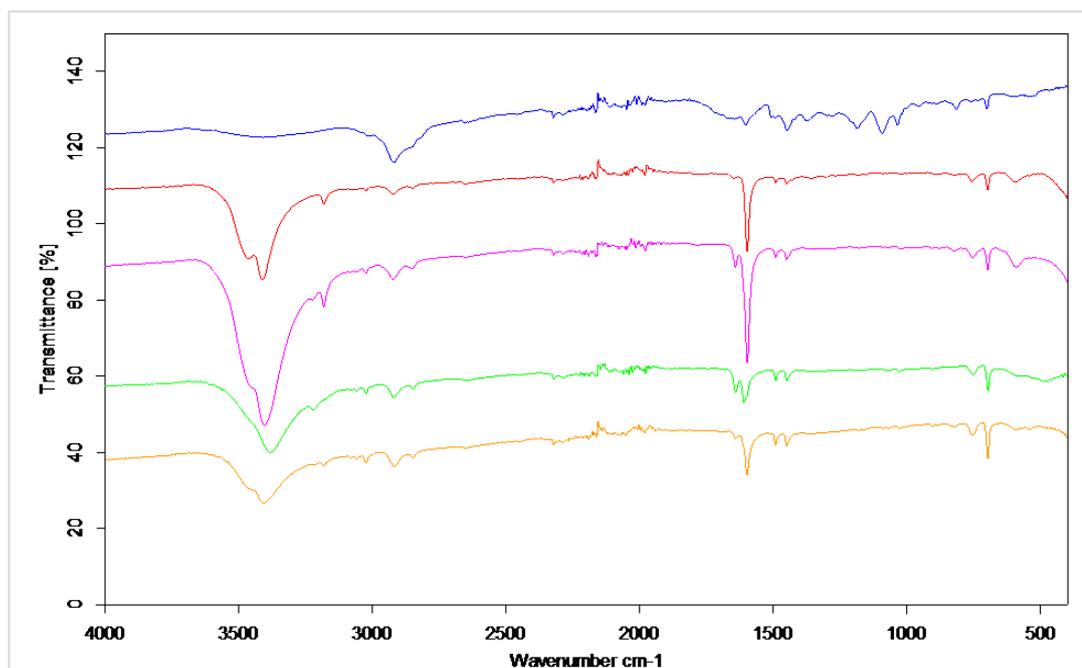
WEPS (1 g, 9.6 mmol based on repeating styrene units) was dissolved in cyclohexane (15 ml, 138.8 mmol), to which was added a solution of  $\text{FeCl}_3$  (0.5, 1 or 2 molar equivs relative to WEPS) dissolved in cyclohexane (15 ml, 138.8 mmol) and the chosen crosslinker (0.5, 1 or 2 molar equivs relative to WEPS). The reaction was then left to proceed for 3 days with vigorous stirring, after which a brown-black solid had formed. This solid was then isolated via vacuum filtration and washed with HCl (3 x 30 ml), MeOH (3 x 30 ml), acetone (3 x 30 ml), MeOH (3 x 30 ml) and DCM (3 x 30 ml) at which point the filtrate was clear/colourless. The product was then dried in a 60 °C vacuum oven overnight and ground into a powder using a pestle and mortar.

FTIR (ATR corrected,  $\text{cm}^{-1}$ ): 3000 (C-H stretching, aromatic), 2900 (C-H stretching of  $-\text{CH}_2-$  in polymer and crosslinks), 1600 (C=C, aromatic), 1500 (C=C, aromatic), 1450 (C=C, aromatic), 750 (C-H stretching, aromatic), 700 (C-H stretching, aromatic) Based on 1:2:2 DCE, shown in Figure 24).



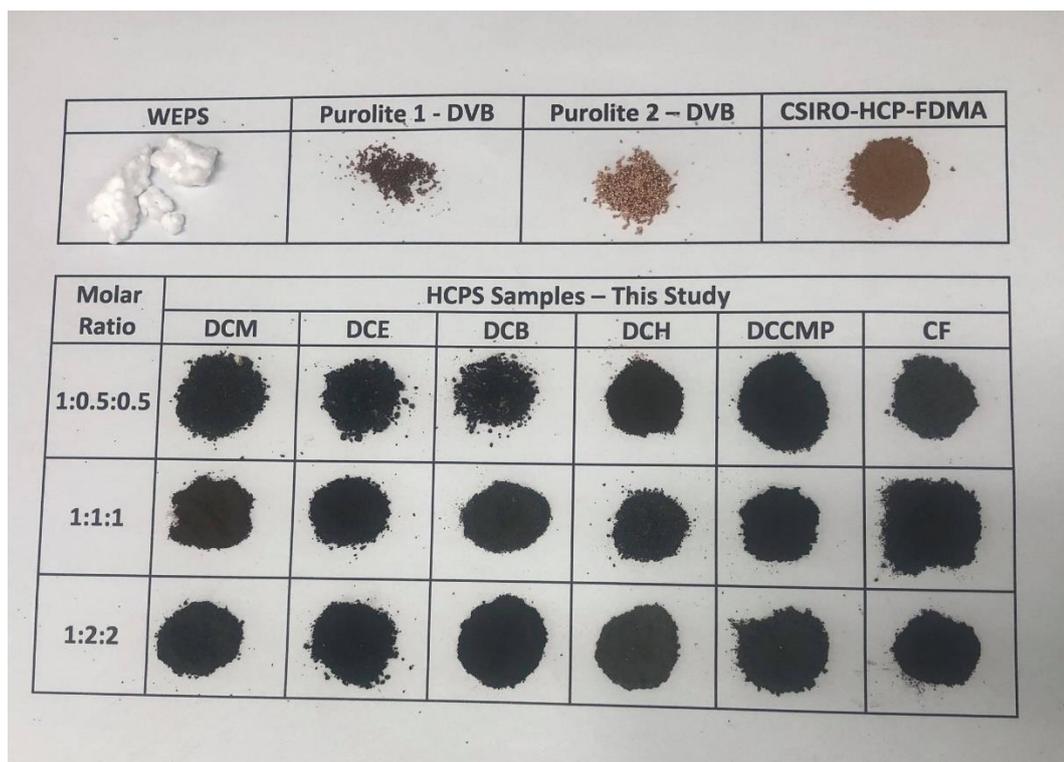
**Figure 24** - ATR corrected FTIR spectra for the various synthesised HCPs. Black = WEPS, Red = 1:0.5, Blue = 1:1 and Green = 1:2, where these ratios indicate the molar ratio of WEPS to crosslinker. Reproduced with permission from Joseph Valerioti's CRM final project thesis.

FTIR spectroscopy results (Figure 24) show characteristic decreases in signals at 700 and 750  $\text{cm}^{-1}$  defined by Fu and co-workers,<sup>50, 51, 91</sup> which are associated with C-H stretching signals from the phenyl rings. As the phenyl ring is substituted (or in this case, crosslinked), the stretching movement of these C-H's is restricted, causing a decrease in the aforementioned signals compared to WEPS.<sup>50, 51, 91</sup> These decreases indicate that HCP was successfully synthesized regardless of crosslinker, and that the most highly crosslinked HCP's for each crosslinker (defined by greatest decreases in the 696 and 756  $\text{cm}^{-1}$  signals) were all 1:2 PS:CL HCPs, followed by the 1:1 HCPs and then the 1:0.5 HCPs. This was expected as increasing the ratio of WEPS to crosslinker would obviously increase the degree of crosslinking, or crosslink density, and is further supported in Figure 25 wherein the earlier HCP<sup>14</sup> (synthesised at a 1:20 PS:CL ratio), shows the greatest decrease in these signals, indicating it is more crosslinked.



*Figure 25 - ATR correct FTIR spectra comparison of earlier HCP to various HCPs synthesised in this work. Blue = earlier HCP, red = DCCMP (1:2) HCP, pink = DCH (1:2) HCP, green = DCB (1:1) HCP and orange = chloroform (1:1) HCP where the ratio represents the molar ratio of WEPS to crosslinker. Reproduced with permission from Joseph Valerioti's CRM final project thesis.*

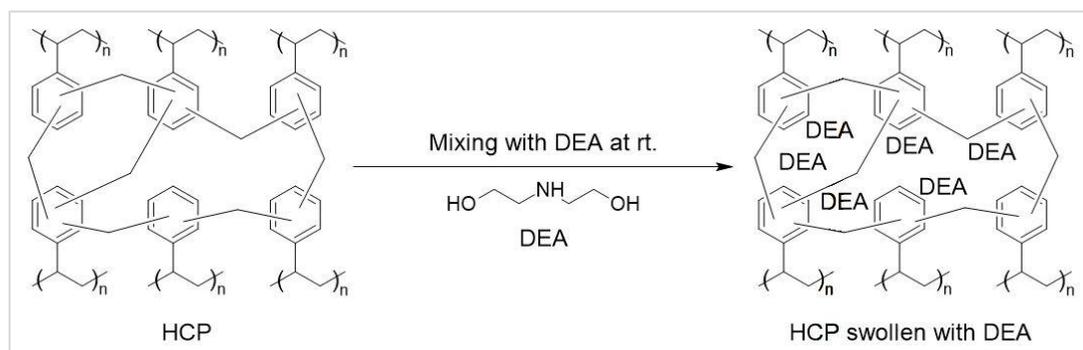
Other significant signals present in the IR spectra (Figure 24) include signals at 3000, 2900, 1600, 1500, and 1450  $\text{cm}^{-1}$  which are associated with C-H stretching (aromatic), C-H stretching of  $-\text{CH}_2-$ 's in the polymer and crosslinks, C=C stretching (aromatic), C=C stretching (aromatic) and C=C stretching (aromatic), respectively.<sup>50, 51, 91</sup> Also present in some spectra is a signal at 1000  $\text{cm}^{-1}$ , which can be associated with a possible side reaction described in the literature.<sup>92, 93</sup> As can be seen in Figure 26, there was no discernible pattern in colour among the HCPs, which was not observed in Fu and co-workers' studies.<sup>50, 51</sup> Furthermore, these HCPs are not the characteristic brown colour observed for other HCPs, such as the earlier HCP<sup>14</sup> and the two purchased Purolite HCPs (Figure 26). It is possible these colour differences and lack of pattern are simply due to interactions between  $\text{FeCl}_3$  and the HCP defined in Fontanals and co-workers' study,<sup>92</sup> as well as residual reactants being present in the HCP network post synthesis.



*Figure 26 - Visual comparison of the various HCPs synthesised in this work vs WEPS, the earlier HCP<sup>14</sup> (labelled CSIRO-HCP-FDMA in picture) and two purchased HCP's (Purolite 1 and 2) which were crosslinked with divinylbenzene.*

### 3.1.3 – HCP/DEA Swelling and CO<sub>2</sub> Capture Experiments Results and Discussion

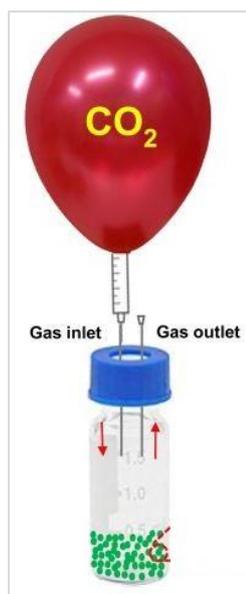
Following the successful syntheses, swelling experiments with DEA were conducted with each of the synthesised HCPs (Figure 27). To do so, the chosen HCP and DEA were simply combined at a 1:2 mass ratio (HCP:DEA) and mixed at room temperature, as per the earlier works procedure.<sup>14</sup> In all cases this resulted in a thick paste rather than the expected powder. This was repeated at a 1:1 and 1:0.5 mass ratio, with only the highest crosslinked HCPs (i.e. the 1:2:2 PS:CL:FeCl<sub>3</sub> HCPs) yielding a free flowing powder at a 1:0.5 mass ratio. These HCP/DEA systems were deemed “successfully swelled”.



**Figure 27** – Scheme of swelling of various HCPs synthesised in this work with DEA at a 1:0.5 HCP to DEA ratio. HCP crosslinked with DCM is used in this figure.

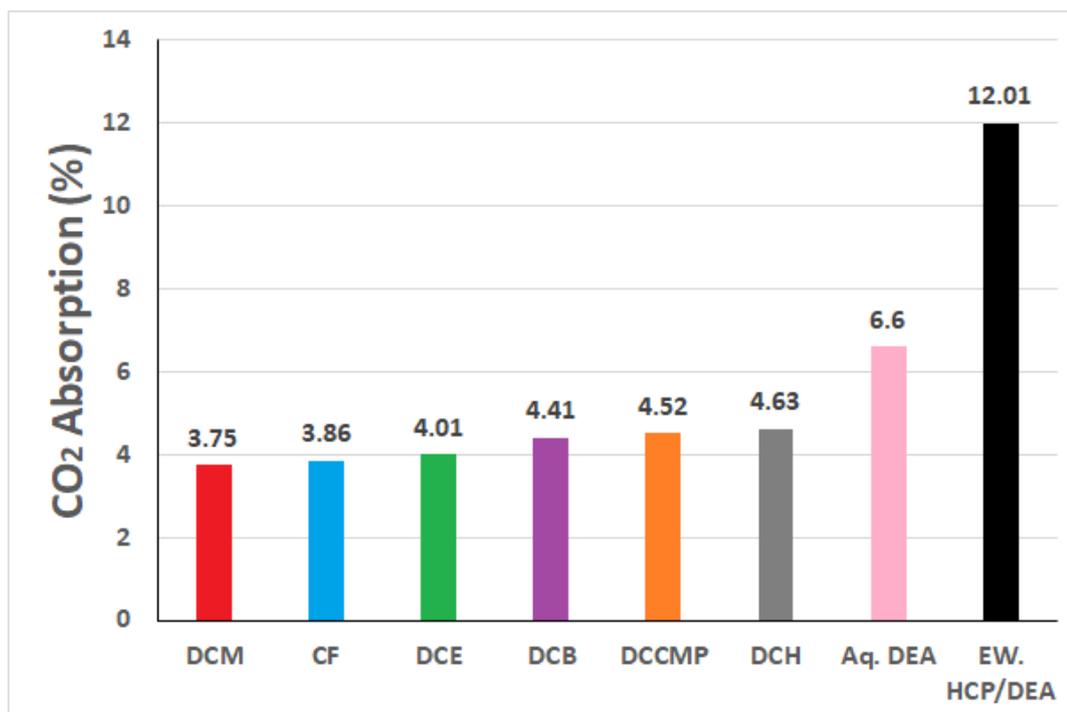
We believe the swelling ratio of the swollen HCPs could be increased by increasing the degree of crosslinking<sup>92</sup> to allow for crosslinking densities similar to the earlier HCP,<sup>14</sup> which displayed a swelling ratio of 1:2 (HCP to DEA), and was synthesised at a 1:20 PS:CL ratio as opposed to the 1:2 WEPS:CL ratios of the HCPs discussed here.<sup>14</sup> The increased crosslinking density of the earlier HCP<sup>14</sup> would thus result in a greater BET surface area within the crosslinking network,<sup>50, 51, 94</sup> allowing for greater swelling.<sup>14, 92</sup> Ideally the BET surface area of these materials would be measured and compared to confirm this, but due to equipment limitations this could not be done.

