Synthesis of Polyethylenimines from the Manganese Catalyzed Coupling of Ethylene Glycol and Ethylenediamine

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Abstract: Polyethyleneimines find many applications in products such as detergents, adhesives, cosmetics, and for processes such as tissue culture, gene therapy, and CO2 capture. The current state-of-the-art technology for the production of the branched polyethyleneimines involves aziridine feedstock which is a highly toxic, volatile and mutagenic chemical and raises significant concern to human health and environment. We report here a novel method for the synthesis of branched polyethyleneimines from ethylene glycol and ethylenediamine feedstock which are much safer, environmentally benign, commercially available and potentially renewable feedstock. The polymerisation reaction is catalysed by a complex of an earth-abundant metal, manganese and liberates H_2O as the only by-product. Our mechanistic studies using DFT computation suggests that the reaction proceeds by the formation and subsequent hydrogenation of imine intermediates.

Introduction

Polyethyleneimines with annual global market of around £400 million are found in linear, branched, and ethoxylated form and have a number of applications such as in detergents, adhesives, cosmetics, and water treatment agents. Recently, they have also been employed for a number of biomedical applications such as tissue culture, drug delivery, gene delivery[1–4] as well as for CO_2 capture[5], and optoelectronic devices.[6] The branched polyethyleneimines are produced from the acid catalysed ring opening polymerisation of ethyleneimine or aziridine (Figure 1). Polyethyleneimine ethoxylated (PEIE) can be formed from the reaction of polyethyleneimine with ethylene oxide (Figure 1).[7] The main drawback of the current synthetic technology is that the feedstock – aziridine - is a highly reactive, toxic, corrosive, mutagenic and volatile chemical.[8] Furthermore, the polymerization process is exothermic and releases a considerable amount of heat that is hazardous and therefore it is difficult to store aziridine or ethylenimine due to the associated risk of auto-polymerisation. Additionally, due to the associated hazard, it can become challenging to take permission from the government regulatory authorities to use this feedstock at the commercial scale.[9] Currently, polyethyleneimines are mainly produced by the BASF and Nippon Shokubai. Thus, the development of an alternative method to make branched polyethylenimines from safer and environmentally benign feedstock will benefit human health, environment and economy.

Catalytic dehydrogenation is a green and atom-economic approach for the synthesis of organic compounds.[10] The synthesis of imines has been reported from the dehydrogenative coupling of alcohols and amines.[11] N-alkylation of amines using alcohols has also been reported using a dehydrogenative strategy.[12] The dehydrogenative coupling approach has also been utilized for the synthesis of polymers. For example, Robertson has reported the synthesis of polyesters from the dehydrogenative coupling of diols using a ruthenium-pincer catalyst.[13] Guan[14] and Milstein[15] have independently reported the synthesis of polyamides from the dehydrogenative coupling of diols and diamines using a ruthenium-

