

Economically competitive Organic Acid-Base mixtures as Catalysts for the Self-Condensation of Diols into Polyethers

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Abstract

Organocatalysts are used in a wide range of polymerization reactions with the advantage of being often more benign or sustainable, while maintaining high catalytic activity. However, the low thermal stability of most of these compounds remain an obstacle for high temperature reactions. It was recently reported that complexes formed from a base such 1,4,7-triazabicyclodecene (TBD) and an acid such as methane sulfonic acid (MSA) demonstrate high thermal stability while efficiently catalysing polycondensation reactions. However, TBD is not cost-efficient neither available at industrial scale, which makes it unfit for scaling up. Herein, eight different bases have been investigated as to replace TBD. First, we confirm the complex formation between the MSA and the bases by nuclear magnetic spectroscopy while confirming the thermal stability of the mixtures by thermogravimetric analysis before evaluating their catalytic activity in the self-condensation of 1,6-hexanediol. Among the different investigated bases, 1,1,3,3-tetramethyl guanidine (TMG) appeared to be the best option since it gathers both high thermal stability and good catalytic activity. These characteristics make TMG suitable for replacing TBD in the self-condensation of diols while opening the way for being used in a wide range of high temperature (de)polymerization reactions.

Introduction

Polyethers are widely studied polymers because of their tunable chemical structures, versatility and wide range of properties which make them excellent candidates for various applications, such as packaging, construction or biomedical materials.¹ The high interest for these polymers is reflected by their industrial production, reaching 8 million tons in 2021 for polyether polyols², such as polyethylene glycol (PEG), polypropylene glycol (PPG) and poly(tetrahydrofuran) (poly(THF)). Polyether polyols remain largely produced through ring opening polymerization (ROP) industrially although efficient alternative methods have been studied such as the self-condensation of aliphatic diols. The main advantage of this method is that all types of hydroxyl-terminated molecules can be polymerized, which means that a wide range of polyethers can be prepared in bulk from readily available polyols. In previous studies from our group, highly crystalline aliphatic polyether polyols from 6- to 12-carbon chains were successfully synthesized following a solvent-free procedure at moderate temperatures (*i.e.* 130-200 °C).^{3,4} The same procedure was used to prepare amorphous polyether and copolyether polyols from the cyclic aliphatic 1,4-cyclohexanedimethanol.⁵

Self-condensation of diols is more efficient while catalyzed by an acid.⁶ In pioneer studies, strong acids such as sulfamic or sulfuric acid were employed in conjunction with very high temperatures (up to 300 °C) and vacuum for efficiently eliminating water and promoting the polycondensation, but this approach is limited by the high volatility and decomposition of these acids along the polymerization process.⁷ To overcome these issues, our group and others have demonstrated that such synthesis can be mediated by stable organic catalysts based on the mixture of an organic acid and an organic base. Acid-base mixture catalysts are prepared by simple mixing of the two components, in both stoichiometric and non-stoichiometric proportions to form a stable complex. The resulting acid-base catalyst considerably outperforms the thermal stability of the lone components while demonstrating good to excellent catalytic activity in polymerization^{3,8-12} and depolymerization¹³⁻¹⁶ reactions.¹⁷

Particularly, the mixtures based on 1,4,7-triazabicyclodecene (TBD) and methane sulfonic acid (MSA) demonstrates a thermal stability up to 400 °C, whereas both TBD and MSA degrade before 150 °C.^{3,18}

While TBD has been the reference base for such type of reactions, thanks to its exceptional catalytic activity, it remains an expensive molecule which is not produced in sufficient scale to contemplate the industrial exploitation of a reaction catalyzed by the organic base or mixtures including thereof. Alternatives to TBD need to be found to render the process more affordable in the perspective of scaling-up the reaction. Basterretxea *et al.* already employed 4-(dimethylamino)pyridine (DMAP) in association with MSA to successfully synthesis polylactide via ROP of L-lactide¹¹ while Coady *et al.* previously demonstrated that an acid-base mixture based on benzoic acid (BA) and 1,8-diaza[5.4.0] bicycloundec-7-ene (DBU) can efficiently catalyze the same reaction.⁸ These encouraging results open the door to the investigation of other bases to replace TBD while maintaining the catalytic mixture's overall stability and activity.