Using the successfully swelled HCPs from this work, CO<sub>2</sub> capture experiments were then conducted using the simple balloon method procedure as used in the earlier work.<sup>14</sup> The procedure is as follows:



*Figure 28 - Visual representation of the "balloon method" used to determine CO<sub>2</sub> capture capabilities in this work. Reproduced with permission from CSIRO.<sup>65</sup>*

*A known amount of the chosen HCP/amine system was placed into a tared vial capped with a septum lid. A needle attached to a CO<sub>2</sub> filled balloon was then inserted into the septum along with a vent needle, allowing CO<sub>2</sub> to flow through the vial, purging it of air. After 1 minute both needles and the balloon were removed and the mass of the vial was measured again, after which only the needle attached to the balloon was reinserted, pressurising the vial with CO<sub>2</sub> and allowing CO<sub>2</sub> to be absorbed. The mass of the vial without the needle and balloon was then measured every 5 minutes thereafter until changes in mass plateaued, indicating the maximum amount of CO<sub>2</sub> had been absorbed. The balloon was refilled as required throughout the experiment to keep constant pressure, and all experiments were conducted at ambient conditions. All CO<sub>2</sub> capture experiments were performed in triplicate, the averages of which are displayed in Figure 29 (and subsequent figures in other sections).*



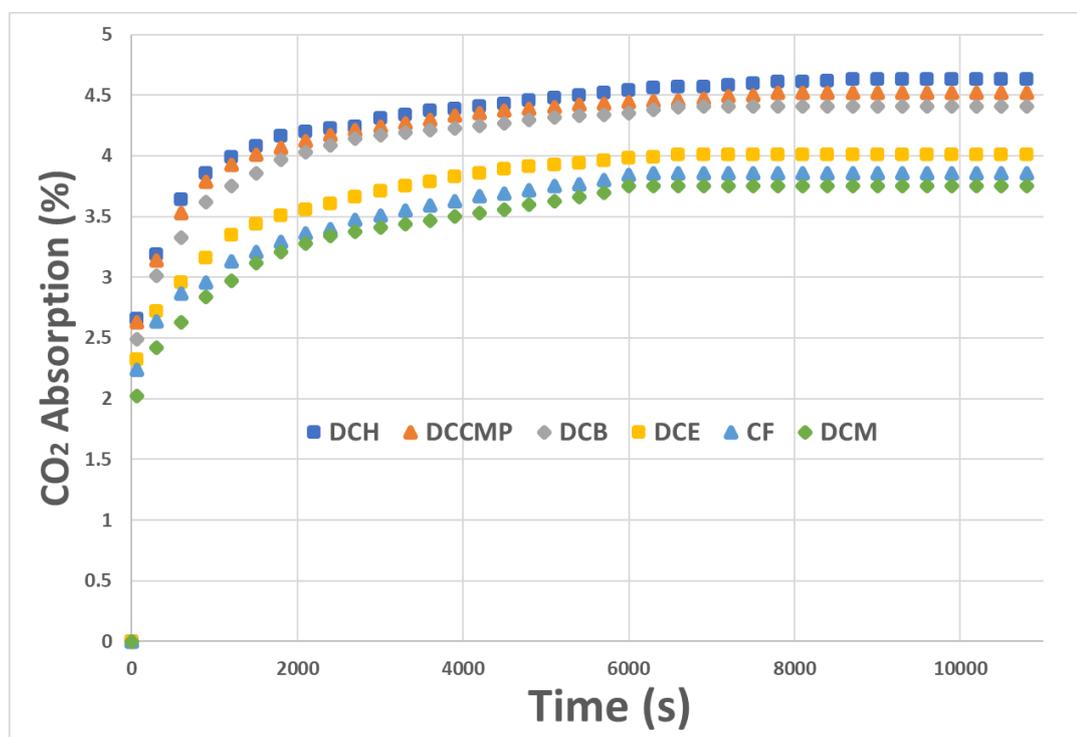
*Figure 29 - CO<sub>2</sub> Absorption (%) comparison of various 1:2 (WEPS to crosslinker) HCPs from this work, which were swollen with 100 wt % DEA at a 1:0.5 HCP to DEA ratio. Aq. DEA<sup>18</sup> and the HCP/DEA system from the earlier work<sup>14</sup> are also included for comparison.*

Figure 29 clearly demonstrates that despite the lower-than-expected swelling ratios, the swelled HCPs were all capable of decent CO<sub>2</sub> uptakes. The highest CO<sub>2</sub> uptakes also correlate to the highest degrees of crosslinking with the DCH HCP, the most crosslinked material (discussed section 4.1.2), displaying the highest uptake of 4.63 wt %, followed by the DCCMP, DCB, DCE, CHCl<sub>3</sub> and DCM HCPs displaying uptakes of 4.52, 4.41, 4.01, 3.86 and 3.75 wt % respectively. The differences in uptakes are simply due to the differences in crosslinking, with higher degrees of crosslinking increasing the internal surface area of the HCP and therefore increasing the gas to sorbent contact area when the DEA occupies this surface area, allowing for greater uptakes.

It is also evident that longer crosslinks generated by the longer crosslinking agents had a positive effect on CO<sub>2</sub> uptake, with CO<sub>2</sub> uptake increasing as crosslinker agent length increases, wherein the ascending crosslinker length of DCM and CF < DCE < DCB < DCH directly correlates to the ascending CO<sub>2</sub> uptake values of DCM < DCE < DCB < DCH. This is simply because, as discussed above, the longer crosslinkers

resulted in greater internal surface area, and therefore greater CO<sub>2</sub> uptakes. Interestingly DCCMP appears to not fit this trend, having a crosslinker length between DCE and DCB of effectively a 3-carbon alkyl chain from Cl to Cl, but a CO<sub>2</sub> uptake between those of DCB and DCH. This is likely due to the fact that DCCMP is trifunctional, and thus has the potential to form crosslinks of greater surface area by substituting to more phenyl rings than the DCB despite its shorter crosslink length.

As with swelling capabilities these uptakes could likely be increased by increasing the crosslinking density, similar to the earlier HCP,<sup>14</sup> thus granting greater internal surface area and therefore greater gas to sorbent contact area and CO<sub>2</sub> uptake.



*Figure 30 - CO<sub>2</sub> absorption breakthrough curves for various 1:2 (WEPS to crosslinker) HCPs synthesised in this work, which were swollen with DEA at a 1:0.5 HCP to DEA ratio.*

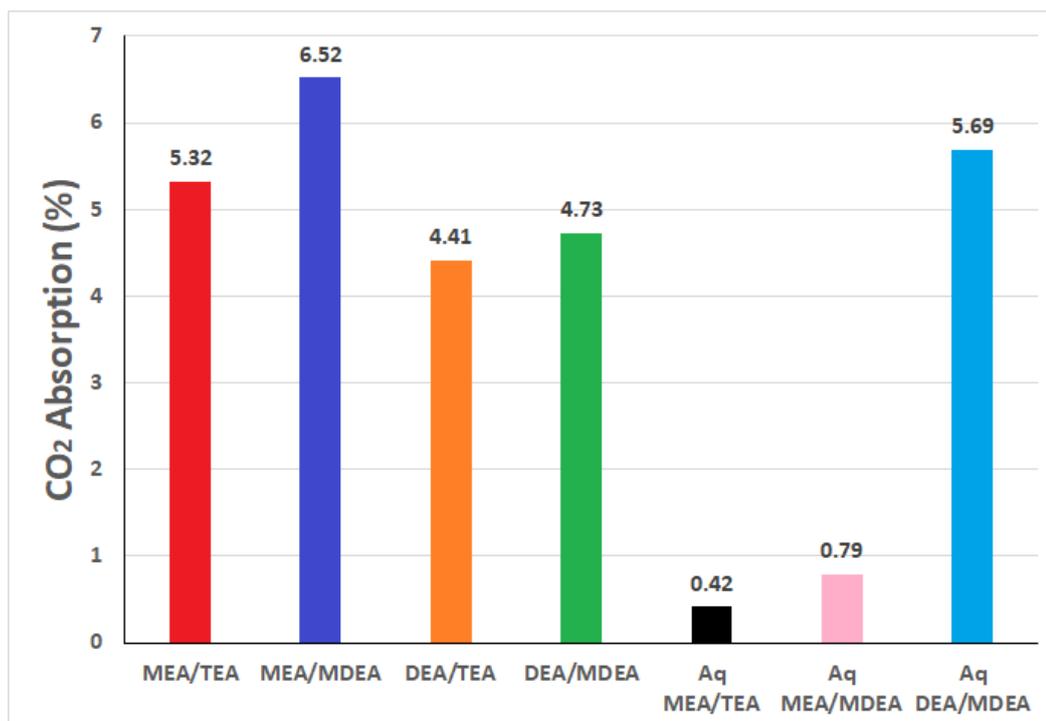
From the CO<sub>2</sub> absorption breakthrough curves in Figure 30 it was found that the synthesised HCPs achieved 90% of their total uptake capacity in 1800, 1800, 1800, 2400, 2700 and 2700 seconds for the DCH, DCCMP, DCB, DCE, CF and DCM HCPs respectively. Thus, it is evident that there is also a correlation between CO<sub>2</sub> uptake rate and the degree of crosslinking, with higher crosslinked HCPs achieving

more rapid CO<sub>2</sub> uptake. The order of slowest to fastest 90% of total CO<sub>2</sub> uptake is thus DCH, DCCMP, and DCB > DCE > CF and DCM. The differences in uptake rate are again simply due to increasing crosslinking resulting in increasing internal surface area and therefore greater gas to sorbent contact area and more rapid CO<sub>2</sub> uptake. This is also why there are two distinct groupings of the DCH/DCCMP/DCB and DCM/DCE/CF crosslinkers observed in the breakthrough curves, with DCM and CF sharing similar breakthrough curves due to their nearly identical crosslinking length and structure, and DCE having only a slightly different breakthrough curve due to the single additional -CH<sub>2</sub>- present in its crosslinking structure. The same can also be said for the DCH, DCCMP and DCB HCPs, which again display similar breakthrough curves due to their similar length and structure.

Since no changes that could affect recyclability were made to the HCPs from this thesis as compared to the earlier work,<sup>14</sup> the HCPs from this thesis were not tested for recyclability, though it is likely they are equally as unrecyclable as the HCP systems from the earlier study due to iron catalysed degradation discussed in section 1.5.<sup>77</sup>

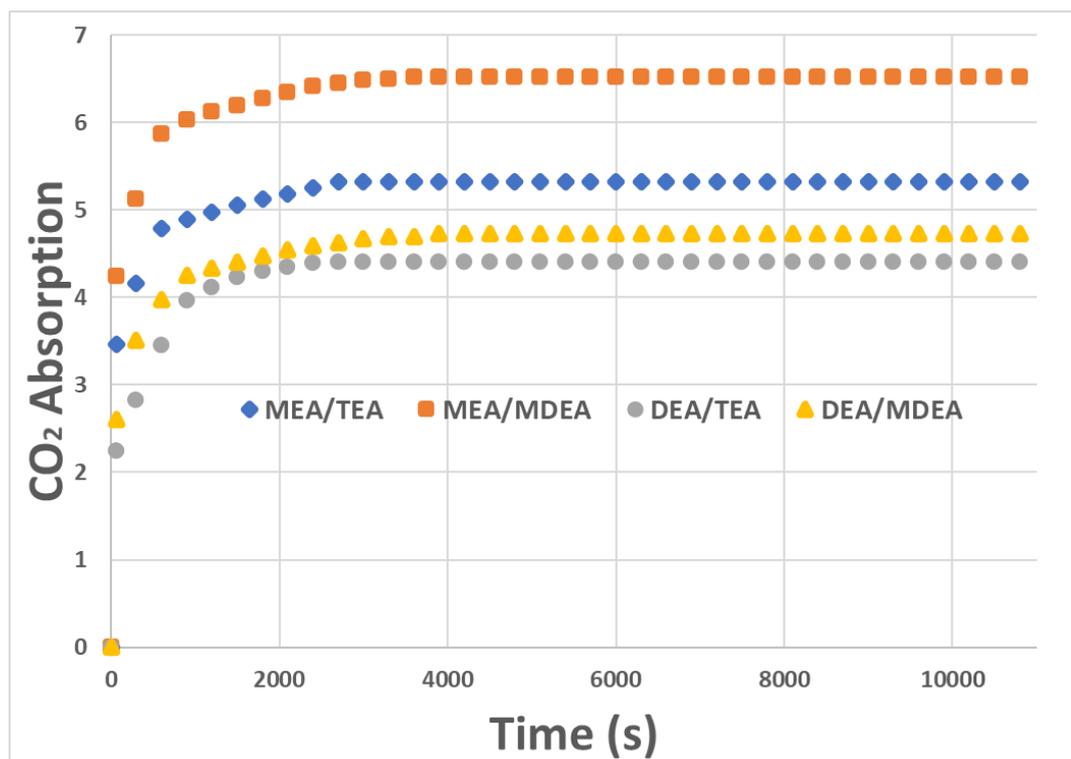
#### 3.1.4 – HCP/Amine Blends Swelling and CO<sub>2</sub> Capture Experiments Results and Discussion

For this study we decided to examine the use of amine blends with HCP due to the theoretical benefits blends can provide over 100 wt % amine solutions, as discussed in section 1.2.1.<sup>23-25</sup> Similarly, to the 100 wt % amine systems, it was decided that the water component of traditional amine blends<sup>23-25</sup> (discussed section 1.2.1) be removed, thus each of the blends used were comprised of 30 wt % primary amine and 70 wt % tertiary amine, with the chosen blends being MEA/MDEA, MEA/TEA, DEA/MDEA and DEA/TEA. For this series of experiments, we chose to use an HCP of much higher crosslinking density prepared from the reaction of WEPS with DCE at a WEPS to DCE ratio of 1:20, an order of magnitude higher than the HCPs used above. This was done, as discussed above, so that higher swelling ratios and CO<sub>2</sub> uptakes could be achieved. Swelling was conducted in the same manner as above,<sup>14</sup> by simply mixing the chosen amine blend with the HCP at a 1:2 HCP to blend mass ratio at ambient conditions, until a free-flowing powder was produced. CO<sub>2</sub> uptake experiments were then performed using the aforementioned “balloon method”.<sup>14</sup>



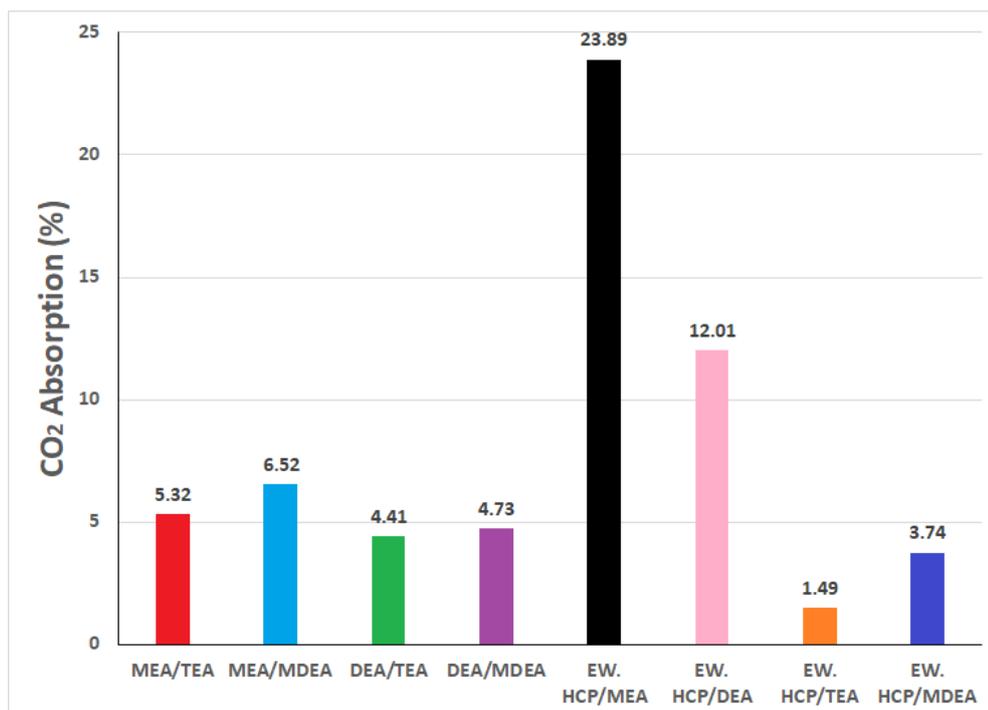
*Figure 31 - CO<sub>2</sub> absorption (%) comparison of the various amine blends (30% primary/secondary amine, 70% tertiary amine) swollen into the higher crosslinked HCP from this work and the aqueous blends discussed in section 1.2.1.*

As seen in Figure 31 the amine blends achieved acceptable uptake capacities of 5.32, 6.52, 4.41 and 4.73 wt % for the MEA/TEA, MEA/MDEA, DEA/TEA and DEA/MDEA blends respectively, achieving 90% of their total CO<sub>2</sub> uptake capacity in 600, 600, 900 and 900 seconds respectively (Figure 32). As expected, the MEA based blends outperformed the DEA based blends in both uptake capacity and rate, which is simply due to the MEA in the blend being a primary amine and therefore more reactive than DEA, a secondary amine. Similarly, the MDEA blends outperformed the TEA blends in uptake capacity due to MDEA's higher reactivity over TEA.