pincer catalyst. We[16,17], Robertson,[18] and Liu[19] independently reported the synthesis of polyureas from the dehydrogenative coupling of diamines and methanol/diformamides using Macho-type pincer complexes. To the best of our knowledge, the synthesis of branched polyethyleneimines from alcohols, and amines feedstock has not been reported in peer-reviewed literature. The only precedence can be found in patents published by BASF where the preparation of polyethylenimines has been claimed from diols and diamines or amino alcohols in the presence of precious metals-based catalysts such as ruthenium or iridium and H_2 gas.[20,21] Another patent claims the synthesis of branched polyethyleneimines through the formation of linear polyethyleneimines followed by their subsequent alkylation using β-chlorethylene or β-aminoethylsulphate.[22] The preparation of branched polyethyleneimines directly from 2-chloroethylamine in a one-pot two-stage process has also been reported. In this approach, the 2-chloroethylamine is first dehydrochlorinated to form aziridine which is then polymerised to form the branched polyethyleneimine. Here, we report a direct synthesis of branched polyethylenimines from the manganese catalysed coupling of ethylene glycol and ethylene diamine (Figure 1). Both ethylene glycol and ethylene diamine are environmentally benign, commercially available and can be sourced from biomass[23,24] making the reported method a greener and sustainable alternative to the current state-of-the-art process.
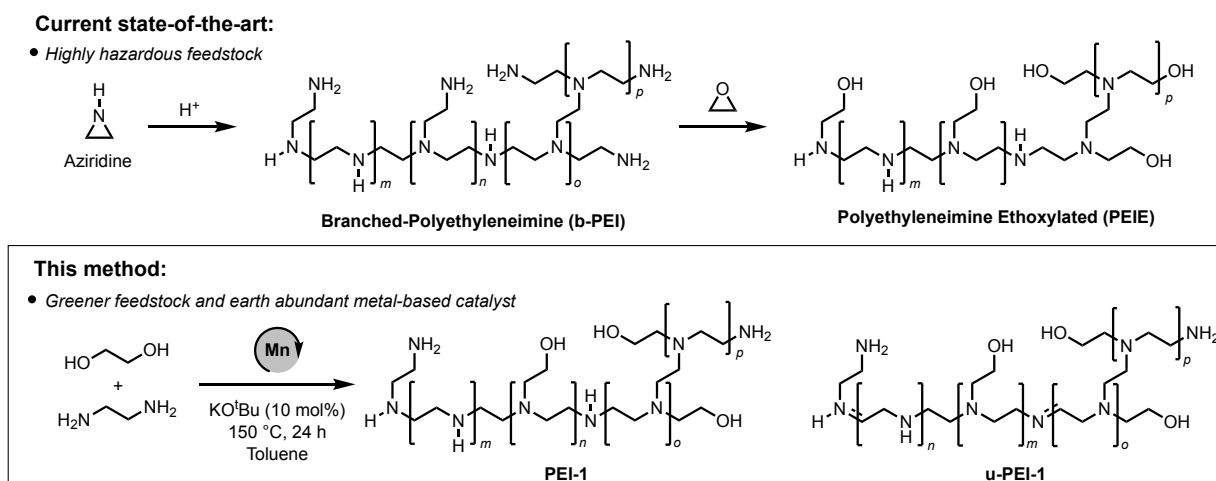

Figure 1 Preparation of branched and ethoxylated polyethyleneimine using the current state-of-the-art process and the method reported herein along with the structure of unsaturated polyethyleneimine (u-PEI-1).

Results and Discussion

We started our investigation by studying a variety of transition metal catalysts, supported by pincer-motif, from groups 7, 8 and 9 (complexes **1-5**) that are known for their activity towards catalytic (de)hydrogenation reactions.[25] These unoptimized reactions were performed in the presence of a base (e.g. K_2CO_3) at 150 °C for 24 h in THF solvent (Table 1) in a sealed 250 mL Young's flask. Of the precatalysts screened, Mn(PN^{H}P-iPr)(CO)$_2$Br (**1**, Mn-MACHO-iPr) and Ru(PN^{H}P^{Ph})(CO)ClH (**4**, Ru-MACHO) successfully mediated the formation of polymer, generating a mixture of unsaturated-poly(ethyleneimine) [u-PEI-1, unsaturation is due to the presence of C=N bond], poly(ethyleneimine) [PEI-1] and poly(ethyleneamide) [PA, $(C_2H_3NO)_n$] products (Figure 1, Table 1). IR and ^{13}C NMR spectra suggested the formation of branched over linear polyethyleneimine.[26] NMR spectra (^{1}H NMR, δ_H: 3.5-4 ppm, ^{13}C NMR, δ_C: ~60-70 ppm), IR spectra (brm ~3200-3300 cm^{-1}), and ESI-MS (Figure S84-87) analysis confirmed the presence of ethoxy groups in the polymer chain (see SI). Of note, when the tert-butyl derivative (**2**, Mn-MACHO-tBu) instead of **1** was used, no coupling products were observed and the reaction returned unreacted starting materials. In all cases and under the conditions shown in Table 1,

the conversion to polymeric products was low, as indicated by low isolated yields, measured gas released, and the requirement to remove residual ethylene glycol (identified by ^{1}H and ^{13}C NMR spectroscopies)[27] from the product mixture by distillation. As higher conversion was obtained using complex **1**, this earth-abundant Mn-precatalyst was taken forward for optimization studies.