In this work, eight bases were chosen for their commercial availability at large scale and lower prices compared to TBD, which have been combined with MSA to prepare catalysts analogous to TBD:MSA. The catalysts were prepared and characterized by means of ¹H NMR spectroscopy and thermogravimetric analysis (TGA) to confirm the complex formation and the thermal stability of the mixture. Density Functional Theory (DFT) was used to correlate the thermal stability with the corresponding dissociation energy of each complex, demonstrating a clear correlation between the dissociation energy and the thermal stability of the catalyst. The catalytic efficiency of each catalyst was then investigated in the self-condensation of the 1,6-hexanediol (HDO) into poly(1,6-hexanediol) (PolyHDO). The most interesting catalysts were prepared in different acid to base ratios to evaluate the influence of the mixture's acidity on the polymerization rate and the final polyether polyol's structure.

Results and discussion

Organocatalytic mixtures were prepared by mixing MSA with the corresponding base in the non-stoichiometric ratio base to MSA (1:2) at 90 °C for 30 min.³ (**Figure 1a**) Six common organic bases were screened, *i.e.* pyridine, DMAP, DBU, diazabicyclo[4.3.0]non-5-ene (DBN), *N*-methylimidazole (NMI), and 1,1,3,3-tetramethyl guanidine (TMG) as well as two biobased derivatives of pyridine, *i.e.* nicotinic acid (NicAc) and nicotinamide (NicAm) which are forms of vitamin B3, which naturally occurs in various plants and animals.¹⁹ (**Figure 1b**) The formation of a complex is expected from the proton exchange reaction from the acid to the base. The different mixtures were analyzed through ¹H NMR spectroscopy and TGA for corroborating the formation of a stable complex.

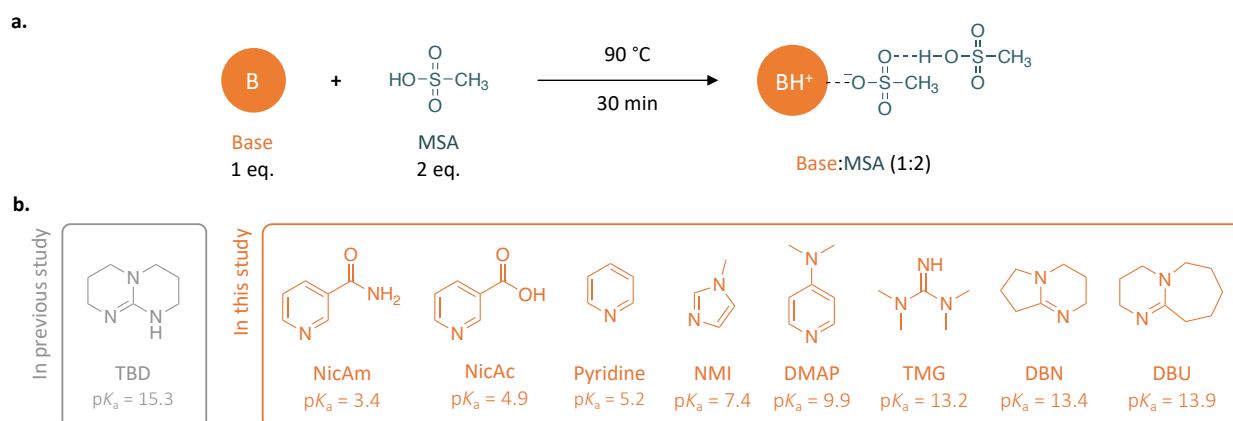


Figure 1. a. Non-stoichiometric reactions between methane sulfonic acid (MSA) and an organic base and, **b.** structures of the organic bases screened in this study with the pK_a of their respective conjugate acids.^{19–21}