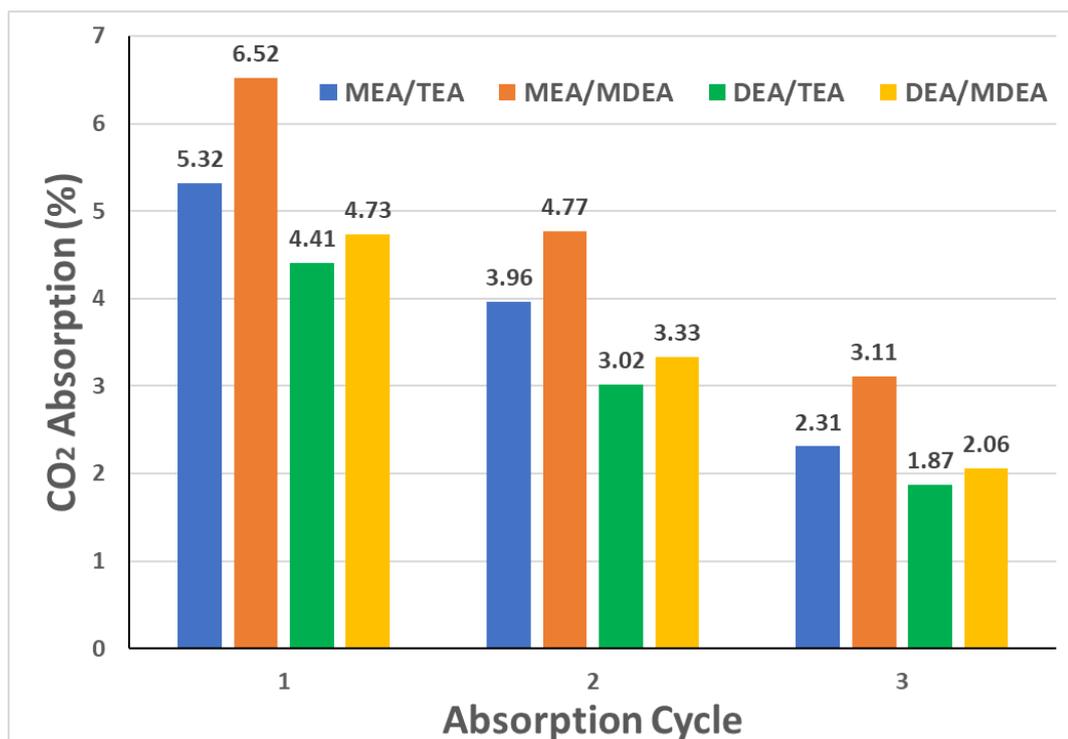
*Figure 32 – CO<sub>2</sub> Absorption breakthrough curves for higher crosslinked HCP swollen with blends of MEA/TEA, MEA/MDEA, DEA/TEA and DEA/MDEA.*

Interestingly, all of the MEA blends tested for this work outperformed their aqueous counterparts discussed in section 1.2.1,<sup>20, 21</sup> with the MEA/MDEA and MEA/TEA blends displaying 825 and 1266 % increased uptake compared to their aqueous counterparts respectively.<sup>20, 21</sup> This is simply due to the increased concentration of MEA present in the blends versus the aqueous counterparts, which would increase uptake capacity compared to those from the literature. The DEA/MDEA blend however, displayed a lower CO<sub>2</sub> capacity compared to its aqueous counterpart.<sup>22</sup> As discussed in section 1.2.1, the aqueous DEA/MDEA achieved its uptakes under 4.9 MPa of pressure, hence its greater uptake compared to the DEA/MDEA blend in this work.<sup>22</sup> As also discussed in section 1.2.1, no aqueous DEA/TEA blend could be found in the literature, hence comparisons cannot be made.



*Figure 33 - CO<sub>2</sub> absorption (%) comparison of the various amine blends from this work and the 100 wt % amines from the earlier work, combined with HCP.<sup>14</sup>*

However, all amine blends achieved lower uptake capacities than the 100 wt % MEA and DEA from the earlier work (Figure 33).<sup>14</sup> This is primarily attributed to the presence of the tertiary amines, which have lower CO<sub>2</sub> uptake capacities and effectively dilute the higher absorbing primary/secondary amine, therefore lowering uptake. The presence of the tertiary amines is also why the blend systems were slightly slower to achieve 90% of their total uptake compared to the 100 wt % MEA system, which achieved 90% of its total CO<sub>2</sub> uptake in 600 seconds,<sup>14</sup> as the tertiary amines lower the overall reactivity of the blend and therefore the absorption rate. Conversely the presence of the MEA and DEA in the blends are responsible for the increased absorption capacities over their 100 wt % MDEA and TEA counterparts (Figure 33),<sup>14</sup> as well as the increased absorption rates over their 100 wt % MDEA and TEA counterparts (which achieved 90% of their total CO<sub>2</sub> uptake in 1200 and 900 seconds respectively),<sup>14</sup> as the increased reactivity of the MEA and DEA increased the overall reactivity of the blend, therefore increasing uptake and uptake rate.

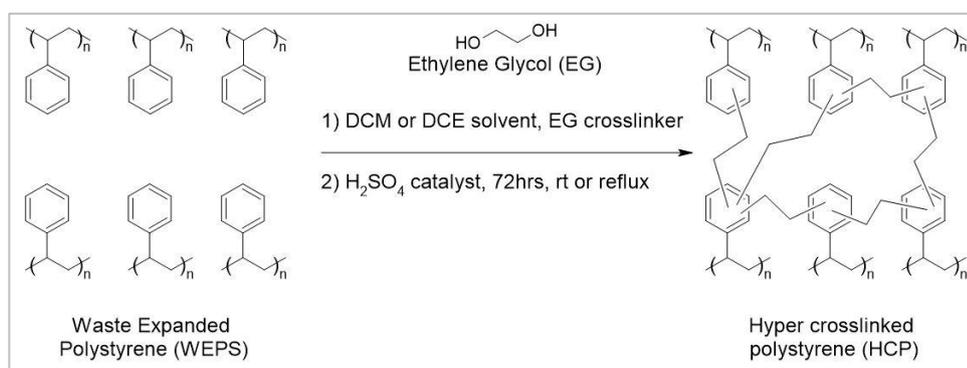


*Figure 34 - Recyclability of the higher crosslinked HCP swollen with amine blends.*

Despite the lower uptake capacities compared to 100 wt % MEA and DEA from the earlier work,<sup>14</sup> it was decided that the blends would be investigated for their recyclability (Figure 34), as it was hypothesized in sections 1.2.1 and 1.6 that the tertiary amine should allow for a more recyclable sorbent.<sup>23-25</sup> Recyclability experiments were conducted by simply absorbing CO<sub>2</sub> via the balloon method, then fully desorbing CO<sub>2</sub> by placing the open vial in a 60°C vacuum oven for 2 hours, followed by reabsorption of CO<sub>2</sub> with the balloon method again. Unfortunately, none of the blends displayed increased recyclability, with CO<sub>2</sub> uptakes reducing by 25.6, 26.9, 31.6 and 29.6 % for the MEA/TEA, MEA/MDEA, DEA/TEA and DEA/MDEA blends respectively after just one cycle (Figure 34). These decreases in uptake capacity are likely due to the rapid degradation of the MEA/DEA in the blends,<sup>76-78, 80</sup> as discussed in section 1.5, as well as the degradation of the tertiary amines as observed elsewhere in the literature.<sup>79</sup>

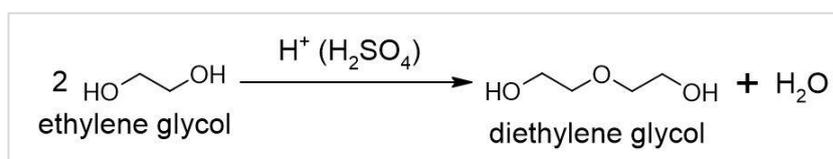
### 3.2 – HCP from Alternative Friedel Crafts Reaction

For this thesis an alternative synthesis<sup>83-88</sup> based on mechanisms found in the literature<sup>83-88</sup> for HCP synthesis from WEPS, difunctional alcohols and a sulfuric acid catalyst was also investigated (Figure 35). Given the simplicity of the reaction (Figure 35) and low cost, wide availability of multi-functional alcohols such as ethylene glycol and poly(ethylene glycol)s, such a synthesis could provide a desirable alternative to the higher cost, higher difficulty traditional synthesis of HCP. Initial experiments, detailed below, were unsuccessful regardless of reaction conditions such as varying reaction temperature and EG/H<sub>2</sub>SO<sub>4</sub> concentration, and so further experiments were not pursued. Reactions were likely unsuccessful due to ether formation from the ethylene glycol dominating the reaction (Figure 36).



**Figure 35** - Alternative synthesis of HCP from WEPS using ethylene glycol as the crosslinker, DCM or DCE as the solvent and H<sub>2</sub>SO<sub>4</sub> as the acid catalyst, performed at room temperature or at reflux over 72 hours.

WEPS (1 g, 9.6 mmol based on repeating styrene units) was dissolved in the chosen solvent (DCM or DCE, 15 ml), to which was added ethylene glycol (15 ml, 268 mmol) followed by dropwise addition of H<sub>2</sub>SO<sub>4</sub> (98 %, 0.3/0.6/1.2/3 ml, 5.6/11.2/22.4/56 mmol) resulting in a clear/colourless solution. The reaction proceeded for 3 days at room temperature or reflux. In all cases no visible reaction occurred after 3 days.



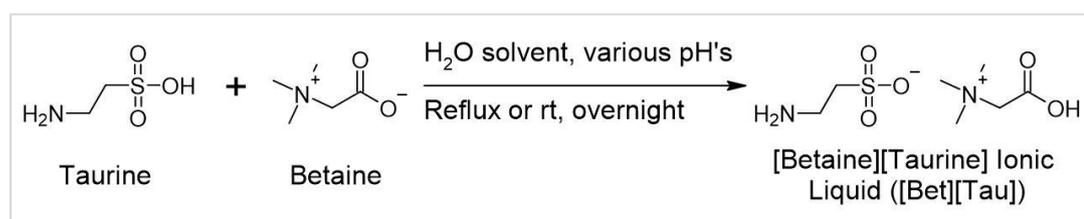
**Figure 36** - Formation of an ether (diethylene glycol) from ethylene glycol via dehydration reaction with H<sub>2</sub>SO<sub>4</sub>.

## 4 – [Bet][Tau] Ionic Liquid

### 4.1 – Synthesis and Discussion

#### 4.1.1 – [Bet][Tau] Synthesis Results and Discussion

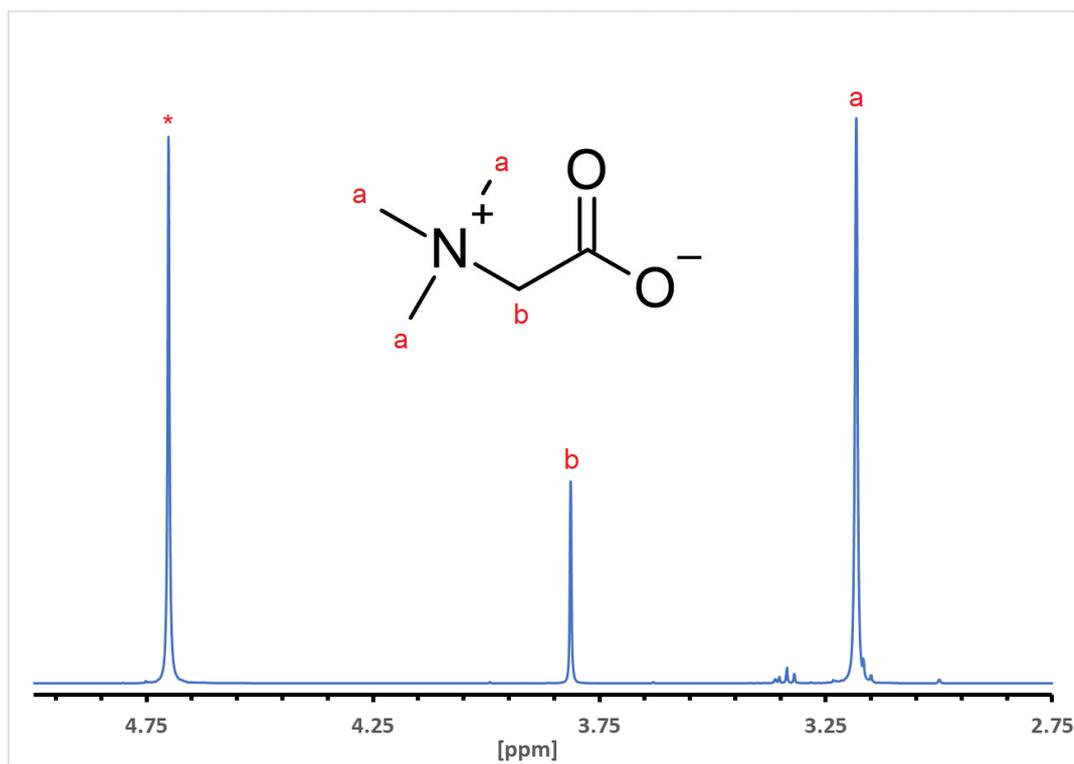
To synthesise [Bet][Tau] the procedure from the literature source was employed (Figure 37).<sup>41</sup> Regardless of reaction conditions, all syntheses resulted in a crystalline solid and small amount of clear/colourless liquid being produced. <sup>1</sup>H NMR spectroscopic shifts from the liquid (Figure 38) at 3.82 and 3.19 ppm correlating respectively to the methylene and methyl groups in betaine confirm the syntheses were unsuccessful, and are corroborated by values found in the literature source.<sup>41</sup> We believe these syntheses were unsuccessful because the synthesis proposed by the literature source<sup>41</sup> is not valid, and provide evidence to support this in the section below.