Table 1. Optimisation of precatalyst choice for the coupling of ethylenediamine and ethylene glycol.[a]
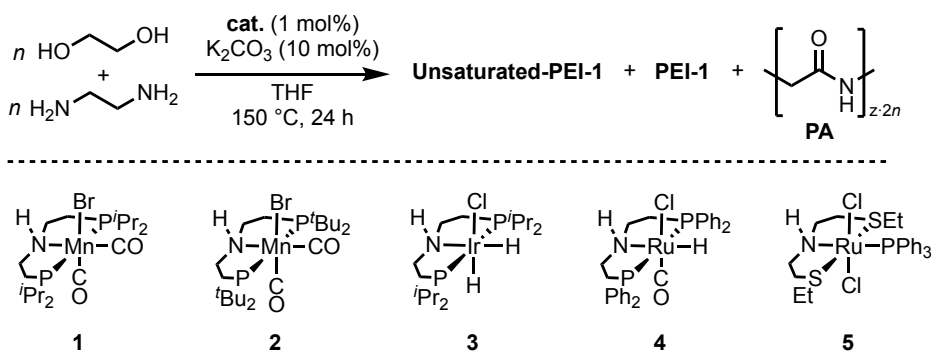
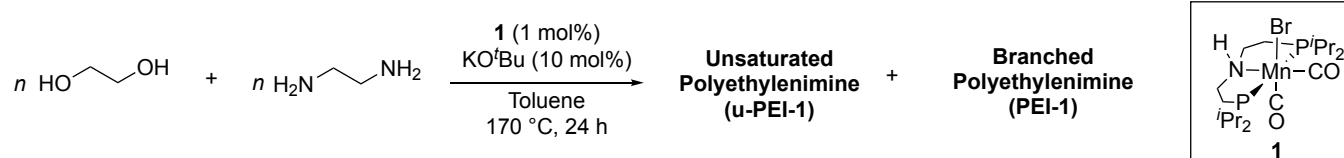| Entry	cat.	H_2 released / mL	Isolated Yield /mg (%)[b]	Products
1	**1**	<5	44 (27)	u-PEI-1 / PEI-1, PA
2	**2**	0	-	-
3	**3**	<5	6	Complex mixture
4	**4**	<5	25 (15)	u-PEI-1 / PEI-1, PA
5	**5**	<5	10 (6)	PA

[a] Experimental conditions: **1** (1 mol%), K_2CO_3 (10 mol%), ethylene glycol (2 mmol), ethylene diamine (2 mmol), 150 °C, 24 h, sealed 250 mL system; [b] theoretical yield based on exclusive formation of major product, u-PEI-1.

Decreasing the reaction vessel size to 100 mL and increasing the temperature to 170 °C resulted in a similar yield (26 %) and selectivity of the reaction, producing a mixture of u-PEI-1, PEI-1 and polyamide, and releasing 40 mL of gas (Table 2, Entry 1). A $^{13}C\{^1H\}$ NMR (in D_2O) of the reaction products shows signals at δ_C 179.8 and 155.4 ppm, attributed to amide (PA) and imine functionalities, respectively. Infrared analysis of the product mixture showed the presence of bands at v1634 cm^{-1} and v1577 cm^{-1}, attributed to C=N/C=O for u-PEI-1 and PA and N-H for PEI-1 and PA, respectively. Doubling the reaction time to 48 h did not improve the isolated yields obtained, however the volume of H_2 evolved did halve in this time, which could indicate further conversion to polyethyleneimine (PEI-1) from unsaturated polyethyleneimine (u-PEI-1) intermediate – although both were still present in the resulting mixture (Table 2; Entry 2). Increasing the loading of K_2CO_3 from 10 mol% to 50 mol% (Table 2; Entry 3) resulted in a similar volume of H_2 being evolved, however, the presence of residual K_2CO_3 obfuscated spectroscopic analysis.

Reduction of the temperature to 150 °C (Entry 4) in a 100 mL sealed system improved selectivity of the reaction to a mixture of water-soluble PEI-1 and u-PEI-1 (*i.e.* no polyamide observed). A $^{13}C\{^1H\}$ NMR (D_2O) spectrum obtained of this product mixture showed a signal at δ_C 164.6 ppm, attributed to the imine functionality of u-PEI-1. Using 2 mol% of complex **1** and 10 mol% of K_2CO_3 for 24 h at 170 °C resulted in a mixture of u-PEI-1 and PEI-1 with moderate yield (44%), releasing 15 mL of H_2 gas (Table