In general, a similar trend can be observed for all mixtures, in the presence of MSA, the signals corresponding to the base's protons are deshielded compared to the individual base while extra signals appear in the range $\delta = 15$ to 7 ppm which are associated to the two acidic protons of the MSA. (Figures S1 to S6) However two distinct behaviors can be segregated depending on the base employed. For DBN, pyridine, NicAc and NicAm, a unique signal corresponding to the acidic protons is observed. (**Figure 2a**) This signal integrates for two

hydrogens in the case of DBN, pyridine and NicAm whereas for NicAc it integrates for three hydrogens, the additional acidic proton corresponding to the carboxyl group. For DBU, DMAP, NMI and TMG, two different signals, each of them integrating for one proton, are visible in the spectra. (**Figure 2b**) This behavior was already reported for DMAP:MSA and TBD:MSA mixtures.^{3,11} The signal at higher field corresponds to the proton involved in the acid-base interaction while the signal at lower field is characteristic of the acidic proton of the second equivalent of MSA. DBU and TMG behave similarly, the complex DBU:MSA (1:2) presenting two singlets at $\delta = 9.58$ and 8.68 ppm, while the spectra of the complex formed out of TMG and MSA exhibits two singlets at $\delta = 13.04$ and 7.73 ppm. In the case of NMI, the two signals were slightly more shifted to downfield, at $\delta = 14.31$ and 14.08 ppm. These observations support the formation of an acid-base complex between the base and the MSA for all mixtures.