**Figure 37** - Synthesis of [Bet][Tau] ionic liquid<sup>41</sup> from betaine and taurine with H<sub>2</sub>O solvent (pH 1, 5, 6, 7 and 12), performed at room temperature or reflux overnight.

Betaine (1 g, 8.5 mmol) was dissolved in water (15 ml, pH 1/5/6/7/12), to which a solution of taurine (1.07 g, 8.5 mmol) dissolved in water (15 ml, pH 1/5/6/7/12) was added dropwise. The reaction was then allowed to proceed overnight at room temperature or reflux, after which the water was removed from the solution by placing the solution in a vacuum oven at 60 °C overnight. After removal of the water a crystalline solid with a small amount of clear/colourless liquid (<1 ml) was present in the reaction vessel.

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ (ppm): 4.70 (solvent), 3.82 (s, -CH<sub>2</sub>-), 3.19 (s, N(CH<sub>3</sub>)<sub>3</sub>).



*Figure 38 –  $^1\text{H}$  NMR Spectra of the clear/colorless liquid present after attempted syntheses of [Bet][Tau] ionic liquid.*

#### 4.2 – Evidence against validity of literature procedure

Henderson Hasselbalch equations (Figure 39, Equations 1-5) for taurine and betaine reveal that at pH values of 1.5 or lower the taurine is present in its sulfonic acid state (Equation 1), while at pH values of 2.33 or lower the betaine is present in its carboxylic acid state (Equation 4), which are incapable of reacting via the mechanism suggested by Lu and co-workers (Figure 37).<sup>41</sup> Similarly at pH values between 3 and 9 (Equations 2 and 5), both the taurine and betaine would be present as zwitterions, which are similarly incapable of reacting via this mechanism (Figure 37).<sup>41</sup> Finally at pH values above pH 9 (Equations 3 and 5) the taurine is present as a sulfonate (amine) and the betaine as a zwitterion, which are also incapable of reacting via the proposed mechanism (Figure 37).<sup>41</sup>

Given:  $pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$ , Taurine  $pK_a$ 's = 1.5 (Sulfonic Acid group) & 8.8 (Amino group) and Betaine  $pK_a$ 's = 2.33 (Carboxylic Acid group). Then:

$$(1) \text{ For Tau if } pH \leq 1.5 \rightarrow \log_{10} \frac{[\text{Zwitterion}]}{[\text{Sulfonic Acid}]} \leq 0 \therefore [\text{Zwitterion}] \leq [\text{Sulfonic Acid}]$$

$$(2) \text{ For Tau if } 1.5 \leq pH \leq 8.8 \rightarrow 0 \leq \log_{10} \frac{[\text{Zwitterion}]}{[\text{Sulfonic Acid}]} \leq \log_{10} \frac{[\text{Amine}]}{[\text{Zwitterion}]}$$

$$\therefore [\text{Sulfonic Acid}] < [\text{Zwitterion}] > [\text{Amine}]$$

$$(3) \text{ For Tau if } pH \geq 8.8 \rightarrow \log_{10} \frac{[\text{Amine}]}{[\text{Zwitterion}]} \geq 0 \therefore [\text{Amine}] \geq [\text{Zwitterion}]$$

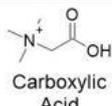
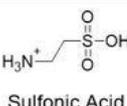
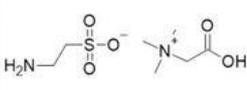
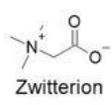
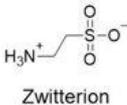
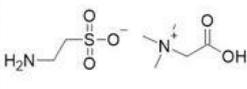
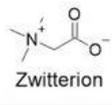
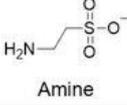
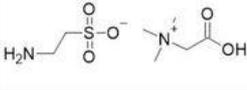
$$(4) \text{ For Bet if } pH \leq 2.33 \rightarrow \log_{10} \frac{[\text{Zwitterion}]}{[\text{Carboxylic Acid}]} \leq 0$$

$$\therefore [\text{Carboxylic Acid}] \geq [\text{Zwitterion}]$$

$$(5) \text{ For Bet if } pH \geq 2.33 \rightarrow \log_{10} \frac{[\text{Zwitterion}]}{[\text{Carboxylic Acid}]} \geq 0$$

$$\therefore [\text{Carboxylic Acid}] \leq [\text{Zwitterion}]$$

Thus:

pH Range	Betaine (Major Form)	Taurine (Major Form)	Can Ion Exchange Occur?	[Bet][Tau] Ionic Liquid
~0-2	 Carboxylic Acid	 Sulfonic Acid	X No	
~3-9	 Zwitterion	 Zwitterion	X No	
~9+	 Zwitterion	 Amine	X No	

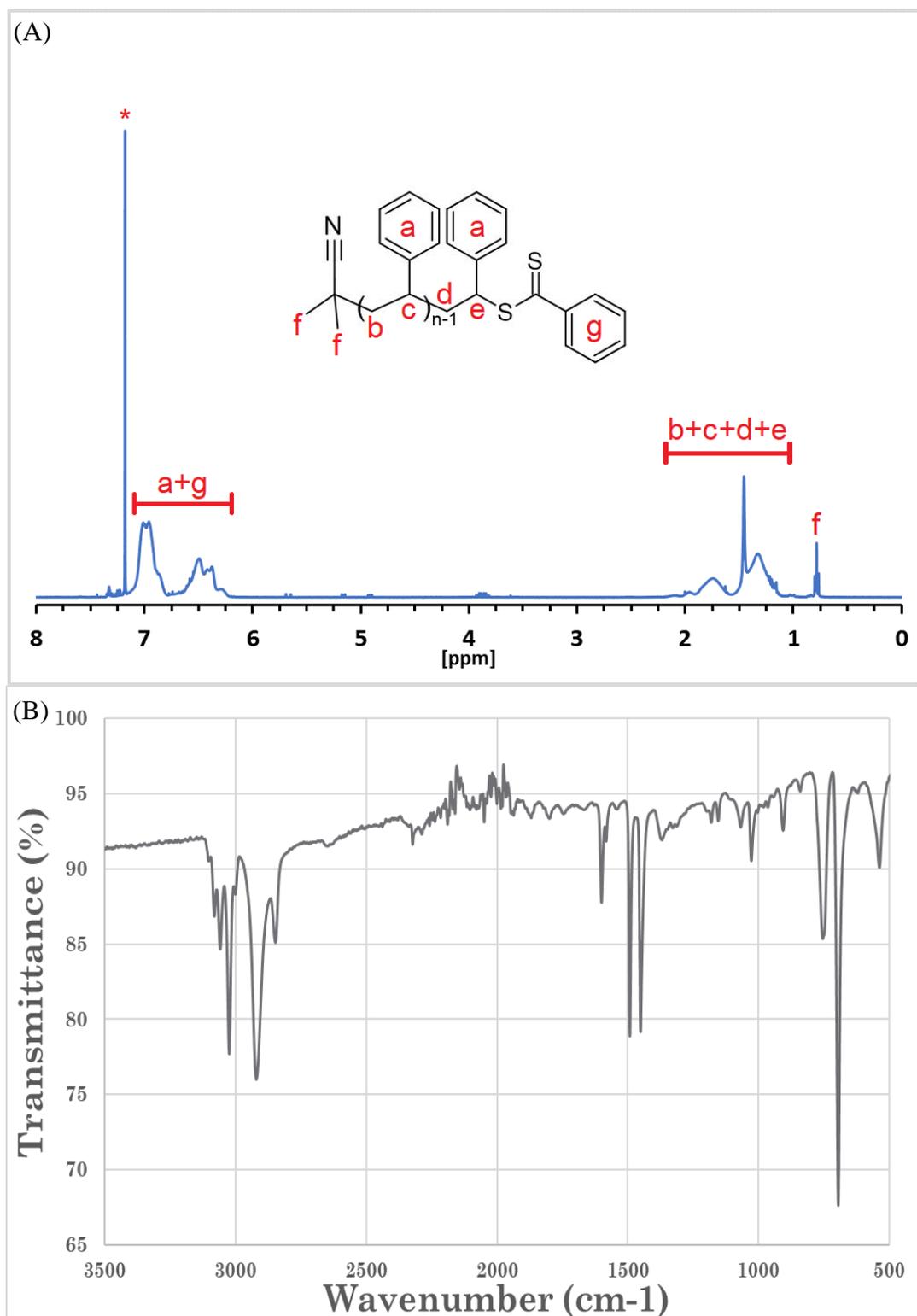
**Figure 39** – Henderson Hasselbalch equations demonstrating the major forms of betaine and taurine at certain pH values and a table graphically representing their ability to form the [Bet][Tau] ionic liquid at particular pH ranges.

These results from the Henderson Hasselbalch equations are corroborated from different studies focussing on betaine and taurine,<sup>95, 96</sup> wherein Lambert and co-workers state that at physiological pH values (i.e., pH 7.4, as defined in their work) taurine is present mainly as a zwitterion, with higher pH values resulting in greater anion (sulfonate/amine) concentration.<sup>96</sup> Similarly, Rivoira and co-workers show that betaine is present as a cation at pH values lower than 2, and a zwitterion at pH values in the physiological range (i.e., pH 7.4).<sup>95</sup> It is also interesting to note that Görbitz and co-workers have confirmed by X-ray diffraction crystallography that taurine exists naturally in its zwitterionic state,<sup>97</sup> and not the non-ionic state required for the



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.18 (solvent), 7.15-6.25 (m, 150H, Ph-H in polymer), 2.00-1.00 (m, 11H,  $\text{R}_3\text{C-H}$  and  $-\text{CH}_2-$  of polymer chain), 0.83-0.80 (t, 3H,  $-\text{CH}_3$ ).

FTIR (ATR corrected,  $\text{cm}^{-1}$ ): 3000 (C-H stretching, aromatic), 2900 (C-H stretching of  $\text{CH}_2$ 's), 1600 (C=C stretching, aromatic), 1500 (C=C stretching, aromatic), 1450 (C=C stretching, aromatic), 750 (C-H stretching, aromatic), 700 (C-H stretching, aromatic).



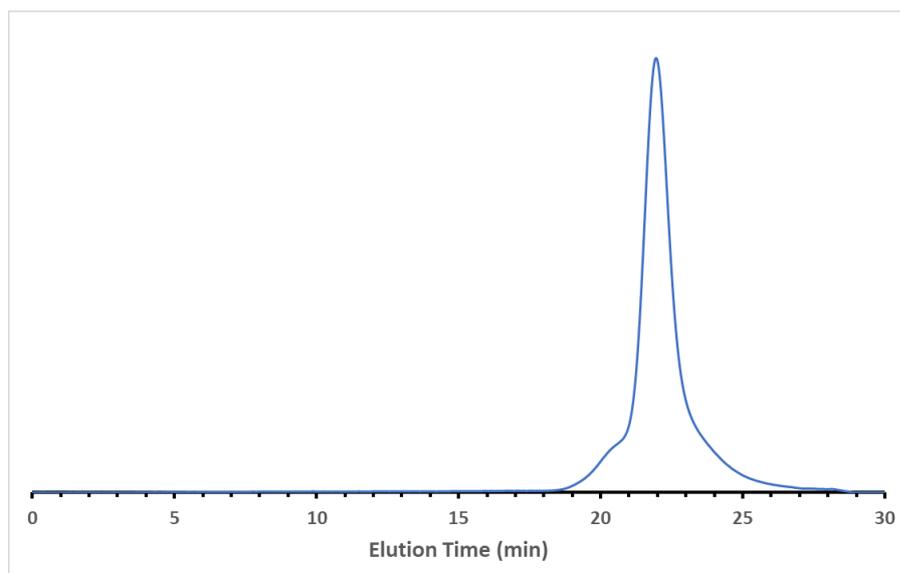
**Figure 41** - (A)  $^1\text{H}$  NMR spectra of the synthesised 10,700 MW polystyrene-mCTA. (B) ATR corrected FTIR spectra of the synthesised 10,700 MW polystyrene-mCTA.

As can be seen in the NMR spectrum (Figure 41A), most signals confirming the synthesis of the PS-mCTA were broad in nature, which is to be expected due to the high MW, repetitive structure of the material causing broad, multiple signals.<sup>98-102</sup> Specifically, though, the NMR signals at  $\delta$  7.15-6.25, 2.00-1.00 and 0.83-0.80 ppm corresponding to the Ph-H, R<sub>3</sub>C-H and -CH<sub>2</sub>-, and -CH<sub>3</sub> in the polystyrene mCTA respectively, confirm the successful synthesis of the PS-mCTA.<sup>91, 94</sup> This is also confirmed by signals in the IR spectrum (Figure 41B) at 3000, 2900, 1600, 1500, 1450, 750 and 700 cm<sup>-1</sup> corresponding to the C-H stretching (aromatic), C-H stretching of -CH<sub>2</sub>-, C=C stretching (aromatic), C=C stretching (aromatic), C=C stretching (aromatic), C-H stretching (aromatic) and C-H stretching (aromatic) in the polystyrene mCTA.<sup>91, 94</sup> These values are corroborated by values found in the literature, confirming successful synthesis.<sup>94</sup>

The above procedure was conducted at varying temperatures of 55, 60, 65, 70 and 75 °C to determine the effect of temperature on the PS-mCTA produced. Initial experiments were performed over 8 hrs, but it was found that the MW of the PS-mCTA produced, regardless of temperature, was lower than the target MW. For example, reactions conducted at 60 and 65 °C yielded products with SEC-measured M<sub>n</sub>s of ~4,800 and 5,450, dispersity's of 1.06 and 1.04 and yields of 32 and 34 % respectively. To increase the MW of the product, all reactions were conducted again over a 24-hour period. Polymerisations performed at 60 and 65 °C yielded products with SEC-measured M<sub>n</sub>s of ~7,500 and 10,700, dispersity's of 1.03 and 1.18 and yields of 37 and 40 % respectively. These results are summarised in Table 1, and an example SEC chromatogram of the 10,700 M<sub>n</sub> PS-mCTA is shown in Figure 42. As seen in Table 1, all successfully synthesised polymers had low dispersity's, as expected of RAFT polymerisation.<sup>98-102</sup>

*Table 2 - Summary of results from various syntheses of Polystyrene mCTA.*

Temperature (°C)	Reaction Time (hrs)	M <sub>n</sub>	M <sub>w</sub>	Disperisty (M <sub>w</sub> /M <sub>n</sub> )	Yield (%)
60	8	4800	5080	1.06	32
65	8	5450	5650	1.04	34
60	24	7500	7700	1.03	37
65	24	10700	12600	1.18	40

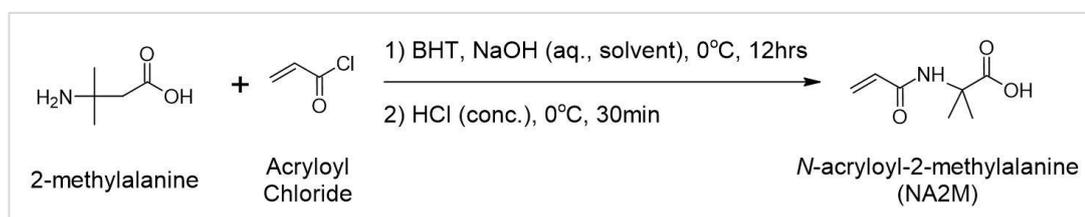


**Figure 42** – Example chromatogram generated by SEC of  $\sim 10,700 M_n$  polystyrene *m*CTA synthesized as per the above procedure at  $65^\circ\text{C}$  over 24 hours.