2; Entry 5). Unsaturation under these conditions is spectroscopically indicated by a strong absorbance at v1655 cm^{-1} and weak signal at δ_C 164.6 ppm indicative of an imine functionality. A further increase in selectivity to saturated PEI-1 is gained through application of KO^{t}Bu, rather than K$_2$CO$_3$, as a base (Table 2; Entry 6), indicated through a reduction in the shoulder corresponding to $v_{C=N}$ in the resulting infrared spectrum (see SI, Figure S12F). However, isolated yields remain relatively unchanged (*c.f.* 26% and 28% for K$_2$CO$_3$ and KO^{t}Bu, respectively). These data suggest the significance of base in a hydrogen borrowing process for the synthesis of PEI-1 via formation and hydrogenation of imines; a phenomenon that has been commented upon before.[12,28,29] The role of potassium *tert*butoxide in lowering the barrier for aldehyde hydrogenation through aiding alcohol release from the metal center has also been recently reported.[30] Indeed, performing the reaction at 150 °C with KO^{t}Bu (10 mol%) now almost exclusively forms PEI-1 (Table 2; Entry 7), albeit with very poor conversion (isolated yield 18%).

Table 2. Optimisation of reaction conditions for the dehydrogenative coupling of ethylene glycol and ethylene diamine with complex **1**.[a]

n HO-CH$_2$CH$_2$-OH + n H$_2$N-CH$_2$CH$_2$-NH$_2$ → (1 (1 mol%), KO^{t}Bu (10 mol%), Toluene, 170 °C, 24 h) → Unsaturated Polyethylenimine (u-PEI-1) + Branched Polyethylenimine (PEI-1)

Entry	1 /mol%	Base (mol%)	Solvent	H$_2$ released /mL	Product(s)	Yield /mg (%)[b]	M$_n$ [c] /g mol^{-1}	Đ [c]	T$_g$ /°C	T$_m$ /°C	T$_d$ [d] /°C
1	1	K$_2$CO$_3$ (10)	THF	40	u-PEI-1, PEI, PA	42 (26)	-	-	-	139.6	245
2[e]	1	K$_2$CO$_3$ (10)	THF	20	**u-PEI-1**, PEI-1, PA	22 (13)	38,500	1.4	-	182.8, 187.9	260
3	1	K$_2$CO$_3$ (50)	THF	15	N/A	110[f]	-	-	-	139.4	261
4[g]	1	K$_2$CO$_3$ (10)	THF	<5	u- PEI-1, PEI-1	50 (29)	58,600	1.2	-	169.5, 180.8	229
5	2	K$_2$CO$_3$ (10)	THF	15	**u-PEI-1**, PEI-1	75 (44)	58,600	1.2	-	180.9, 191.8	259
6	1	KO^{t}Bu (10)	THF	<5	u-PEI-1, **PEI-1**	49 (28)	48,400	1.2	−32.9	-	269
7[g]	1	KO^{t}Bu (10)	THF	<1	**PEI-1**	32 (18)	22,600	1.4	-	-	250
8[h]	1	KO^{t}Bu (10)	THF	<5	u-PEI-1, **PEI-1**	55 (32)	24,100	1.3	-	176.1, 181.8	254
9[i]	1	KO^{t}Bu (10)	THF	<5	u-PEI-1, **PEI-1**	44 (26)	27,000	1.3	−36.5	179.6, 191.6	240
10[g]	1	KO^{t}Bu (10)	Toluene	<1	**PEI-1**	160 (92)	59,000	1.1	−31.3	189.8	235
11	1	K$_2$CO$_3$ (10)	Toluene	<5	u-PEI-1, **PEI-1**	164 (95)	26,900	1.9	-	166.5	238
12[j]	1	KO^{t}Bu (10)	-	<5	**PEI-1**, i[k]	113 (65)	61,600	1.1	−30.7	151.4	237
13[l]	1	KO^{t}Bu (10)	Toluene	<5	**PEI-1**	116 (67)	63,700	1.1	−32.2	176.0	238
14[m]	1	KO^{t}Bu (10)	Toluene	<5	**PEI-1**	99 (57)	62,300	1.1	-	-	250

[a] Experimental conditions: 170 °C, 24 h, 2 mmol C$_2$H$_6$O$_2$ [0.5 M in THF or toluene], sealed 100 cm^3 system; [b] Based on major product (indicated in bold), all yields are isolated yields; [c] Determined by GPC – see text for limitations; [d] Defined as 5% mass loss after solvent loss; [e] 48 h; [f] contains residual K$_2$CO$_3$; [g] 150 °C; [h] 4:1 [C$_2$H$_6$O$_2$]:[C$_2$H$_8$N$_2$]; [i] 250 mL sealed system; [j] no solvent; [k] unidentified impurity; [l] 1.0 M [C$_2$H$_6$O$_2$]; [m] H$_2$O (2 eq. to C$_2$H$_6$O$_2$).