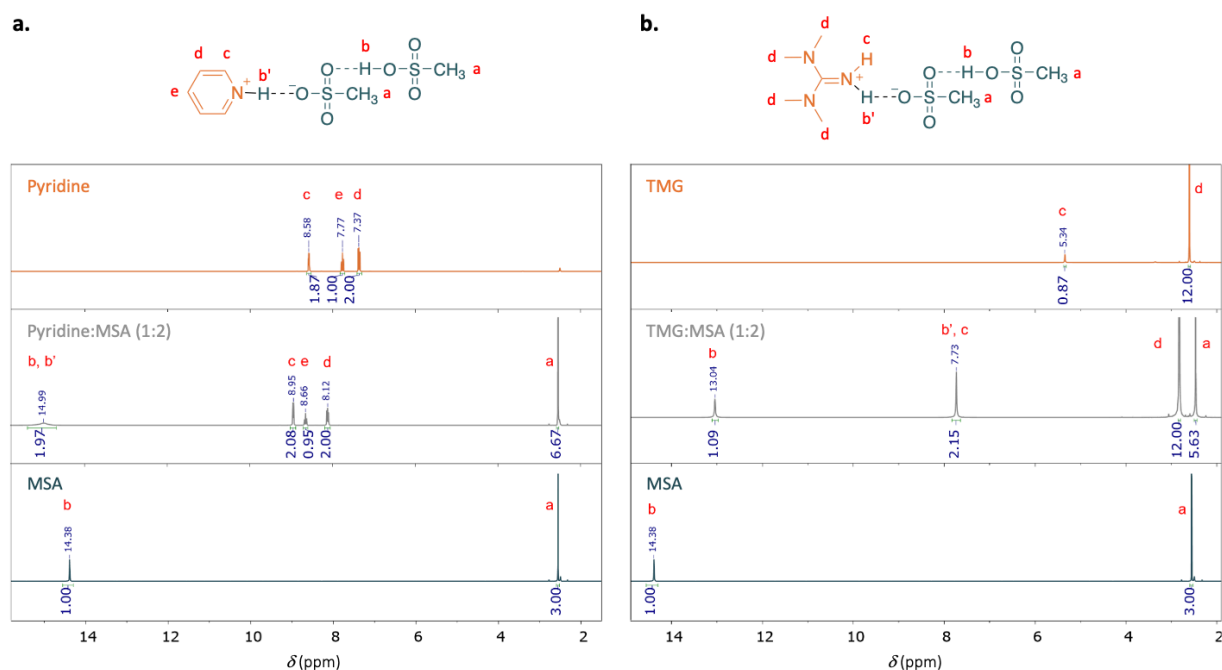


Figure 2. ^1H NMR spectra of **a.** pyridine, MSA and complex pyridine:MSA (1:2) and **b.** TMG, MSA and complex TMG:MSA (1:2) (300 MHz, $\text{DMSO}-d_6$, 293 K).

TGA was performed on the catalytic mixtures to further confirm the acid-base complex formation and investigate their thermal behavior. Acid-base complexes usually present an enhanced thermal stability compared to the lone acid and base.^{3,11,22} The thermograms were recorded for every lone base as well as for the corresponding base:MSA (1:2) mixtures. (**Figure 3**)

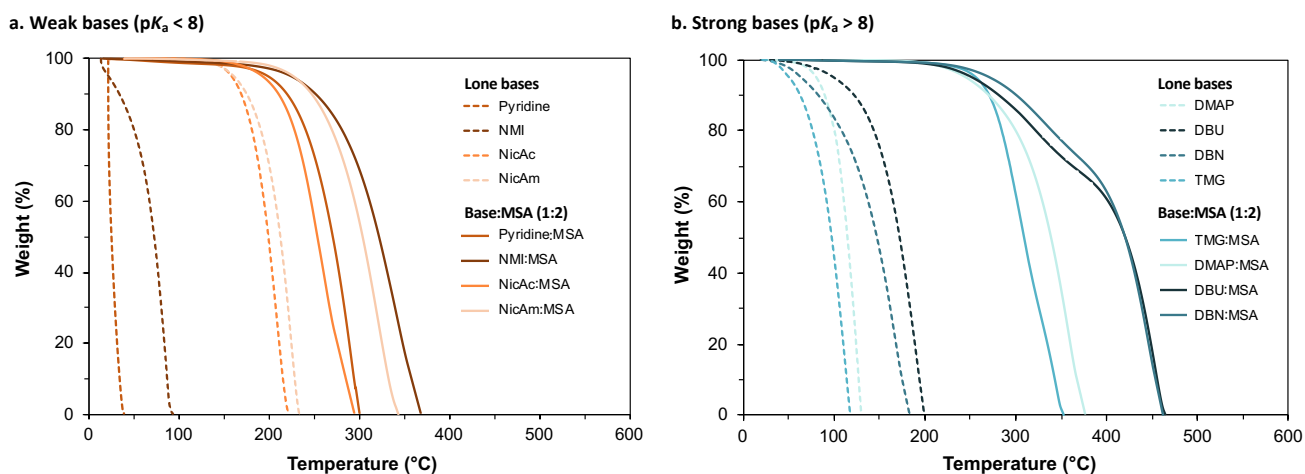


Figure 3. TGA thermograms of the lone bases (dash lines) and the corresponding base:MSA (1:2) (plain lines) mixture for the bases with **a.** $\text{p}K_a < 8$ and **b.** $\text{p}K_a > 8$ (in water at 25 °C), 40 °C to 600 °C, $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

On one hand, each mixture largely overpasses the performances of the corresponding lone base, with an improvement in thermal stability of about 200 °C in most of the cases. (Table S1) On the other hand, no clear correlation could be established between the relative thermal stability of each base and the corresponding complexes. It is noteworthy that all the acid-base mixtures barely have degraded at 180 °C, which will be the maximum operative temperature in the following study, making them all excellent candidates for the present study. (Table S1)