## 5.2 – VDMA Monomer Synthesis

### 5.2.1 – VDMA Synthesis and Discussion.

VDMA was synthesized according to a 2-step literature procedure by Prai-in and co-workers.<sup>103</sup> Slight variations were made to the procedure, in that the amount of BHT used was doubled for both steps, the purification procedures for the second step were changed and the second step was performed under nitrogen rather than argon. The overall procedure yields VDMA in a 39.05% overall yield, which differs from the literature by -4.15%,<sup>103</sup> which is primarily due to the differences in purification of VDMA.<sup>103</sup> The 2-step procedure for the synthesis of VDMA was thus as follows:

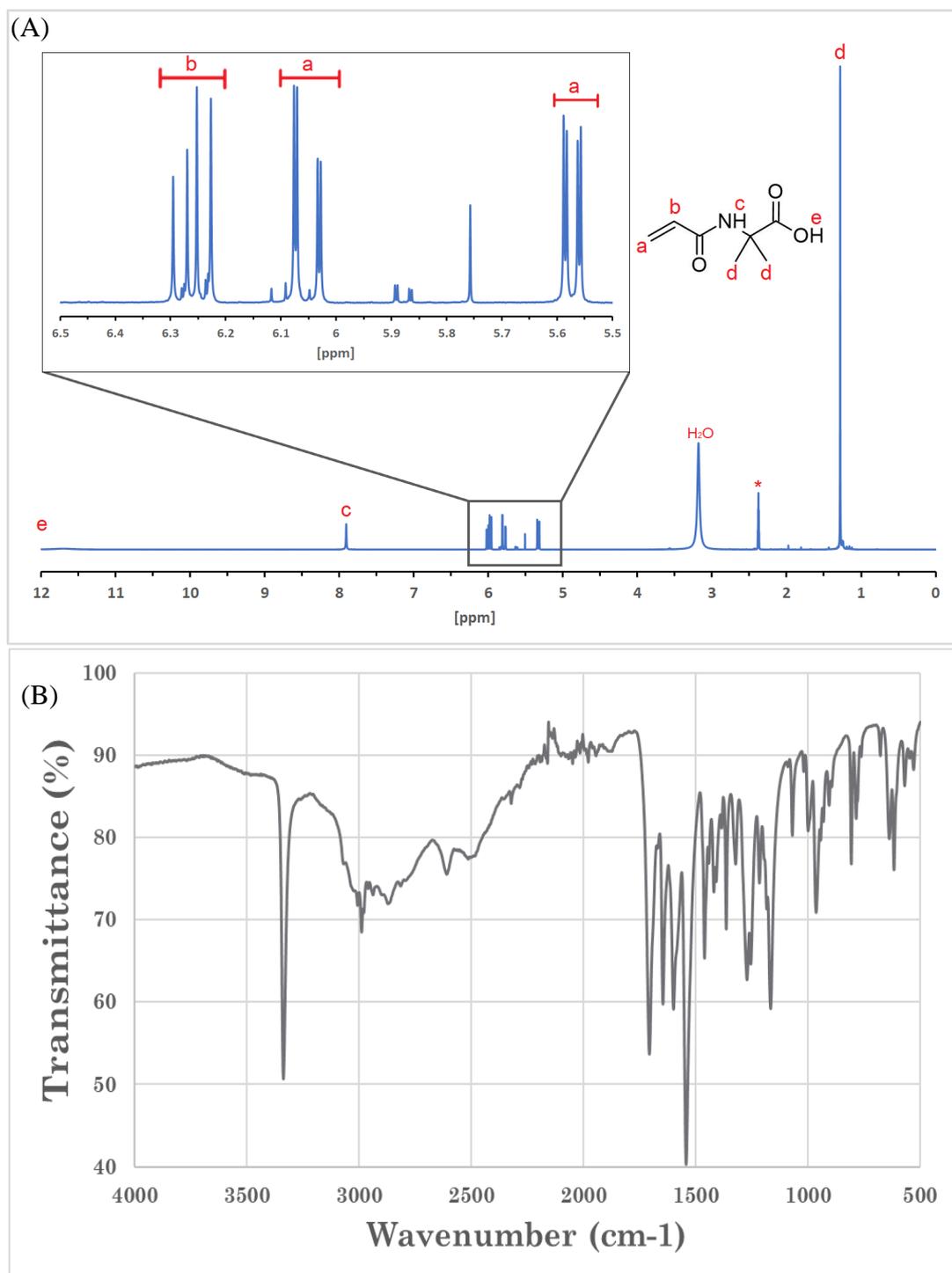


**Figure 43** - Synthesis of *N*-acryloyl-2-methylalanine (NA2M) from 2-methylalanine and acryloyl chloride with butylated hydroxytoluene (BHT) as a polymerisation inhibitor and *aq.* NaOH as the solvent.

**(1)** 2-Methylalanine (6 g, 58 mmol) and BHT (0.055 g, 0.25 mmol) were dissolved in aqueous NaOH (4.65 g, 116 mmol, in 15 ml of water) at 0 °C, to which acryloyl chloride (5.3 g/5.9 ml, 58 mmol) was added dropwise. The reaction was then allowed to proceed overnight, after which a white precipitate had formed. HCl (8 ml, conc. (32%), 72 mmol) was then added to the reaction at 0 °C and stirred for 30 min before isolating the white product via vacuum filtration, washing with water (3 x 30 ml) and drying in a 60 °C vacuum oven overnight to yield a white powder (yield = 71%).

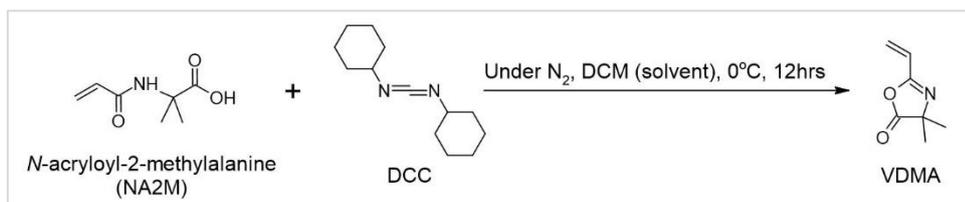
$^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  (ppm): 1.37 (s, 6H, (C(CH<sub>3</sub>)<sub>2</sub>)), 2.51 (Solvent), 3.34 (H<sub>2</sub>O impurity), 5.55-5.59 (dd, 1H, CH<sub>2</sub>=CH), 6.03-6.08 (dd, 1H, CH<sub>2</sub>=CH), 6.23-6.29 (dd, 1H, CH<sub>2</sub>=CH), 8.25 (s, 1H, NH), 12.20 (s, 1H, COOH).

FTIR (ATR Corrected,  $\text{cm}^{-1}$ ): ~3300 (N-H Stretching), ~1700 (C=O of COOH), ~1650 (C=O of amide), 1600 (C=C stretching), 1550 (N-H bending).



**Figure 44** - (A)  $^1\text{H}$  NMR spectra of the synthesised NA2M. (B) ATR Corrected FTIR spectra of the synthesised NA2M.

As stated above, the NA2M product was synthesised with a yield of 71%, falling within the expected yield range of 69-72% from the literature.<sup>103</sup> As can be seen from the NMR spectrum (Figure 44A), there were slight H<sub>2</sub>O contaminations at 3.34ppm, partially due to using water as a solvent and in the washing procedures, as well as the difficulties related to drying DMSO solvents. Also present were some slight impurities at 5.75 and 5.85-5.9. Despite this the NMR signals at 1.37, 5.55-5.59, 6.03-6.08, 6.23-6.29, 8.25 and 12.20 ppm corresponding to -C(CH<sub>3</sub>)<sub>2</sub>, -CH<sub>2</sub>=CH, -CH<sub>2</sub>=CH, -CH<sub>2</sub>=CH, -NH and -COOH in the NA2M respectively indicate the successful synthesis of NA2M.<sup>103</sup> Similarly, IR spectroscopic signals (Figure 44B) at ~3300, 1700, 1650, 1600 and 1550 cm<sup>-1</sup> corresponding to the N-H stretching, C=O (of COOH), C=O (of amide), C=C stretching and N-H bending indicate successful synthesis as well.<sup>103</sup> Both the NMR and IR spectroscopy results corroborate to those found in the literature procedure, confirming NA2M was successfully synthesized in good yield.<sup>103</sup>

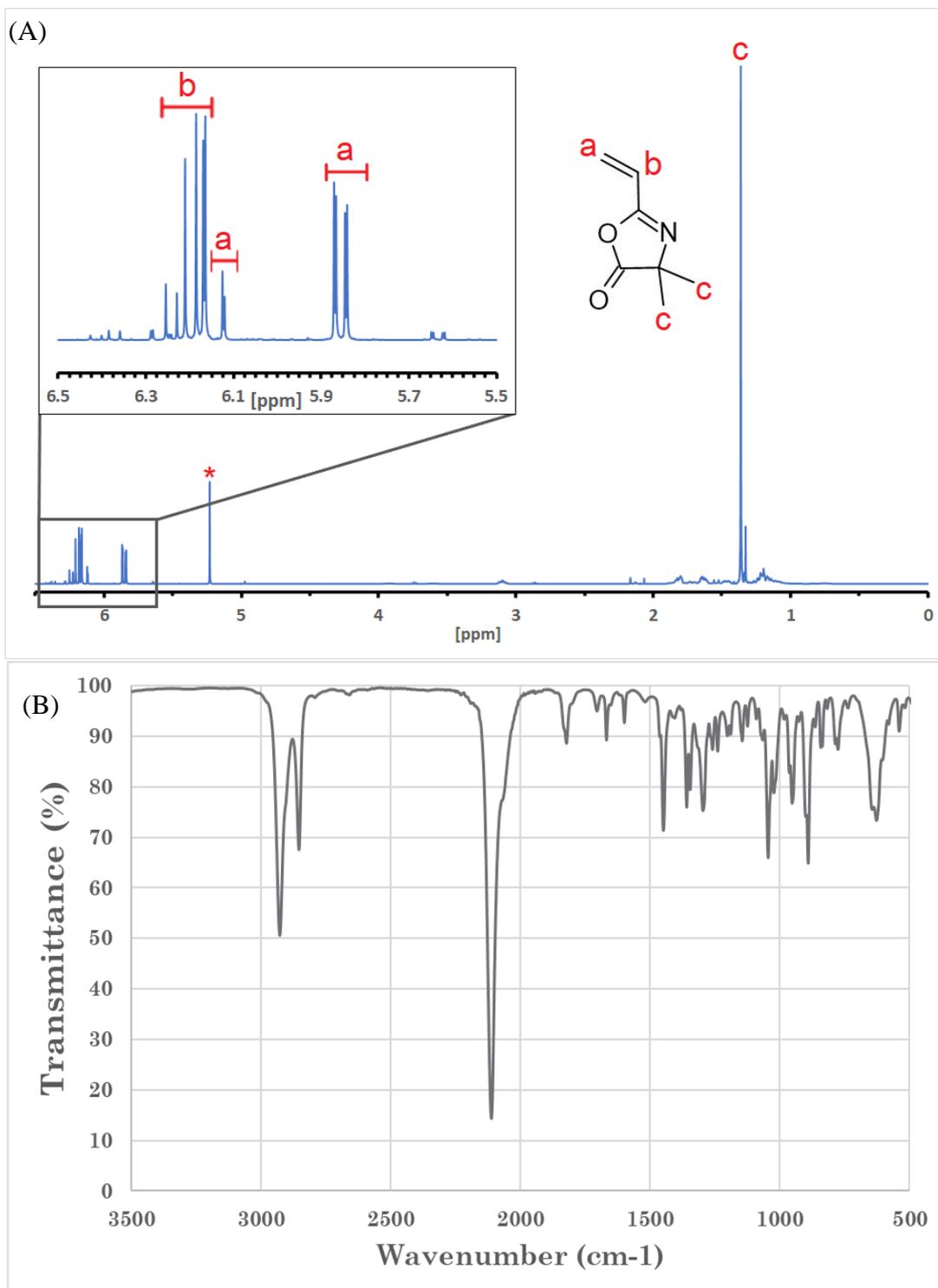


**Figure 45** - Synthesis of 2-vinyl-4,4-dimethylazlactone (VDMA) from N-acryloyl-2-methylalanine (NA2M) using N,N'-dicyclohexylcarbodiimide (DCC) as a coupling agent.

(2) NA2M (5 g, 31.8 mmol) and BHT (0.11g, 0.5 mmol) were dissolved in DCM (30 ml) and mixed at 0 °C under nitrogen to form a “colloidal dispersion”, to which a solution of DCC (7.2 g, 34.9 mmol) in DCM (40 ml) was added. The reaction was then left to proceed overnight at 0 °C, after which a white solid was present. The mixture was then filtered using syringe micro-filters before being passed through a basic alumina column. Following this, the solvent was removed under vacuum from the clear/colourless solution yielding a cloudy white mixture. This mixture was then filtered again using micro-filters to yield a clear colourless liquid (yield = 55%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 1.36 (s, 6H, (C(CH<sub>3</sub>)<sub>2</sub>)), 5.24 (Solvent), 5.85-5.88 (dd, 1H, CH<sub>2</sub>=CH), 6.12-6.17 (dd, 1H, CH<sub>2</sub>=CH), 6.19-6.26 (dd, 1H, CH<sub>2</sub>=CH).

FTIR (ATR corrected,  $\text{cm}^{-1}$ ):  $\sim 2900$  (C-H stretching),  $\sim 2850$  (C-H),  $\sim 2100$  (C=N),  $\sim 1800$  (C=O stretching),  $\sim 1650$  (C=N stretching),  $\sim 1200$  (C-O-C stretching).



**Figure 46** - (A)  $^1\text{H}$  NMR spectra of the synthesised VDMA. (B) ATR Corrected FTIR spectra of the synthesised VDMA.