Increasing the vessel size from 100 mL to 250 mL or changing the ratio of ethylene glycol : ethylene diamine from 1:1 to 1:4 made little difference to the yield obtained and did not change the observed

selectivity significantly (Table 2; Entries 8 and 9, respectively). Remarkably, a significant increase to the reaction yield was obtained through the use of toluene as a solvent with KO^{t}Bu base, allowing selective formation of branched-polyethyleneimine (PEI-1) exclusively (v_{N-H} 1577 cm^{-1}) with isolated yield of 92% (Table 2; Entry 10). Use of toluene with K_2CO_3 base retains a high yield (95%), but some degree of unsaturation remains ($v_{C=N}$ 1649 cm^{-1} and δ_C 164.6 ppm), as shown in Table 2; Entry 11.

As both substrates for this transformation are liquids, we also attempted the reaction in the absence of solvent. However, alongside the generation of PEI-1, performing the reaction neat produces some unidentified side-product (Table 2; Entry 12). This may be due to poor mixing of these small scale (2 mmol) reactions. As such, the reaction was also conducted at higher concentration (1M vs 0.5 M [substrate]), which did retain selectivity, but a drop in isolated yield to 67% (*c.f.* 92%) at this higher concentration was noted (Table 2; Entry 13). Addition of water to the reaction (2 eq. to diol) at the onset results in the formation of PEI-1 in moderate yield (Entry 14, 57%). Additionally, no conversion to PEI-1 or u-PEI-1 was observed when the reaction was carried out under open conditions (see ESI), or in the absence of any of: catalyst, base, or ethylene glycol, with these control reactions all returning unreacted starting materials. **Therefore, the optimized conditions for the coupling of ethylene glycol and ethylene diamine to PEI-1 are as follows**: **1** (1 mol%), KO^{t}Bu (10 mol%), 24 h, toluene [0.5 M ethylene glycol/ethylene diamine], 150 °C.

Thermal gravimetric analysis of the PEI-1 samples obtained often displayed the presence of entrained water/solvent in several samples through a small (<10%) mass loss around 100–120 °C, despite drying the samples under reduced pressure at 120 °C for several hours post work-up. After this initial mass loss, the samples were relatively stable up to ~230 °C, after which decomposition began. Decomposition temperature, T_d (defined as 5% mass loss, after solvent loss) of the isolated polymers were found to be in the range of 235–269 °C. Differential scanning calorimetry performed on the prepared samples (–50–200 °C) revealed low temperature glass transition around –32°C (when observed) and T_m ranging between 167–192 °C. Where mixtures of PEI-1 and u-PEI-1 were produced, two exothermic events, which could be attributed to localized melting regions, were observed. The presence of significant amounts of PA or impurities lead to a reduction in the observed melting temperature. These observed thermal characteristics are in line with those previously reported samples of polyethyleneimines.[6,7,26]