As previously reported, no linear correlation can be established between the pK_a of the different bases and the thermal stability of the corresponding acid-base mixture but on a general overview, the weakest bases, with $pK_a < 8$ seems to present the lowest thermal stability (**Figure 3a**) while the strongest bases present superior thermal stability (**Figure 3b**).¹² Additionally for the strongest bases, *i.e.* TMG, DBU and DBN, the thermal profiles depict two degradation events. It is clear for DBU and DBN, and, although they are more difficult to observe on the thermogram because they are very close, the complex based on TMG also experiences two degradation events. A first loss of counting 30-35% of the weight seems to correspond to the degradation of one molecule of MSA while the second event leads to complete degradation of the remaining (1:1) complex.

Finally, Density Functional Theory (DFT) was employed for calculating the dissociation energy of the different mixtures which will be compared to the thermal profiles obtained, while providing insight on the preferred dissociated pathway. (**Figure 4**) In general, although a linear correlation cannot be established, the dissociation energy calculated for each complex are coherent with the thermograms obtained, the highest dissociation energy being associated to the complexes which have the highest thermal stability.

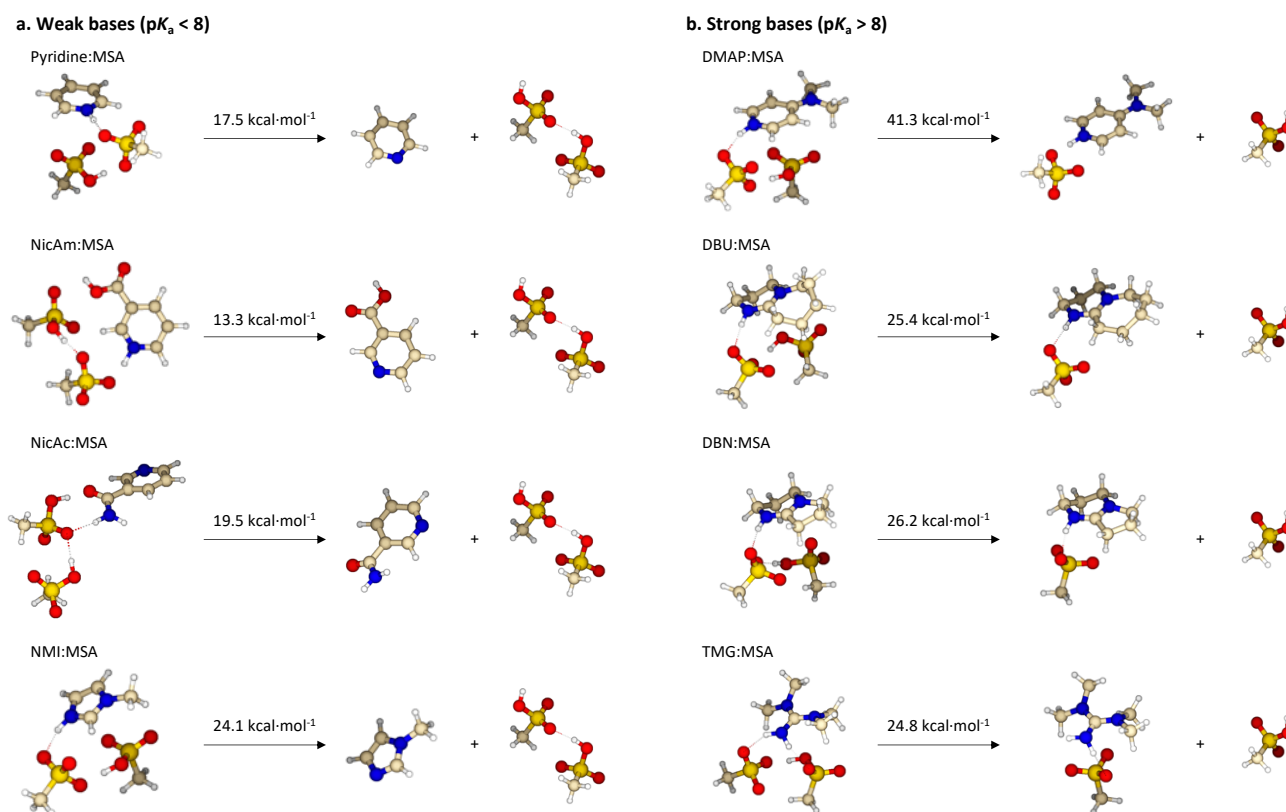
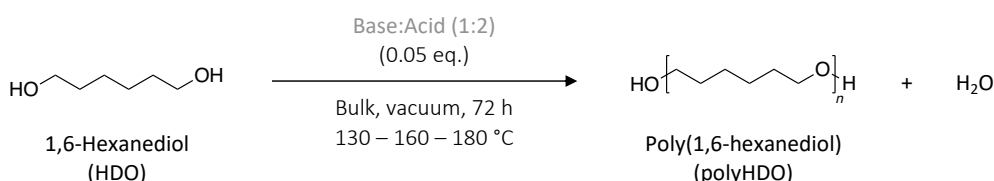