As stated above, the VDMA product was synthesized with a yield of 55%, differing from the literature by -6%.<sup>103</sup> This is likely due to differences in the procedures used, but most specifically due to the basic-alumina column and syringe filter purification rather than the vacuum distillation performed in the literature.<sup>103</sup> Regardless, peaks in the NMR spectrum (Figure 46A) present at 1.36, 5.85-5.88, 6.12-6.17 and 6.19-6.26 ppm corresponding to the  $C(CH_3)_2$ ,  $\underline{CH}_2=CH$ ,  $\underline{CH}_2=CH$  and  $CH_2=CH$  in the VDMA respectively indicate successful synthesis of VDMA.<sup>103</sup> Signals in the IR spectrum (Figure 46B) at  $\sim 2900$ , 2850, 1800, 1650 and  $1200\text{ cm}^{-1}$  corresponding to the C-H stretching, C-H, C=O stretching, C=N stretching and C-O-C stretching respectively also indicate successful synthesis.<sup>103</sup> The NMR and IR spectroscopy results mostly match those from the literature, confirming VDMA was successfully synthesized, with the exception of the C=N vibration present in the IR spectrum at  $\sim 2100\text{ cm}^{-1}$ , which is not present in the literature.<sup>103</sup> The reason for this is unknown.

### 5.3 – Copolymer and Nanogel Formation

Due to time constraints, no experiments were conducted for the formation of copolymers of PS and VDMA, nor were any experiments conducted for nanogel formation. Since the nanogel was not synthesized, this similarly means that no CO<sub>2</sub> uptake experiments were conducted. However, the above sections should form the basis of possible future work.

## 6 – Conclusions

### 6.1 – New HCPs Conclusions

As demonstrated by the IR spectra, swelling and CO<sub>2</sub> capture results, the procedure used for synthesis of low stoichiometric ratio HCP is a viable method of obtaining acceptable CO<sub>2</sub> absorbent materials. These results also demonstrate the viability of synthesis of HCPs using several previously (to my knowledge) unused crosslinkers, such as the DCB, DCCMP and DCH. Perhaps most beneficial is the demonstration of viable HCP synthesis via methods wherein the crosslinking agent is not the solvent, which will greatly assist in syntheses of HCPs where the cost of the crosslinking agent is an issue and thus cannot be used in excess as in traditional methods.<sup>50, 51</sup> Also demonstrated was the unviability of the alternative mechanism,<sup>83-88</sup> which is likely not able to be improved upon.

Future research should focus on increasing the WEPS:CL ratio used in the detailed syntheses so that HCPs with higher crosslinking densities similar to the earlier work's HCP<sup>14</sup> may be produced using the crosslinkers featured in this thesis. Other crosslinkers could also be investigated using this method as well. These changes could, potentially, result in HCP materials with greater BET surface area, swelling and CO<sub>2</sub> capture capabilities than even the earlier work's HCP. The investigation of higher resolution IR and solid-state <sup>13</sup>C NMR spectroscopic techniques to more absolutely determine the degrees of crosslinking may also be beneficial for determining optimal synthesis conditions, such as optimal crosslinker and WEPS:CL ratios, in order to produce HCP systems with the greatest BET surface area, swelling and CO<sub>2</sub> uptakes. Finally, future research should investigate the viability of further cross linking an already crosslinked material such as the Purolite HCPs. This may prove as a viable way to produce HCP at lower cost, as lowly crosslinked HCPs synthesised from different, cheaper procedures (such as the Purolite HCPs) could be produced or bought and then simply further crosslinked until effective for swelling and CO<sub>2</sub> capture.

This thesis also demonstrated the potential viability of 100 wt % amine blend systems, with all blends featured in section 3.1.4 either outperforming or achieving CO<sub>2</sub> uptakes close to their aqueous counterparts discussed in section 1.2.1,<sup>20-22</sup> and their 100 wt % tertiary amine counterparts from the earlier work.<sup>14</sup> Unfortunately, however it was also demonstrated that the presence of the tertiary amines within the blends did not have a significant impact on the recyclability nor the iron catalysed degradation of the amines as previously discussed.<sup>76, 77</sup>

HCP/amine and HCP/amine blend systems could be improved in a variety of ways. Future research may find benefit in investigating the use of different amines<sup>18, 104</sup> with the HCP, particularly sterically hindered amines which demonstrate increased recyclability.<sup>104</sup> Additionally, changing the amine concentration or composition within the blends could also be investigated as this may affect recyclability and CO<sub>2</sub> uptake.<sup>105-109</sup> Amine-ionic liquid blends could also be investigated, but as discussed in section 1.2.3 this would come with other immediate issues related to recyclability.<sup>40</sup> Future studies would likely, however, see the greatest benefits from either investigating other sorbent liquids such as ionic liquids<sup>26-32, 110-114</sup> (particularly hydrophobic ionic liquids, discussed below), PEI and TEPA,<sup>67-69</sup> or by investigating

the addition of chelating agents to the amines/amine blends prior to swelling, which would chelate with the residual iron in the HCP and thus prevent the iron catalysed degradation of the amines observed thus far, drastically increasing recyclability.<sup>77</sup>

### 6.2 – [Bet][Tau] Ionic Liquid Conclusions

We believe the evidence presented in this thesis clearly demonstrates that the proposed synthesis from the literature procedure<sup>41</sup> is not valid. Rather than focussing on other methods to synthesise [Bet][Tau], future research should instead investigate other ionic liquids which could be combined with HCP for CO<sub>2</sub> capture applications instead, such as the imidazolium based ionic liquids [bmim][Tf<sub>2</sub>N] and [bmim][PF<sub>6</sub>] as discussed in section 1.2.2.<sup>27, 28</sup> Hydrophobic ionic liquids such as [bmim][Tf<sub>2</sub>N] should be especially investigated as their hydrophobicity may help to overcome the water-based recyclability and stability issues of ionic liquids discussed in section 1.2.2.<sup>110</sup> The hydrophobic imidazolium based 1-butyl-3-methylimidazolium hexafluoroacetylacetonate [bmim][hfac] also has the ability to coordinate metals due to the hexafluoroacetylacetonate [hfac] anion, and thus could also be combined with HCP both by itself and in blends with amines to achieve a similar effect to chelating agents.<sup>111</sup> Other amino acid based hydrophobic ionic liquids should also be investigated, such as 1-ethyl-3-methylimidazolium lysinate [emim][Lys] and 1-ethyl-3-methylimidazolium glycinate [emim][Gly], as described by Ohno and co-workers,<sup>113</sup> as their wide availability and generally cheap/easy syntheses are of particular benefit to CO<sub>2</sub> capture applications.

### 6.3 – RAFT Nanogel Conclusions

It is evident from the yield and spectral analyses that the method used in section 3.1.1 is suitable for small scale syntheses of the polystyrene m-CTA. This is not a novel concept, as RAFT homopolymerisation of styrene is a fairly generic procedure,<sup>94, 98, 115</sup> and has been reported elsewhere in the literature on a larger scale by Lowe and co-workers.<sup>115</sup> This procedure is likely unsuitable for larger scale syntheses, as Lowe and co-workers performed a synthesis similar to the one performed in this work at a 30 g scale but at 110 °C.<sup>115</sup> It is also worth noting that despite the low dispersity, since no solvent was used in this work there is an increased chance of self-coupling termination reactions, which may make the procedure used in this work undesirable when self-coupling is to be avoided.<sup>98</sup>

Future research should employ a similar synthesis to that used by Lowe and co-workers,<sup>115</sup> as a larger scale reaction (and thus larger, by mass, yields) is simply more convenient. Other RAFT agents may also be explored, such as 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid and 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl)pentanoic acid as used by Ratvijitvech and co-workers in their study on RAFT prepared HCPs,<sup>94</sup> though this may affect the ability to form copolymers with VDMA.<sup>103, 116, 117</sup> Usage of a solvent, such as THF, may also be employed to reduce self-coupling, but for this particular procedure wherein the polymer is to be crosslinked anyways this is likely unnecessary.

Despite having slightly lower yields compared to the adapted literature procedure, the procedure used to synthesis VDMA in section 3.2.1 displays obvious viability as a simpler method for this synthesis due to the use of a basic alumina column over a vacuum distillation.<sup>103, 116, 117</sup> This difference in yield can likely be overcome by simply adjusting the alumina column size, and thus only further demonstrates the viability of this simpler procedure. The synthesis performed in this thesis becomes increasingly attractive when compared to other literature syntheses of VDMA, such as Levere et al.<sup>117</sup> and Duong et al.'s<sup>116</sup> syntheses that only yielded VDMA in a 29.4 % overall yield, with considerably more difficult syntheses.<sup>116, 117</sup>

Future research should look to scale up the procedure featured in this synthesis, as despite its good % yield and simplicity, the actual mass of VDMA yielded is still quite low. It is unlikely that step 1 of the procedure can be improved upon, having already simple steps and a very high yield, and thus future research should investigate improving step 2 of the synthesis. This could be done by through the usage of different coupling reagents over DCC, as this may positively affect yield thus making for a more efficient synthesis, especially when scaled up. Alternatively, VDMA could be synthesised using or adapting the original synthesis developed by 3M, wherein VDMA is synthesised from NA2M using ethyl chloroformate as a dehydrating agent, with reported yields of up to 80%.<sup>118</sup>

Nanogel formation could be completed by first completing the copolymerisation of PS and pVDMA, which can simply be done via generic RAFT polymerisation techniques. Next, micelle formation should be accomplished by using cyclohexane as a solvent for the PS-b-PVDMA copolymer, and hexane as a solvent for the

PVDMA-b-PS copolymer, as suggested by Pascual et al.<sup>119</sup> and Tully et al.<sup>120</sup> respectively. Finally crosslinking should be performed such that the hyper crosslinking is performed first so that the basic crosslinks formed by VDMA crosslinking do not inhibit the FCA reaction required for hyper crosslinking. It thus follows that VDMA crosslinking be performed by simply immersing the hyper-crosslinked nanogel in TEPA, allowing crosslinks to form via aminolysis. Successful nanogel formation could then be confirmed by dynamic light scattering and CO<sub>2</sub> capture tests, and the nanogels could be furthermore combined with sorbent liquids or a solvent (e.g. water or ethylene glycol) to potentially improve CO<sub>2</sub> uptake. Future research could also explore the use of easier/cheaper to synthesise monomers instead of VDMA, such as the p(tBA) as used in the literature source that inspired this work.<sup>52</sup> Direct functionalisation of the HCP rather than indirect functionalisation could also be investigated. Li and co-workers, for example, employ a methodology in which the phenyl rings of the HCP are first hydroxylated, activating the phenyl rings and allowing for hyper crosslinking to be performed as normal despite the presence of the -OH groups.<sup>54</sup> These -OH groups are also, theoretically, capable of CO<sub>2</sub> capture (discussed section 1.2.3),<sup>37-39</sup> and thus may provide a promising material for CO<sub>2</sub> capture. Liao and co-workers also demonstrate the ability to directly ionically functionalise HCP (discussed section 1.3.2),<sup>53</sup> which may hold promise for CO<sub>2</sub> capture depending on the counterions used for the synthesis.

#### 6.4 – Overall Conclusions

From the data presented in this thesis it is clear that swollen HCP systems provide facile platforms to produce effective CO<sub>2</sub> capture materials, with even small changes to crosslinking density, crosslinking agent and sorbent liquid affecting the CO<sub>2</sub> uptake of the resulting materials. In particular the results generated in section 2 and section 5, as well as the suggestions for improvement given above, provide solid foundations for future research looking to improve upon the HCP systems featured in this thesis, whether by optimisation of crosslinking structure, changing of the sorbent liquid or functionalisation of the HCP via copolymerisation with VDMA. Expanding further, given their flexible, facile nature, with the correct optimisation or functionalisation these HCP systems may find use in other fields such as hydrogen sulphide capture<sup>121</sup> and hydrogen storage<sup>122</sup> and should be investigated for such applications in future research as well.

## 7 - Glossary

[Bet][Tau]	[Betaine][taurine] ionic liquid
[BF <sub>4</sub> ]	Tetrafluoroborate
[bmim]	1-butyl-3-methylimidazolium
[C <sub>2</sub> -mim]	1-ethyl-3-methylimidazolium
[C <sub>8</sub> -mim]	1-octyl-3-methylimidazolium
[emim]	Also 1-ethyl-3-methylimidazolium
[EtSO <sub>4</sub> ]	Ethyl sulfate
[hfac]	Hexafluoroacetylacetonate
[PF <sub>6</sub> ]	Hexafluorophosphate
[Tf <sub>2</sub> N]	Bis(trifluoromethylsulfonyl)imide
2C2PBD	2-cyano-2-propylbenzodithioate
2MA	2-methylalanine
AIBN	Azobisisobutyronitrile
AIH	Amine infused hydrogel
BET	Brunauer–Emmett–Teller
BHT	Butylated hydroxytoluene
CF	Chloroform
CL	Crosslinker
DAC	Direct air capture
DCB	Dichlorobutane
DCC	N,N'-dicyclohexylcarbodiimide
DCCMP	1,3-dichloro-2-(chloromethyl)-2-methylpropane
DCE	Dichloroethane
DCH	Dichlorohexane
DCM	Dichloromethane
DEA	Diethanolamine
EG	Ethylene glycol
EW	Earlier work
FCA	Friedel-Crafts alkylation
HCP	Hyper crosslinked polystyrene
LysK	Potassium lysinate
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MetK	Potassium 2-methylalaninate
M <sub>n</sub>	Number average molecular weight
MOF	Metal organic framework
M <sub>w</sub>	Weight average molecular weight
NA2M	N-acryloyl-2-methylalanine
p(tBA)	Poly( <i>tert</i> -butyl acrylate)
PAM	Polyacrylamide
PE	2-piperidineethanol
PEI	Polyethyleneimine
PHEAA	Poly( <i>N</i> -2-hydroxyethyl acrylamide)
POPs	Porous organic polymers
PS	Polystyrene
PS-mCTA	Polystyrene macro chain transfer agent
RAFT	Reversible addition-fragmentation chain transfer
SarK	Potassium sarcosinate
SEC	Size exclusion chromatography
TEA	Triethanolamine
TEPA	Tetraethylenepentamine
TrzPOP	Triazine porous organic polymer
VDMA	2-vinyl-4,4-dimethylazlactone
WEPS	Waste expanded polystyrene

## 8 – References

1. Masson-Delmotte, V., P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, and B. Zhou, Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. *Cambridge University Press, IPCC* **2021**.
2. Masson-Delmotte, V., P. Zhai, A. Pirani, S.L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M.I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T.K. Maycock, T. Waterfield, O. Yelekçi, R. Yu, and B. Zhou, Summary for Policymakers. In: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. *Cambridge University Press, IPCC* **2021**.
3. Heldebrant, D. J.; Koech, P. K.; Glezakou, V.-A.; Rousseau, R.; Malhotra, D.; Cantu, D. C., Water-Lean Solvents for Post-Combustion CO<sub>2</sub> Capture: Fundamentals, Uncertainties, Opportunities, and Outlook. *Chemical Reviews* **2017**, *117* (14), 9594-9624.
4. Kvamsdal, H. M.; Chikukwa, A.; Hillestad, M.; Zakeri, A.; Einbu, A., A comparison of different parameter correlation models and the validation of an MEA-based absorber model. *Energy Procedia* **2011**, *4*, 1526-1533.
5. MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P., An overview of CO<sub>2</sub> capture technologies. *Energy & Environmental Science* **2010**, *3* (11), 1645-1669.
6. Mazari, S. A.; Si Ali, B.; Jan, B. M.; Saeed, I. M.; Nizamuddin, S., An overview of solvent management and emissions of amine-based CO<sub>2</sub> capture technology. *International Journal of Greenhouse Gas Control* **2015**, *34*, 129-140.
7. Riboldi, L.; Bolland, O., Overview on Pressure Swing Adsorption (PSA) as CO<sub>2</sub> Capture Technology: State-of-the-Art, Limits and Potentials. *Energy Procedia* **2017**, *114*, 2390-2400.
8. Rufford, T. E.; Smart, S.; Watson, G. C. Y.; Graham, B. F.; Boxall, J.; Diniz da Costa, J. C.; May, E. F., The removal of CO<sub>2</sub> and N<sub>2</sub> from natural gas: A review of conventional and emerging process technologies. *Journal of Petroleum Science and Engineering* **2012**, *94-95*, 123-154.
9. Salvinder, K. M. S.; Zabiri, H.; Taqvi, S. A.; Ramasamy, M.; Isa, F.; Rozali, N. E. M.; Suleman, H.; Maulud, A.; Shariff, A. M., An overview on control strategies for CO<sub>2</sub> capture using absorption/stripping system. *Chemical Engineering Research and Design* **2019**, *147*, 319-337.
10. Keith, D. W.; Holmes, G.; St. Angelo, D.; Heidel, K., A Process for Capturing CO<sub>2</sub> from the Atmosphere. *Joule* **2018**, *2* (8), 1573-1594.
11. McQueen, N.; Gomes, K. V.; McCormick, C.; Blumanthal, K.; Pisciotta, M.; Wilcox, J., A review of direct air capture (DAC): scaling up commercial technologies and innovating for the future. *Progress in Energy* **2021**, *3* (3), 032001.
12. Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W., Direct Capture of CO<sub>2</sub> from Ambient Air. *Chemical Reviews* **2016**, *116* (19), 11840-11876.
13. Zeman, F., Energy and Material Balance of CO<sub>2</sub> Capture from Ambient Air. *Environmental Science & Technology* **2007**, *41* (21), 7558-7563.
14. Adam, E.; Myers, M.; Lowe, A. B., Polymers and Solvent Systems for the Direct Air Capture of Atmospheric Carbon Dioxide. *Curtin Internal* **2020**.

