JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Communication

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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b00235 • Publication Date (Web): 28 Feb 2017

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Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Design of Aminopolymer Structure to Enhance Performance and Stability of CO_2 Sorbents: Poly(propylenimine) vs. Poly(ethylenimine)

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Supporting Information Placeholder

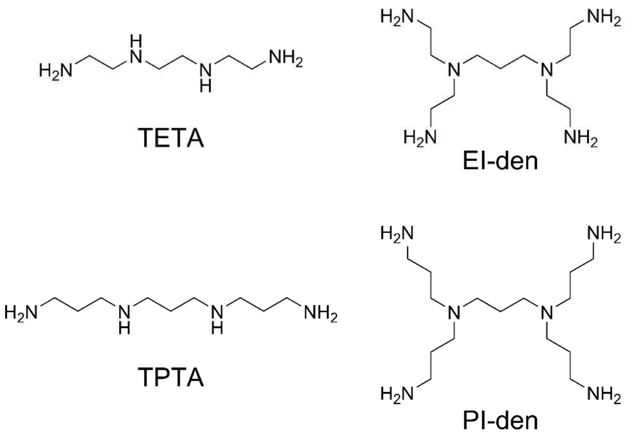
ABSTRACT: Studies on aminopolymer/oxide composite materials for direct CO_2 capture from air have often focused on the prototypical poly(ethylenimine) (PEI) as the aminopolymer. However, it is known that PEI will oxidatively degrade at elevated temperatures. This degradation has been ascribed to the presence of secondary amines, which, when oxidized, lose their CO_2 capture capacity. Here, we demonstrate the use of small molecule poly(propylenimine) (PPI) in linear and dendritic architectures supported in silica as adsorbent materials for direct CO_2 capture from air. Regardless of amine loading or aminopolymer architecture, the PPI-based sorbents are found to be more efficient for CO_2 capture than PEI-based sorbents. Moreover, PPI is found to be more resistant to oxidative degradation than PEI, even while containing secondary amines, as supported by FTIR, NMR, and ESI-MS studies. These results suggest that PPI-based CO_2 sorbents may allow for longer sorbent working lifetimes due to an increased tolerance to sorbent regeneration conditions, and suggest that the presence of secondary amines may not mean that all aminopolymers will oxidatively degrade.

Significant recent research on materials for direct capture of CO_2 from ambient air has focused on amines supported on oxide or polymeric materials.[1–3] Materials involving impregnation of an aminopolymer into a porous oxide support such as silica or alumina have been well-studied due to the high density of amines present in the material,[4–11] leading to high heats of adsorption, and thus, high CO_2 capture efficiencies, even from ultradilute streams such as ambient air (400 ppm).[12–15] The prototypical aminopolymer used in these studies is a randomly-branched poly(ethylenimine), PEI. However, PEI is known to oxidatively degrade in the presence of oxygen at elevated temperatures,[16–19] leading to development of processes that require sorbent regeneration (CO_2 desorption) be performed in environments free of O_2, such as vacuum or steam. These regeneration conditions impose additional costs and can still lead to the possibility of leaching of PEI from the material and loss of CO_2 capture capacity.[20–22]

Studies performed on aminosilanes grafted onto oxide supports have been used to determine the nature of oxidative degradation of various amines.[16,23,24] In particular, primary and tertiary amines appeared to be stable against oxidation but secondary amines degraded via imine and amide formation. Furthermore, degraded secondary amines also negatively impacted the CO_2 capture capability of neighboring primary amines, for grafted amines with an ethylenediamine structure. Though aminosilanes with only primary amines were found to be resistant to oxidation, the amine density achievable in these amine-grafted materials is typically lower than in the supported aminopolymer-based materials,[25,26] making them less desirable for industrial application.