Figure 4. Dissociation energies of the complexes base:MSA (1:2) obtained from DFT with the ω B97XD functional in conjunction with the 6-31+G(d,p) basis set for all atoms.

It also appears that for the weakest bases, *i.e.* Pyridine, NicAm, NicAc and NMI, the dissociation preferably occurs on the acid/base interaction, the complex splitting into the base and a complex formed by two MSA molecules. (**Figure 4a**) On the contrary, for the stronger bases, *i.e.* DMAP, DBU, DBN and TMG, the favored pathway involves the dissociation of the complex into the (1:1) complex and a lone molecule of acid. (**Figure 4b**) More interestingly, in the case DBN, DBU and TMG which were presenting two degradation events, a significantly higher dissociation energy is found for the (1:1) mixture compared to the (1:2) (Figure S8) which

could explain that two thermal events are identified in the thermogram, first, the dissociation of the (1:2) complex into one molecule of MSA and the stable (1:1) complex, second, the degradation of (1:1). This is not observed for DMAP as the (1:2) mixture is remarkably more stable than the (1:1) complex, although the mixture dissociates into the (1:1) mixture and MSA, the stoichiometric complex, less stable, would decompose instantaneously, so only one thermal degradation is visible on the thermogram.

The catalytic activity of each acid-base mixture was investigated for the polycondensation of HDO into the corresponding polyether, *i.e.* polyHDO. All experiments were conducted for 72 h under vacuum following a temperature range of 130 °C (24 h), 160 °C (24 h) and 180 °C (24 h), with 0.05 eq. of the catalytic mixture, as previously reported.³ (Scheme 1) ¹H NMR spectroscopy (300 MHz, 293 K, CDCl₃) was employed to monitor the reactions and characterize the resulting polymers (Table 1). The conversion was evaluated through the diagnostic disappearance of the HDO protons' adjacent to the hydroxyl group, *i.e.* triplet at δ = 3.63 ppm, and the concomitant appearance of a signal at δ = 3.33 ppm attributed to the repeating methylene protons of the etheric sequence. (Figure S9)



Scheme 1. Self-condensation of 1,6-hexanediol into poly(1,6-hexanediol) catalysed by an organic acid-base mixture.

Table 1. Screened data for the self-condensation of 1,6-hexanediol using different base:MSA (1:2) mixtures (0.05 eq.) as organocatalyst for 72 h at 130 – 160 – 180 °C.