15. Caplow, M., Kinetics of carbamate formation and breakdown. *Journal of the American Chemical Society* **2002**, *90* (24), 6795-6803.
16. Danckwerts, P. V., The reaction of CO<sub>2</sub> with ethanolamines. *Chemical Engineering Science* **1979**, *34* (4), 443-446.
17. Stowe, H. M.; Hwang, G. S., Fundamental Understanding of CO<sub>2</sub> Capture and Regeneration in Aqueous Amines from First-Principles Studies: Recent Progress and Remaining Challenges. *Industrial & Engineering Chemistry Research* **2017**, *56* (24), 6887-6899.
18. El Hadri, N.; Quang, D. V.; Goetheer, E. L. V.; Abu Zahra, M. R. M., Aqueous amine solution characterization for post-combustion CO<sub>2</sub> capture process. *Applied Energy* **2017**, *185*, 1433-1449.
19. Kim, Y. E.; Lim, J. A.; Jeong, S. K.; Yoon, Y. I.; Bae, S. T.; Nam, S. C., Comparison of Carbon Dioxide Absorption in Aqueous MEA, DEA, TEA, and AMP Solutions. *Bulletin of the Korean Chemical Society* **2013**, *34* (3), 783-787.
20. Horng, S.-Y.; Li, M.-H., Kinetics of Absorption of Carbon Dioxide into Aqueous Solutions of Monoethanolamine + Triethanolamine. *Industrial & Engineering Chemistry Research* **2001**, *41* (2), 257-266.
21. Liao, C.-H.; Li, M.-H., Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine+N-methyldiethanolamine. *Chemical Engineering Science* **2002**, *57* (21), 4569-4582.
22. Zhang, X.; Zhang, C.-F.; Liu, Y., Kinetics of Absorption of CO<sub>2</sub> into Aqueous Solution of MDEA Blended with DEA. *Industrial & Engineering Chemistry Research* **2002**, *41* (5), 1135-1141.
23. Adeosun, A.; Abu-Zahra, M. R. M., Evaluation of amine-blend solvent systems for CO<sub>2</sub> post-combustion capture applications. *Energy Procedia* **2013**, *37*, 211-218.
24. Lu, J.-G.; Zheng, Y.-F.; Cheng, M.-D.; Wang, L.-J., Effects of activators on mass-transfer enhancement in a hollow fiber contactor using activated alkanolamine solutions. *Journal of Membrane Science* **2007**, *289* (1-2), 138-149.
25. Zoghi, A. T.; Feyzi, F.; Zarrinpashneh, S., Experimental investigation on the effect of addition of amine activators to aqueous solutions of N-methyldiethanolamine on the rate of carbon dioxide absorption. *International Journal of Greenhouse Gas Control* **2012**, *7*, 12-19.
26. Aghaie, M.; Rezaei, N.; Zendehboudi, S., A systematic review on CO<sub>2</sub> capture with ionic liquids: Current status and future prospects. *Renewable and Sustainable Energy Reviews* **2018**, *96*, 502-525.
27. Aki, S. N. V. K.; Mellein, B. R.; Saurer, E. M.; Brennecke, J. F., High-Pressure Phase Behavior of Carbon Dioxide with Imidazolium-Based Ionic Liquids. *The Journal of Physical Chemistry B* **2004**, *108* (52), 20355-20365.
28. Blanchard, L. A.; Gu, Z.; Brennecke, J. F., High-Pressure Phase Behavior of Ionic Liquid/CO<sub>2</sub> Systems. *The Journal of Physical Chemistry B* **2001**, *105* (12), 2437-2444.
29. Ramdin, M.; de Loos, T. W.; Vlugt, T. J. H., State-of-the-Art of CO<sub>2</sub> Capture with Ionic Liquids. *Industrial & Engineering Chemistry Research* **2012**, *51* (24), 8149-8177.
30. Shiflett, M. B.; Yokozeki, A., Solubilities and Diffusivities of Carbon Dioxide in Ionic Liquids: [bmim][PF<sub>6</sub>] and [bmim][BF<sub>4</sub>]. *Industrial & Engineering Chemistry Research* **2005**, *44* (12), 4453-4464.
31. Shin, E.-K.; Lee, B.-C.; Lim, J. S., High-pressure solubilities of carbon dioxide in ionic liquids: 1-Alkyl-3-methylimidazolium

- bis(trifluoromethylsulfonyl)imide. *The Journal of Supercritical Fluids* **2008**, *45* (3), 282-292.
32. Shukla, S. K.; Khokarale, S. G.; Bui, T. Q.; Mikkola, J.-P. T., Ionic Liquids: Potential Materials for Carbon Dioxide Capture and Utilization. *Frontiers in Materials* **2019**, *6*, 42.
33. Huang, Q.; Bhatnagar, S.; Remias, J. E.; Selegue, J. P.; Liu, K., Thermal degradation of amino acid salts in CO<sub>2</sub> capture. *International Journal of Greenhouse Gas Control* **2013**, *19*, 243-250.
34. Ramezani, R.; Mazinani, S.; Di Felice, R., State-of-the-art of CO<sub>2</sub> capture with amino acid salt solutions. *Reviews in Chemical Engineering* **2020**, *0* (0).
35. Xu, X.; Myers, M. B.; Versteeg, F. G.; Adam, E.; White, C.; Croke, E.; Wood, C. D., Next generation amino acid technology for CO<sub>2</sub> capture. *Journal of Materials Chemistry A* **2021**, *9* (3), 1692-1704.
36. Shen, X.; Du, H.; Mullins, R. H.; Kommalapati, R. R., Polyethylenimine Applications in Carbon Dioxide Capture and Separation: From Theoretical Study to Experimental Work. *Energy Technology* **2017**, *5* (6), 822-833.
37. Han, S.-J.; Yoo, M.; Kim, D.-W.; Wee, J.-H., Carbon Dioxide Capture Using Calcium Hydroxide Aqueous Solution as the Absorbent. *Energy & Fuels* **2011**, *25* (8), 3825-3834.
38. Salmón, I.; Cambier, N.; Luis, P., CO<sub>2</sub> Capture by Alkaline Solution for Carbonate Production: A Comparison between a Packed Column and a Membrane Contactor. *Applied Sciences* **2018**, *8* (6), 996.
39. Yoo, M.; Han, S.-J.; Wee, J.-H., Carbon dioxide capture capacity of sodium hydroxide aqueous solution. *Journal of Environmental Management* **2013**, *114*, 512-519.
40. Perumal, M.; Jayaraman, D., Amine-Ionic Liquid Blends in CO<sub>2</sub> Capture Process for Sustainable Energy and Environment. *Energy & Environment* **2022**.
41. Lu, B.; Yi, M.; Hu, S.; Wu, D.; Zhu, Z.; Wu, C.; Wang, Z.; Li, Y.; Zhang, J., Taurine-Based Ionic Liquids for Transdermal Protein Delivery and Enhanced Anticancer Activity. *ACS Sustainable Chemistry & Engineering* **2021**, *9* (17), 5991-6000.
42. Barkakaty, B.; Browning, K. L.; Sumpter, B.; Uhrig, D.; Karpisova, I.; Harman, K. W.; Ivanov, I.; Hensley, D. K.; Messman, J. M.; Kilbey, S. M.; Lokitz, B. S., Amidine-Functionalized Poly(2-vinyl-4,4-dimethylazlactone) for Selective and Efficient CO<sub>2</sub> Fixing. *Macromolecules* **2016**, *49* (5), 1523-1531.
43. Das, S. K.; Bhanja, P.; Kundu, S. K.; Mondal, S.; Bhaumik, A., Role of Surface Phenolic-OH Groups in N-Rich Porous Organic Polymers for Enhancing the CO<sub>2</sub> Uptake and CO<sub>2</sub>/N<sub>2</sub> Selectivity: Experimental and Computational Studies. *ACS Applied Materials & Interfaces* **2018**, *10* (28), 23813-23824.
44. Wang, J.; Wang, L.; Wang, Y.; Zhang, D.; Xiao, Q.; Huang, J.; Liu, Y.-N., Recent progress in porous organic polymers and their application for CO<sub>2</sub> capture. *Chinese Journal of Chemical Engineering* **2022**, *42*, 91-103.
45. Wang, W.; Zhou, M.; Yuan, D., Carbon dioxide capture in amorphous porous organic polymers. *Journal of Materials Chemistry A* **2017**, *5* (4), 1334-1347.
46. Xu, X.; Myers, M. B.; Versteeg, F. G.; Pejcic, B.; Heath, C.; Wood, C. D., Direct air capture (DAC) of CO<sub>2</sub> using polyethylenimine (PEI) “snow”: a scalable strategy. *Chemical Communications* **2020**, *56* (52), 7151-7154.
47. Xu, X.; Pejcic, B.; Heath, C.; Myers, M. B.; Doherty, C.; Gozukara, Y.; Wood, C. D., Polyethylenimine “Snow”: An Emerging Material for Efficient Carbon Removal. *ACS Applied Materials & Interfaces* **2019**, *11* (30), 26770-26780.

48. Xu, X.; Pejcic, B.; Heath, C.; Wood, C. D., Carbon capture with polyethylenimine hydrogel beads (PEI HBs). *Journal of Materials Chemistry A* **2018**, *6* (43), 21468-21474.
49. Davankov, V. A.; Tsyurupa, M. P., Structure and properties of hypercrosslinked polystyrene—the first representative of a new class of polymer networks. *Reactive Polymers* **1990**, *13* (1-2), 27-42.
50. Fu, Z.; Jia, J.; Li, J.; Liu, C., Transforming waste expanded polystyrene foam into hyper-crosslinked polymers for carbon dioxide capture and separation. *Chemical Engineering Journal* **2017**, *323*, 557-564.
51. Fu, Z.; Mohamed, I. M. A.; Li, J.; Liu, C., Novel adsorbents derived from recycled waste polystyrene via cross-linking reaction for enhanced adsorption capacity and separation selectivity of CO<sub>2</sub>. *Journal of the Taiwan Institute of Chemical Engineers* **2019**, *97*, 381-388.
52. Pan, Y.; Xu, Z.; Tan, W.; Zhu, Y.; Wang, Y.; Li, P.; Chen, X.; Sun, Z.; Li, C.; Jiang, B., Novel amino-functionalized hypercrosslinked polymer nanoparticles constructed from commercial macromolecule polystyrene via a two-step strategy for CO<sub>2</sub> adsorption. *New Journal of Chemistry* **2020**, *44* (48), 21125-21133.
53. Liao, X.; Pei, B.; Ma, R.; Kong, L.; Gao, X.; He, J.; Luo, X.; Lin, J., Hypercrosslinked Ionic Polymers with High Ionic Content for Efficient Conversion of Carbon Dioxide into Cyclic Carbonates. *Catalysts* **2022**, *12* (1).
54. Li, F.; Liu, J.; Liu, W.; Xu, Y.; Cao, Y.; Chen, B.; Xu, M., Preparation of hyper-cross-linked hydroxylated polystyrene for adsorptive removal of methylene blue. *RSC Advances* **2021**, *11* (41), 25551-25560.
55. Kumar, A.; Madden, D. G.; Lusi, M.; Chen, K. J.; Daniels, E. A.; Curtin, T.; Perry, J. J.; Zaworotko, M. J., Direct Air Capture of CO<sub>2</sub> by Physisorbent Materials. *Angewandte Chemie International Edition* **2015**, *54* (48), 14372-14377.
56. Lin, R.-B.; Chen, D.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M., A Zeolite-Like Zinc Triazolate Framework with High Gas Adsorption and Separation Performance. *Inorganic Chemistry* **2012**, *51* (18), 9950-9955.
57. Lin, Y.; Kong, C.; Chen, L., Amine-functionalized metal-organic frameworks: structure, synthesis and applications. *RSC Advances* **2016**, *6* (39), 32598-32614.
58. McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R., Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal-Organic Framework mmen-Mg<sub>2</sub>(dobpdc). *Journal of the American Chemical Society* **2012**, *134* (16), 7056-7065.
59. Shekhah, O.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Cairns, A. J.; Eddaoudi, M., A facile solvent-free synthesis route for the assembly of a highly CO<sub>2</sub> selective and H<sub>2</sub>S tolerant NiSIFSIX metal-organic framework. *Chemical Communications* **2015**, *51* (71), 13595-13598.
60. Shekhah, O.; Belmabkhout, Y.; Chen, Z.; Guillerm, V.; Cairns, A.; Adil, K.; Eddaoudi, M., Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture. *Nature Communications* **2014**, *5* (1), 4228.
61. Si, X.; Jiao, C.; Li, F.; Zhang, J.; Wang, S.; Liu, S.; Li, Z.; Sun, L.; Xu, F.; Gabelica, Z.; Schick, C., High and selective CO<sub>2</sub> uptake, H<sub>2</sub> storage and methanol sensing on the amine-decorated 12-connected MOF CAU-1. *Energy & Environmental Science* **2011**, *4* (11), 4522-4527.