In this study, we sought to utilize aminopolymer structures that had improved stability against oxidative degradation, which we hypothesized would be dendritic structures that consisted of only primary and tertiary amines. Linear aminopolymers containing secondary amines were also explored as control materials. Linear and dendritic aminopolymers with either ethylene or propylene spacers (Scheme 1) were supported inside mesoporous silica SBA-15, a model silica support characterized by long, straight cylindrical 8 nm diameter pores (Figure S1). The dendritic structures used in this study, termed EI-den and PI-den, were synthesized in house (see Supporting Information). Unexpectedly, PPI-based aminopolymers were found to behave quite differently, in an advantageous way, than traditional PEI-based aminopolymers.

Scheme 1. Linear and Dendritic Poly(ethylenimine) and Poly(propylenimine) in this Study



Results from nitrogen physisorption experiments confirm that the impregnated aminopolymers resided in the mesopores of SBA-15 (Table S1 and Figure S2). CO_2 capture was performed at 35 °C with simulated air (400 ppm CO_2/N_2) in a TGA and the quantity of CO_2 adsorbed was monitored by measuring the mass increase after the degassed sample was exposed to a flow of simulated air for 3 h. As shown in Figure 1, the amine efficiency and CO_2 capture capacity (Figure S3) increased as a function of amine loading for all molecules studied. Additionally, linear and dendritic aminopolymers appeared to have similar amine efficiencies for a given alkyl spacer length when normalized to the number of amines that are hypothetically active for CO_2 capture under dry conditions, suggesting no significant branching-dependence in capture capability for these small molecules.

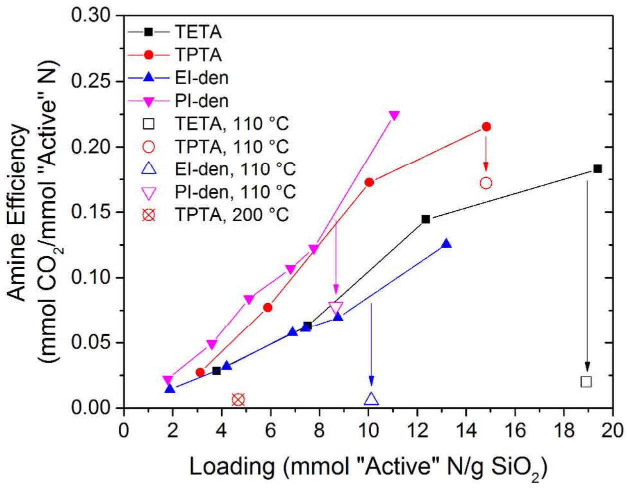


Figure 1. Amine efficiencies of aminopolymers impregnated in SBA-15 at 400 ppm CO_2/N_2 and 35 °C over a range of amine loading, normalized to the number of amines that are active for CO_2 capture under dry conditions (1° and 2° only). Open symbols indicate samples exposed to oxidative treatment at the listed temperature.

It was additionally observed that for both the linear and dendritic aminopolymers, the poly(propylenimines), TPTA and PI-den, were more efficient at CO_2 capture than the corresponding poly(ethylenimines), TETA and EI-den. This increased amine efficiency may be related to the basicity (pKa) of the various amines and nearest neighbor interactions between the amines. As the length of the alkyl spacer increased, the pKa of the amines was previously observed to increase and the extent of nearest neighbor interactions decreased.[27,28] Since CO_2 capture involves an acid-base interaction, it is possible that the increased basicity and decreased nearest neighbor interactions associated with increasing alkyl spacer length would increase the CO_2 capture capacity and efficiency.

The CO_2 capture capacities and amine efficiencies reported here (for TPTA, TETA, and PI-den) are higher than or (for EI-den) equivalent to those for randomly-branched PEI/SBA-15 systems at similar amine loadings, which reach approximately 0.1 mmol CO_2/mmol N at the highest amine loadings tested.[13,29] In general, small molecule aminopolymers have been shown to have higher amine efficiencies than randomly-branched PEI due to their lack of tertiary amines, which are inactive for CO_2 capture under dry conditions.[30] However, amine efficiencies up to 0.25 mmol CO_2/mmol N have been observed for other PEI/silica composites that utilize silica supports with higher pore volume, such as commercially-available CARiACT silicas.[12,31] The best amine efficiency achieved here, 0.21 mmol CO_2/mmol N for TPTA/SBA-15, approaches this value.