Entry	Base	pK _a ^a	Base:Acid	Conversion (%) ^{b,c}	M _n ^{NMR} (g·mol ⁻¹) ^b	M _n ^{GPC} (g·mol ⁻¹) ^d	$\bar{D}$ ^d	Sulfonate end-chain (%) ^b
1	TBD	15.3	1:3	94	1 800	3 000	2.13	<1
2	DBU	13.9	1:2	68	400	700	1.94	<1
3	DBN	13.4	1:2	70	400	1 000	2.00	<1
4	TMG	13.2	1:2	93	1 600	4 200	1.47	2
5	DMAP	9.9	1:2	91	1 200	1 600	2.80	3
6	NMI	7.4	1:2	93	1 500	2 000	2.65	4
7	Pyridine	5.2	1:2	96	2 800	8 900	1.73	36
8	Nicotinic Acid	4.9	1:2	90	1 000	1 200	3.39	5
9	Nicotinamide	3.4	1:2	80	500	1 100	2.22	<1

^aIn water at 25 °C. ^bDetermined by ¹H NMR spectroscopy (300 MHz, 293 K, CDCl₃). ^cConversions are average values obtained from various run for ensuring repeatability - error = $\pm$ 1.5%. ^dDetermined by GPC in CHCl₃, $\bar{D}$ = M_w/M_n.

Each catalyst evaluated demonstrates moderate to high monomer conversion after 72 h. The catalysts prepared with DBU, DBN and NicAm demonstrate poor efficiency compared to the other mixtures, inferior to 80%, while the rest of the mixture provide very good to excellent conversions, from 90 to 96%. (Table 1)

The catalysts promoting the lowest conversions also led to very low molecular weights, *i.e.* M_n = 400 g·mol⁻¹, for both DBN:MSA (1:2) and DBU:MSA (1:2) and M_n = 500 g·mol⁻¹ for NicAm. DMAP:MSA (1:2) was a suitable candidate as it previously demonstrated great thermal stability as well as high efficiency and selectivity but finally the polymer obtained exhibited lower molecular weight than while TBD:MSA is used, with M_n = 1200 g·mol⁻¹. Similarly, NicAc only provides moderate performances with a molecular weight which is not exceeding 1000 g·mol⁻¹. The mixtures based on pyridine, NMI and TMG demonstrated the best performances. The molecular weight of the resulting polyether was significantly higher while employing pyridine:MSA (1:2) (2800 g·mol⁻¹) compared to TBD:MSA (1:3) (1800 g·mol⁻¹), NMI:MSA (1:2) (1500 g·mol⁻¹) and TMG:MSA (1:2) (1600 g·mol⁻¹). It can be noticed that the excellent thermal stability of a complex is not correlated with its catalytic activity on the self-condensation of HDO. For instance, the mixtures based on NicAm and TMG present

a very similar thermal stability but lead to different catalytic activity with molecular weight lower than $500 \text{ g}\cdot\text{mol}^{-1}$ for the former and performances similar to TBD:MSA for the later, *i.e.* $1600 \text{ g}\cdot\text{mol}^{-1}$. Another counter-example is the pyridine:MSA (1:2) which performed the worst in terms of thermal stability but surpasses the catalytic activity of TBD:MSA (1:3) with a final molecular weight of $2600 \text{ g}\cdot\text{mol}^{-1}$. The different materials show variable polydispersity values, ranging from 1.47 for the polyHDO obtained with the TMG:MSA (1:2) catalyst to 3.39 for the polyHDO obtained with NicAc:MSA (1:2) catalyst which was expected as high polydispersity is a common feature in organocatalyzed polycondensations, where values observed often range 2 - 3.^{3,23,24}

Considering only the conversion and the molecular weight of the polyether obtained, the pyridine appears to be the most suitable option to replace TBD in the acid-base mixture catalyst. However, the ^1H NMR spectrum of the crude product of the self-condensation reaction reveals the formation of a side-product resulting in a nucleophilic attack of the MSA on the hydroxyl ending-group of the polyether. The formation of this ending-group is associated with the appearance of an additional triplet at $\delta = 4.22$ ppm, corresponding to the two methylene protons adjacent to the sulfonate end-group, together with a singlet at $\delta = 2.99$ ppm, corresponding to the three protons of the methyl group of the MSA when attached to the chain-end of the polymer. (**Figure 5**) The integrations of these signals in the ^1H NMR spectrum reveals that 36% of the chain ends of the polyether seems to be sulfonated. This result can be correlated with the possible lower stability of the complex formed by the MSA and the pyridine which is a weak base ($\text{pK}_a = 5.2$ in water²¹). The same phenomenon can be observed for the other mixtures in lower proportions, *i.e.* 2, 3 and 4% for TMG, DMAP and NMI, respectively.