The molecular weight and dispersity of each sample of polyethyleneimine was investigated through gel permeation chromatography (relative to PEG/PEO standards) using H_2O eluent. In all cases, high molecular weight material (M_n > 24,000 g mol^{-1}) with narrow polydispersity (Đ 1.1 – 1.4 typically) was produced. Importantly, it should be noted that, under our GPC measurement conditions, a commercial sample of branched PEI (expected molecular weight of 10,000 g mol^{-1}) returned M_n ≈3× higher than reported, and our calibration is only valid between 200 – 50,000 g mol^{-1} due to the size exclusion limitations of our column. Therefore, caution must be applied when considering the molecular weights presented here. Crucially, what can be inferred from the GPC data obtained is that the products obtained are: polymeric in nature; have narrow dispersity and likely have high molecular weight (M_n > 10,000 g mol^{-1}, *c.f.* commercial b-PEI, see SI).
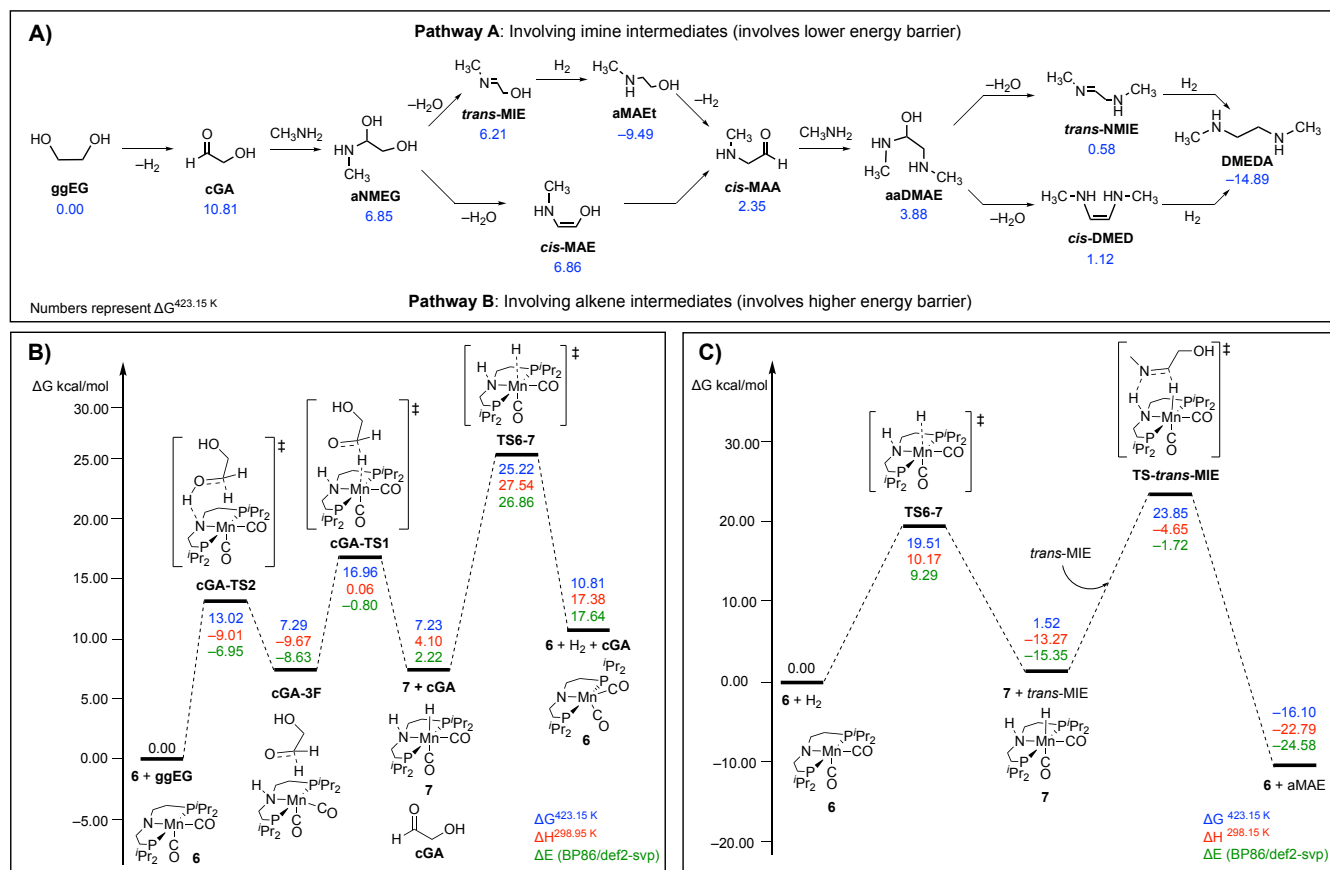
Figure 2 A) Pathways and thermodynamics driving forces for the formation of dimethyl ethylenediamine (DMEDA) from ethylene glycol; **B**) Free energy profiles for the proposed pathways for dehydrogenation of ethylene glycol to give glycol aldehyde (cGA); **C**) Free energy profiles of the proposed pathways for hydrogenation of *trans*-MIE (*trans*-methyl imine ethanol) to give methylamine ethanol, aMAE.