To test the stability of these molecules against oxidative degradation, ultra-zero grade air was bubbled through the liquid aminopolymers at 110 °C for 24 h, and the resulting oxidatively-treated aminopolymers were impregnated into SBA-15. As expected, the amine efficiency and CO_2 capture capacity of TETA decreased significantly (Figures 1 and S3), approximately 90%, due to the presence of secondary amines that were oxidized, whereas PI-den only lost approximately 50% of its amine efficiency. Unexpectedly, TPTA did not lose much efficiency (20% loss) after the oxidative treatment, despite containing secondary amines like TETA. Additionally, EI-den lost over 90% of its amine efficiency, despite having no secondary amines. Thus, it appears that aminopolymers with ethylene linkers were more susceptible to oxidative degradation than those with propylene linkers. We hypothesize that the conditions used during oxidative treatment caused thermal rearrangement reactions between molecules, resulting in production of secondary amines that could oxidize EI-den. This point is explained in greater detail below.

To investigate the structures created during the oxidative treatment, spectroscopic studies were carried out to examine the changes in functional groups. Fourier transform infrared (FTIR) spectra (Figure 2) were normalized to the Si-O-Si framework bending mode at 460 cm^{-1}. For all sorbent materials, the expected stretches above 2500 cm^{-1} corresponding to NH, OH, and CH_2 stretches were observed (Figure S4). After the oxidative treatment, some of these stretches decreased in intensity, but no other peaks appeared, as expected. The stretches near 1640, 1570 and 1475 cm^{-1} correspond to vibrations of the aminopolymers and ammonium carbamate ion pairs formed by capture of CO_2 from ambient air.[25,30,32,33] Below this region, the vibrational spectra are dominated by modes from the silica support, and are therefore not discussed here.

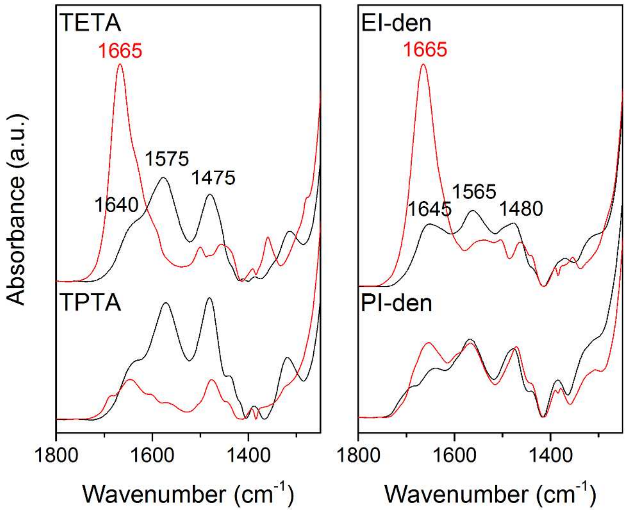


Figure 2. FTIR spectra for SBA-15-supported samples with fresh aminopolymers (black) and aminopolymers oxidatively-treated at 110 °C for 24 h (red). Spectra were acquired under vacuum and normalized to the Si-O-Si framework bending mode at 460 cm^{-1}.

After the oxidative treatment, an intense peak at 1665 cm^{-1} appeared in the spectra for the ethylenimine sorbents TETA and EI-den; this peak has been attributed to the stretching mode of C=N or C=O groups, consistent with oxidation of the aminopolymers.[17,19,23,34,35] This oxidation product is correlated with the sharp loss in CO_2 capacity. In contrast, the peak at 1665 cm^{-1} did not appear with significant intensity for the propylenimine sorbents TPTA and PI-den, consistent with retention of CO_2 capacity as seen in the results above.