62. Zhang, F.; Zou, X.; Gao, X.; Fan, S.; Sun, F.; Ren, H.; Zhu, G., Hydrogen Selective NH<sub>2</sub>-MIL-53(Al) MOF Membranes with High Permeability. *Advanced Functional Materials* **2012**, 22 (17), 3583-3590.
63. Xu, X.; Heath, C.; Pejcic, B.; Wood, C. D., CO<sub>2</sub> capture by amine infused hydrogels (AIHs). *Journal of Materials Chemistry A* **2018**, 6 (11), 4829-4838.
64. Xu, X.; Wood, C. D., A Highly Tunable Approach to Enhance CO<sub>2</sub> Capture with Liquid Alkali/amines. *Environmental Science & Technology* **2018**, 52 (18), 10874-10882.
65. Xu, X.; Yang, Y.; Acencios Falcon, L. P.; Hazewinkel, P.; Wood, C. D., Carbon capture by DEA-infused hydrogels. *International Journal of Greenhouse Gas Control* **2019**, 88, 226-232.
66. White, C.; Adam, E.; Sabri, Y.; Myers, M. B.; Pejcic, B.; Wood, C. D., Amine-Infused Hydrogels with Nonaqueous Solvents: Facile Platforms to Control CO<sub>2</sub> Capture Performance. *Industrial & Engineering Chemistry Research* **2021**, 60 (41), 14758-14767.
67. Liu, F.; Wang, S.; Lin, G.; Chen, S., Development and characterization of amine-functionalized hyper-cross-linked resin for CO<sub>2</sub> capture. *New Journal of Chemistry* **2018**, 42 (1), 420-428.
68. Bai, G.; Han, Y.; Du, P.; Fei, Z.; Chen, X.; Zhang, Z.; Tang, J.; Cui, M.; Liu, Q.; Qiao, X., Polyethylenimine (PEI)-impregnated resin adsorbent with high efficiency and capacity for CO<sub>2</sub> capture from flue gas. *New Journal of Chemistry* **2019**, 43 (46), 18345-18354.
69. Liu, F.; Fu, W.; Chen, S., Adsorption behavior and kinetics of CO<sub>2</sub> on amine-functionalized hyper-crosslinked polymer. *Journal of Applied Polymer Science* **2019**, 137 (12), 48479.
70. Chen, C.; Ahn, W.-S., CO<sub>2</sub> capture using mesoporous alumina prepared by a sol-gel process. *Chemical Engineering Journal* **2011**, 166 (2), 646-651.
71. Martínez, F.; Sanz, R.; Orcajo, G.; Briones, D.; Yáñez, V., Amino-impregnated MOF materials for CO<sub>2</sub> capture at post-combustion conditions. *Chemical Engineering Science* **2016**, 142, 55-61.
72. Ouyang, J.; Zheng, C.; Gu, W.; Zhang, Y.; Yang, H.; Suib, S. L., Textural properties determined CO<sub>2</sub> capture of tetraethylenepentamine loaded SiO<sub>2</sub> nanowires from  $\alpha$ -sepiolite. *Chemical Engineering Journal* **2018**, 337, 342-350.
73. Song, F.; Zhong, Q.; Ding, J.; Zhao, Y.; Bu, Y., Mesoporous TiO<sub>2</sub> as the support of tetraethylenepentamine for CO<sub>2</sub> capture from simulated flue gas. *RSC Advances* **2013**, 3 (45), 23785-23790.
74. Vieira, R. B.; Pastore, H. O., Polyethylenimine-Magadiite Layered Silicate Sorbent for CO<sub>2</sub> Capture. *Environmental Science & Technology* **2014**, 48 (4), 2472-2480.
75. Zhu, J.; Wu, L.; Bu, Z.; Jie, S.; Li, B.-G., Polyethylenimine-Grafted HKUST-Type MOF/PolyHIPE Porous Composites (PEI@PGD-H) as Highly Efficient CO<sub>2</sub> Adsorbents. *Industrial & Engineering Chemistry Research* **2019**, 58 (10), 4257-4266.
76. Fredriksen, S. B.; Jens, K.-J., Oxidative Degradation of Aqueous Amine Solutions of MEA, AMP, MDEA, Pz: A Review. *Energy Procedia* **2013**, 37, 1770-1777.
77. Goff, G. S.; Rochelle, G. T., Oxidation Inhibitors for Copper and Iron Catalyzed Degradation of Monoethanolamine in CO<sub>2</sub> Capture Processes. *Industrial & Engineering Chemistry Research* **2005**, 45 (8), 2513-2521.

78. Lepaumier, H.; Picq, D.; Carrette, P.-L., New Amines for CO<sub>2</sub> Capture. II. Oxidative Degradation Mechanisms. *Industrial & Engineering Chemistry Research* **2009**, *48* (20), 9068-9075.
79. Lepaumier, H.; Martin, S.; Picq, D.; Delfort, B.; Carrette, P.-L., New Amines for CO<sub>2</sub> Capture. III. Effect of Alkyl Chain Length between Amine Functions on Polyamines Degradation. *Industrial & Engineering Chemistry Research* **2010**, *49* (10), 4553-4560.
80. Lepaumier, H.; Picq, D.; Carrette, P.-L., New Amines for CO<sub>2</sub> Capture. I. Mechanisms of Amine Degradation in the Presence of CO<sub>2</sub>. *Industrial & Engineering Chemistry Research* **2009**, *48* (20), 9061-9067.
81. Acosta-Guzmán, P.; Mateus-Gómez, A.; Gamba-Sánchez, D., Direct Transamidation Reactions: Mechanism and Recent Advances. *Molecules* **2018**, *23* (9).
82. Chen, J.; Xia, Y.; Lee, S., Transamidation for the Synthesis of Primary Amides at Room Temperature. *Organic Letters* **2020**, *22* (9), 3504-3508.
83. Smith, M.; March, J., *March's advanced organic chemistry : reactions, mechanisms, and structure*. 6th ed.; Wiley-Interscience: Hoboken, N.J., 2007; p 707.
84. Bardhan, J. C.; Sengupta, S. C., 374. Resin acids. Part I. Synthesis of phenanthrene hydrocarbons derived from d-pimaric acid, and a new route to phenanthrene. *Journal of the Chemical Society (Resumed)* **1932**, 2520-2526.
85. Bogert, M. T., A New Process for the Synthesis of Phenanthrene and of Phenanthrene Derivatives. *Science* **1933**, *77* (1994), 289-289.
86. Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S., Ruthenium-Catalyzed Propargylation of Aromatic Compounds with Propargylic Alcohols. *Journal of the American Chemical Society* **2002**, *124* (40), 11846-11847.
87. Norris, J. F.; Sturgis, B. M., The Condensation of Alcohols, Ethers, and Esters with Aromatic Hydrocarbons in the Presence of Aluminum Chloride. *Journal of the American Chemical Society* **2002**, *61* (6), 1413-1417.
88. Olah, G. A., Carbocations and Electrophilic Reactions. *Angewandte Chemie International Edition in English* **1973**, *12* (3), 173-212.
89. Zhai, H.; Luo, S.; Ye, C.; Ma, Y., A Facile Asymmetric Route to (-)-Aphanorphine. *The Journal of Organic Chemistry* **2003**, *68* (21), 8268-8271.
90. Hansen, C. M., *Hansen solubility parameters : a user's handbook*. 2nd ed.; CRC Press: Boca Raton, 2007; p 519 p.
91. Dean, J. A.; Lange, N. A., *Lange's handbook of chemistry*. McGraw-Hill: New York, 1973; *15*, 7.41-7.70.
92. Fontanals, N.; Cortés, J.; Galià, M.; Maria Marcé, R.; Cormack, P. A. G.; Borrull, F.; Sherrington, D. C., Synthesis of Davankov-type hypercrosslinked resins using different isomer compositions of vinylbenzyl chloride monomer, and application in the solid-phase extraction of polar compounds. *Journal of Polymer Science Part A: Polymer Chemistry* **2005**, *43* (8), 1718-1728.
93. Jang, B. N.; Wilkie, C. A., The thermal degradation of polystyrene nanocomposite. *Polymer* **2005**, *46* (9), 2933-2942.
94. Ratvijitvech, T.; Barrow, M.; Cooper, A. I.; Adams, D. J., The effect of molecular weight on the porosity of hypercrosslinked polystyrene. *Polymer Chemistry* **2015**, *6* (41), 7280-7285.
95. Rivoira, L.; Studzińska, S.; Szultka-Młyńska, M.; Bruzzoniti, M. C.; Buszewski, B., New approaches for extraction and determination of betaine from *Beta vulgaris* samples by hydrophilic interaction liquid chromatography-tandem

- mass spectrometry. *Analytical and Bioanalytical Chemistry* **2017**, 409 (21), 5133-5141.
96. Lambert, I. H.; Hansen, D. B., Regulation of Taurine Transport Systems by Protein Kinase CK2 in Mammalian Cells. *Cellular Physiology and Biochemistry* **2011**, 28 (6), 1099-1110.
97. Görbitz, C. H.; Prydz, K.; Ugland, S., Taurine. *Acta Crystallographica Section C Crystal Structure Communications* **2000**, 56 (1), e23-e24.
98. Matyjaszewski, K.; American Chemical Society. Division of Polymer Chemistry.; American Chemical Society. Meeting, *Advances in controlled/living radical polymerization*. American Chemical Society: Washington, D.C., 2003; 688 p.
99. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process - A Second Update. *Australian Journal of Chemistry* **2009**, 62 (11), 1402-1472.
100. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process – A Third Update. *Australian Journal of Chemistry* **2012**, 65 (8), 985-1076.
101. Moad, G.; Rizzardo, E.; Thang, S. H., Living Radical Polymerization by the RAFT Process—A First Update. *Australian Journal of Chemistry* **2006**, 59 (10), 669-692.
102. Moad, G.; Rizzardo, E.; Thang, S. H., RAFT Polymerization and Some of its Applications. *Chemistry - An Asian Journal* **2013**, 8 (8), 1634-1644.
103. Prai-in, Y.; Boonthip, C.; Rutnakornpituk, B.; Wichai, U.; Montembault, V.; Pascual, S.; Fontaine, L.; Rutnakornpituk, M., Recyclable magnetic nanocluster crosslinked with poly(ethylene oxide)-block-poly(2-vinyl-4,4-dimethylazlactone) copolymer for adsorption with antibody. *Materials Science and Engineering: C* **2016**, 67, 285-293.
104. Bougie, F.; Iliuta, M. C., Sterically Hindered Amine-Based Absorbents for the Removal of CO<sub>2</sub> from Gas Streams. *Journal of Chemical & Engineering Data* **2012**, 57 (3), 635-669.
105. Bonenfant, D.; Mimeault, M.; Hausler, R., Estimation of the CO<sub>2</sub> Absorption Capacities in Aqueous 2-(2-Aminoethylamino)ethanol and Its Blends with MDEA and TEA in the Presence of SO<sub>2</sub>. *Industrial & Engineering Chemistry Research* **2007**, 46 (26), 8968-8971.
106. Dubois, L.; Kahasha Mbasha, P.; Thomas, D., CO<sub>2</sub> Absorption into Aqueous Solutions of a Polyamine (PZEA), a Sterically Hindered Amine (AMP), and their Blends. *Chemical Engineering & Technology* **2010**, 33 (3), 461-467.
107. Gómez-Díaz, D.; Muñoz-Mouro, A.; Navaza, J. M.; Rumbo, A., Diamine versus amines blend for CO<sub>2</sub> chemical absorption. *AIChE Journal* **2020**, 67 (1), e17071.
108. Shakir, S. W.; Wiheeb, A. D.; Ahmed, S. A., Tertiary amine blend for CO<sub>2</sub> capture: A kinetic investigation using Monoethanolamine, Triethanolamine and Piperazine. *IOP Conference Series: Materials Science and Engineering* **2021**, 1076 (1).
109. Xu, G.-W.; Zhang, C.-F.; Qin, S.-J.; Gao, W.-H.; Liu, H.-B., Gas-Liquid Equilibrium in a CO<sub>2</sub>-MDEA-H<sub>2</sub>O System and the Effect of Piperazine on It. *Industrial & Engineering Chemistry Research* **1998**, 37 (4), 1473-1477.
110. Fukaya, Y.; Ohno, H., Hydrophobic and polar ionic liquids. *Physical Chemistry Chemical Physics* **2013**, 15 (11), 4066-4072.

111. Mehdi, H.; Binnemans, K.; Van Hecke, K.; Van Meervelt, L.; Nockemann, P., Hydrophobic ionic liquids with strongly coordinating anions. *Chem. Commun.* **2010**, *46* (2), 234-236.
112. Mei, K.; He, X.; Chen, K.; Zhou, X.; Li, H.; Wang, C., Highly Efficient CO<sub>2</sub> Capture by Imidazolium Ionic Liquids through a Reduction in the Formation of the Carbene–CO<sub>2</sub> Complex. *Industrial & Engineering Chemistry Research* **2017**, *56* (28), 8066-8072.
113. Ohno, H.; Fukumoto, K., Amino Acid Ionic Liquids. *Accounts of Chemical Research* **2007**, *40* (11), 1122-1129.
114. Wang, C.; Luo, H.; Luo, X.; Li, H.; Dai, S., Equimolar CO<sub>2</sub> capture by imidazolium-based ionic liquids and superbase systems. *Green Chemistry* **2010**, *12* (11), 2019-2023.
115. Harvison, M. A.; Davis, T. P.; Lowe, A. B., Macromolecular thiolysis of oxiranes: end-group modification of RAFT prepared homopolymers. *Polymer Chemistry* **2011**, *2* (6), 1347-1354.
116. Duong, H. T. T.; Kamarudin, Z. M.; Erlich, R. B.; Li, Y.; Jones, M. W.; Kavallaris, M.; Boyer, C.; Davis, T. P., Intracellular nitric oxide delivery from stable NO-polymeric nanoparticle carriers. *Chem. Commun.* **2013**, *49* (39), 4190-4192.
117. Levere, M. E.; Ho, H. T.; Pascual, S.; Fontaine, L., Stable azlactone-functionalized nanoparticles prepared from thermoresponsive copolymers synthesized by RAFT polymerization. *Polymer Chemistry* **2011**, *2* (12), 2878-2887.
118. Gorodisher, I.; Pocius Alphonsus, V.; Gaddam Babu, N.; Hansen Richard, G. REACTIVE LIQUID MODIFIERS. WO 2010/011714 A2, 2009/07/22, 2010.
119. Pascual, S.; Blin, T.; Saikia, P. J.; Thomas, M.; Gosselin, P.; Fontaine, L., Block copolymers based on 2-vinyl-4,4-dimethyl-5-oxazolone by RAFT polymerization: Experimental and computational studies. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48* (22), 5053-5062.
120. Tully, D. C.; Roberts, M. J.; Geierstanger, B. H.; Grubbs, R. B., Synthesis of Reactive Poly(vinyl oxazolones) via Nitroxide-Mediated “Living” Free Radical Polymerization. *Macromolecules* **2003**, *36* (12), 4302-4308.
121. Vega, F.; Cano, M.; Camino, S.; Fernández, L. M. G.; Portillo, E.; Navarrete, B., Solvents for Carbon Dioxide Capture. In *Carbon Dioxide Chemistry, Capture and Oil Recovery*, 2018.
122. Lee, J. Y.; Wood, C. D.; Bradshaw, D.; Rosseinsky, M. J.; Cooper, A. I., Hydrogen adsorption in microporous hypercrosslinked polymers. *Chem Commun (Camb)* **2006**, (25), 2670-2.