With reaction condition optimization and product characterization in hand, we turned to DFT computation to probe the mechanism of the catalytic coupling of ethylene glycol and ethylene diamine. We first studied thermodynamic driving forces for the reaction of ethylene glycol with methyl amine to form dimethyl ethylenediamine (**DMEDA**) through various pathways at the PBE0-D3[pcm,THF]/def2-TZVP//RI-BP86[pcm,THF]/def2-SVP level of theory. Lowest-lying pathways are shown in Figure 2A (full details in the ESI, Section 2.1, Scheme S1). The reaction starts with the dehydrogenation of ethylene glycol to form the cis conformer of glycol-aldehyde (**cGA**) with ΔG = 10.8 kcal/mol. Methylamine is then added to hydroxyl ethanal to afford the anti-conformer of *N*-methyl ethylene glycol (**aNMEG**) which dehydrates to form either an imine (*trans*-methyl imine ethanol [**trans-MIE**], pathway A) or an alkene (*cis*-methylamine ethenol [**cis-MAE**], pathway B) both leading to form an aldehyde, *cis*-methylamine aldehyde (**cis-MAA**). The reaction of **cis-MAA** with methyl amine followed by dehydration again leads to the formation of an imine (**trans-NMIE**) or an alkene (**cis-DMED**) of similar energy which upon hydrogenation can lead to the formation of **DMEDA**. Our studies showed that the energetics for the formation of the branched oligomer is similar or slightly more favorable than those of the linear oligomers as seen in Schemes S4a and S4b (SI). We then studied the mechanistic pathway involving manganese complexes as described below.

(a) Dehydrogenation of ethylene glycol: Based on well documented literature of pincer chemistry,[31,32] it is likely that the first step is the generation of amido complex **6** from the reaction of precatalyst **1** with base (e.g. KO^tBu). At our level of theory, dehydrogenation of ethylene glycol to give glycol aldehyde

(**cGA**) using complex **6** is similar to that of MeOH as recently reported by us, *i.e.* the reaction proceeds in a stepwise transfer of hydrogen *via* a zwitterionic intermediate, **cGA-3F** (Figure 2B).[17] The highest barrier of the two steps is found for **cGA-TS1** corresponding to the transfer of hydride at $\Delta G^{\ddagger}$ = 17.0 kcal/mol to afford the separated product, **cGA** and the hydrogenated catalyst **7**. The regeneration of the active catalyst **6** from **7** is the rate limiting step with an overall barrier of $\Delta G^{\ddagger}$ = 25.22 kcal/mol at **TS6-7** corresponding to the transfer of hydrogen. This overall barrier is lower than that for methanol dehydrogenation, where $\Delta G^{\ddagger}$ = 32.6 kcal/mol *via* the same TS was obtained,[17] probably because glycol aldehyde formed from ethylene glycol is stabilised by intramolecular H-bonding between the carbonyl O atom and the remaining OH group (formation of **cGA** is endergonic by ΔG = 10.8 kcal/mol). We also found that the overall barrier for catalyst regeneration *via* **TS6-7** is further reduced by 2.7 – 5.4 kcal/mol through participation of protic solvents (*e.g.* water).[17]

(b) (De)hydration steps: Many of the elementary steps in Figure 2A involve hydration or dehydration steps interconverting alcohols and corresponding unsaturated intermediates. We first computed the barrier for the uncatalyzed elimination of water (see SI, Scheme S3). Established in literature,[33] the strain in such four-membered transition states in such processes can be alleviated by the involvement of protic substrates acting as proton relays. Interestingly, the involvement of a single water molecule reduces the barriers by ~20 kcal/mol, with $\Delta G^{\ddagger}$ = 38.5 kcal/mol and 39.8 kcal/mol, relative to **ggEG** (see SI, Scheme S3). This is consistent with previous reports by Poater, where the energy barrier to dehydration decreases from 54.2 kcal/mol to 39.5 or 34.1 kcal/mol when assisted by two water or benzyl alcohol molecules, respectively.[34] Realizing the high barrier observed in the dehydration step, we explored the possible involvement of Mn catalysts such as **6** in these processes. In view of the known ability of complex **6** to heterolytically split the OH bond in water,[35] it is reasonable to assume that a corresponding OH activated intermediate can be involved, viz. the [Mn(OH)-N(H)] hydrated complex, **8**. Formation of this complex is slightly exergonic by ΔG = –0.59 kcal/mol (see SI, section 2.6). Our computational studies showed that the barrier for the formation of an imine product (*e.g.* ***trans*-MIE**, $\Delta G^{\ddagger}$ = 26.35 kcal/mol or ***trans*-NMIE**, $\Delta G^{\ddagger}$ = 25.1 kcal/mol) is much lower than that of an alkene product *e.g.* (***cis*-MAE**, $\Delta G^{\ddagger}$ = 41.78 kcal/mol or ***cis*-DMED**, $\Delta G^{\ddagger}$ = 36.8 kcal/mol). Full details on the pathways and barriers for the manganese catalysed (de)hydration steps can be found in the SI (section 2.6).