To confirm that the oxidation trends observed here were not due the use of liquid-phase aminopolymers, essentially identical oxidation experiments were performed after impregnating the

SBA-15 with aminopolymer molecules (Figure S7). The results of the liquid-phase and impregnated sorbent oxidation experiments resulted in similar changes in all cases – a peak at 1665 cm^{-1} appeared in the spectra for both TETA and EI-den. Experiments were also performed with a longer chain linear poly(ethylenimine), pentaethylenehexamine (PEHA), and identical results to TETA were observed, as expected. TPTA and PI-den still did not appear to oxidize to a significant extent, but the intensity of the stretches for TPTA decreased significantly, indicating loss of organic content due to evaporation during the 110 °C thermal treatment.

To investigate the chemistry occurring during oxidative treatment, solution-phase NMR was performed on the neat and oxidatively-treated liquid aminopolymers (Figure 3). Prior to the oxidative treatment, TETA showed peaks at 2.81, 2.74, 2.68 ppm corresponding to the three types of methylene protons in the molecules. After exposure to the oxidative treatment, many peaks appeared in the 2.0-4.5 ppm region, indicating the formation of many new types of methylene protons. ^{13}C spectra (Figure S8) also indicated the formation of many types of methylene carbons detected in the 35-55 ppm region, supporting the formation of oxidized or thermally-rearranged species. Importantly, peaks in the 8.0-8.3 ppm region of the ^{1}H spectrum appeared, suggesting formation of imine (–CH=N–) and/or amide (–C(=O)NH–) species. These assignments are supported by the appearance of carbon shifts at 160-165 ppm, which have also been previously assigned to imine and amide species formed after oxidation of aminopolymers.[18]

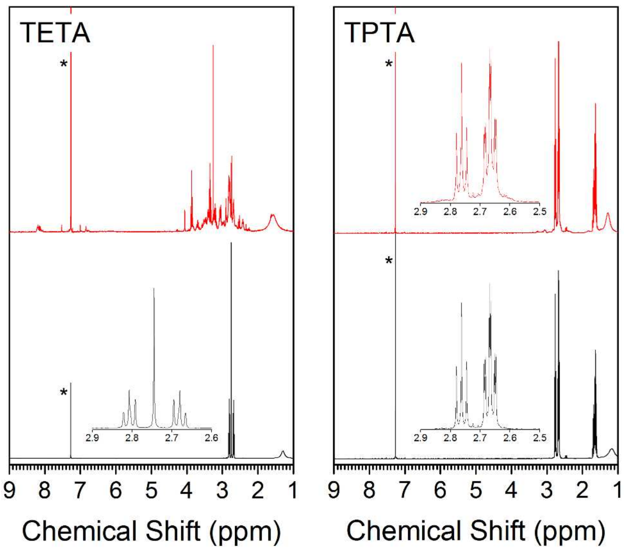


Figure 3. ^{1}H NMR spectra for linear aminopolymers TETA and TPTA, acquired in $CDCl_3$ (solvent peak indicated by asterisks). Black, lower: fresh aminopolymers; red, upper: aminopolymers oxidatively-treated at 110 °C for 24 h. Inset for TPTA: higher resolution methylene region, showing very little change after the oxidative treatment.

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed to examine the formation of oxidized and thermally-rearranged products (Figure S9). TETA was characterized by a single peak at m/z = 147, corresponding to singly protonated TETA, as expected. After oxidation, this peak disappeared completely and was replaced by peaks at m/z = 169 and 165, suggesting that all of the TETA molecules had been oxidized. These masses are consistent with thermal rearrangement and/or dehydrogenation reactions and addition of up to two oxygen atoms, consistent with formation of imines and amides, in agreement with IR and NMR studies.

In contrast, there was very little change in the TPTA ^{1}H and ^{13}C NMR spectra after oxidative treatment and the m/z = 189 peak was retained in ESI-MS, corroborating the observations from the IR spectra that TPTA was not oxidized significantly. Interestingly, some higher and lower molecular weight species were observed in the ESI-MS, indicating that TPTA did undergo some small amount of thermal rearrangement during the treatment (see Figure S9 for additional discussion). Thus, from the IR, NMR, and ESI-MS studies, the 20% decrease in CO_2 capture capacity for TPTA after the oxidative treatment is likely not associated with oxidation, but rather reaction between TPTA molecules at the elevated temperatures within an oxidizing environment.

As expected from the IR results, similar oxidation trends were observed for the dendritic species in ^{1}H NMR (Figure S10). Particularly striking for EI-den was the appearance of additional peaks in the 2.0-4.5 and 7.5-8.5 ppm regions, suggesting that significant oxidation occurred, in agreement with IR results and the over 90% decrease in the amine efficiency for sorbents based on this molecule. Some small additional peaks in the 2.0-4.5 ppm region also appeared for PI-den.

We hypothesize that similar types of oxygen-assisted thermal rearrangement reactions occurred for all molecules, resulting in intramolecular cyclization and/or alkylamine chain transfer reactions, as has been suggested previously.[36,37] These kinds of reactions could result in generation of secondary amines from the dendritic species, explaining the oxidation of EI-den. We also hypothesize that these thermal rearrangements are facilitated by the presence of primary amines, which have a higher density on the dendritic structures than the linear structures and may more easily form degradation products. This helps to explain why there was a larger decrease in amine efficiency and CO_2 capture capacity observed after the oxidative treatment for PI-den than TPTA.

Though TPTA appeared to be more resistant to oxidation under relatively mild (110 °C) conditions, it was still possible to oxidize the propylene-containing molecule at higher temperature (200 °C). The resulting compound was difficult to dissolve in methanol for impregnation in SBA-15 or chloroform-d for analysis via NMR, suggesting that the polarity of the resulting thermally-rearranged compound was significantly different from the parent molecule. The methanol-soluble fraction was impregnated into SBA-15 (Fig. 1) and had essentially no CO_2 capture capacity. However, these harsh, high-temperature thermal treatments are outside the typical operating envelope for post-combustion CO_2 capture and direct air capture.

These findings have important implications for design of sorbents for CO_2 capture. First, the oft studied randomly-branched poly(ethylenimine), PEI, may be replaced by a molecule with longer spacing in between the amines, poly(propylenimine), PPI, to increase the CO_2 capacity under flue gas or air capture conditions due to the increased basicity of the amines in PPI and the decreased nearest neighbor interactions. This may be achieved with a randomly-branched, dendritic or linear PPI.

Second, the presence of the accepted “bad actors” for deactivation of aminopolymers, the secondary amines, may not mean that the aminopolymer will readily oxidize. That is, it appears that secondary amines linked by propylene spacers still retain much of their CO_2 capture capability even after exposure to oxidation conditions relevant to carbon capture, making them less sensitive to regeneration conditions. This is consistent with oxidative stability studies of poly(allylamine), which also has three carbons in between nearest neighbor amines and which also was not observed to undergo oxidation.[19] However, molecules with amines linked by ethylene spacers, be they aminosilanes[16,23] or randomly-branched PEI, [17–19] have the potential to undergo oxidation regardless of the initial structure due to thermal rearrangement reactions, as was the case shown for EI-den.

In summary, linear and dendritic PPI were found to have higher CO_2 capture capacities and efficiencies compared to PEI. Moreover, these PPI-based sorbents were more resistant to oxidative degradation. These results suggest that development of higher molecular weight poly(propylenimine)-based sorbents, either linear or branched, may be advantageous for direct CO_2 capture from air. These types of sorbent molecules should provide superior CO_2 capture capacity and efficiency compared to their poly(ethylenimine) counterparts and additionally be more resistant to oxidative degradation, making them less sensitive to oxygen during regeneration and allowing for longer sorbent working lifetimes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website.
Detailed information about all materials and synthetic procedures, other figures as described in the text (PDF)

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Notes

Funding for the initial work was provided by Global Thermostat, LLC. Partial support was also provided as part of UNCAGE-ME, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under award no. DE-SC0012577.

ACKNOWLEDGMENT

Funding for this work was provided by Global Thermostat, LLC.

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