(c) Hydrogenation of imine and olefin intermediates:

Finally, we turn to steps involving hydrogenation of unsaturated intermediates. Hydrogenation of imines (C=N) have been reported to be efficiently catalysed by a triazine core-based (PN$_5$P) Mn catalyst through an outer sphere mechanism to afford amines.[36,37] In contrast, hydrogenation of alkenes (C=C) have been reported to be challenging using such complexes, although Kirchner and coworkers have shown that alkyl Mn(I) complexes can be used under base-free conditions to hydrogenate mono- and di-substituted alkenes *via* alkyl migration.[38] We have shown computationally that the dehydrogenation of amides affording ketenes (with a C=N moiety) can be efficiently catalysed by **6**.[17] The same is thus to be expected for the reverse reaction, hydrogenation of imines. We have now corroborated this by explicit study of the formation of methylamine ethanol (**aMAE**) by the hydrogenation of ***trans*-MIE**. This process is initiated by the well-studied H$_2$ activation by complex **6**, followed by H-transfer to ***trans*-MIE** through the transition state **TS-*trans*-MIE** (Figure 2C). The hydrogen transfer process occurs in a concerted manner and the overall barrier for the general process is $\Delta G^{\ddagger}$ = 23.85 kcal/mol as shown in Figure 2C. Similar results are obtained for the catalytic hydrogenation of the C=N double bond in ***trans*-NMIE** affording **DMEDA**. H transfer to ***trans*-NMIE** occurs in a rather concerted fashion *via* ***trans*-NMIE-TS** (Scheme S12) with a barrier of $\Delta G^{\ddagger}$ = 21.92 kcal/mol. In contrast, hydrogenation of non-polar C=C double bond by complex **7** is indicated to be much less favourable. As an illustrative example, that of ***cis*-DMED** to form **DMEDA** (the same final product as obtained from reduction of the imine moiety in trans-NMIE, c.f. Scheme S12) is illustrated in Scheme S13. As with hydration steps of such olefins, a large barrier is computed for hydrogenation by **7** ($\Delta G^{\ddagger}$ = 35.4 kcal/mol).

Conclusion

In conclusion, we present here a new methodology for the synthesis of polyethyleneimines based on manganese catalysed dehydrogenative coupling of ethylene glycol and ethylene diamine. The methodology is significantly greener than the current state-of-the-art as it substitutes a highly toxic feedstock, aziridine with much safer and potentially renewable feedstock (ethylene glycol and ethylene diamine). The use of a catalyst based on earth-abundant metal is an added advantage of the process. The characterisation studies of the polymer shows that the formed polymer is a branched polyethyleneimine (PEI-1) with high molecular weights (M_n > 10,000 g mol^{-1}, and narrow PDI (e.g. 1.1-1.4). Based on the DFT computation and prior studies, we suggest that the reaction proceeds via the dehydrogenative condensation of ethylene glycol with ethylene diamine to form imine intermediates followed by their subsequent hydrogenation to form polyethyleneimine as described in Figure 3.
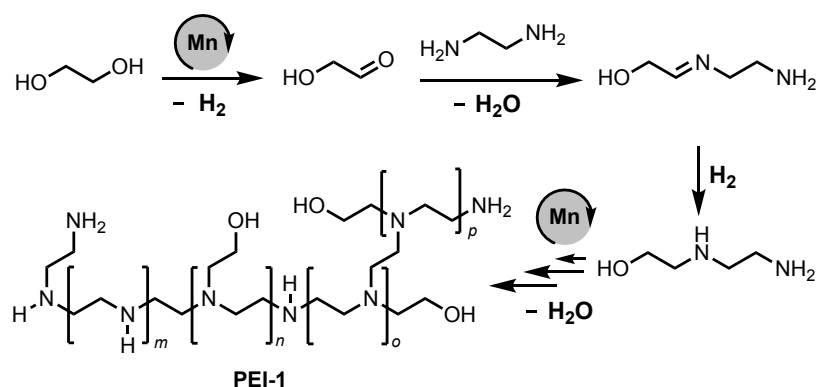

Figure 3. Proposed pathway for the synthesis of branched polyethyleneimines from ethylene glycol and ethylenediamine.

Acknowledgements

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