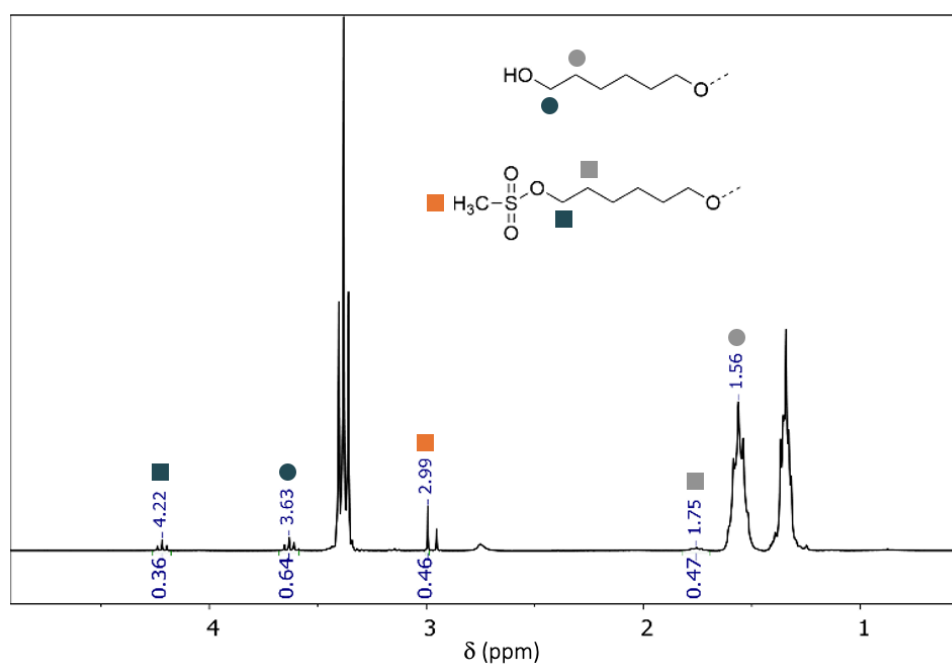


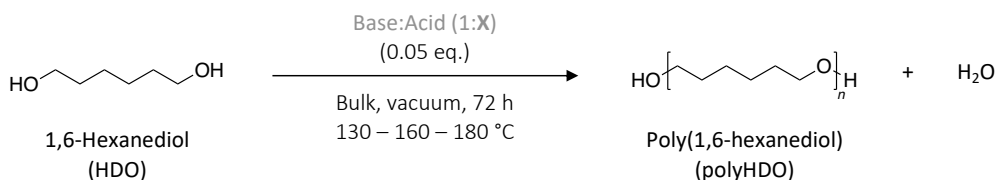
Figure 5. ^1H NMR spectrum of the crude product of the self-condensation of 1,6-hexanediol catalyzed by pyridine:MSA (1:2) (300 MHz, 293 K, CDCl_3).

The use of the NicAc-based mixture resulted also in relatively low content of sulfonate group, *i.e.* 5%, but additional signals in the region $\delta = 4.80 - 4.40$ ppm of the ^1H NMR spectrum suggests that ending-groups of another nature were also formed corresponding to 58% of the chain end. (Figure S11) This observation can be related to the very weak acid-base interaction between the pyridyl group of the NicAc ($\text{pK}_a = 4.9$ in water²⁵) and MSA, as well as the presence of the carboxylic acid in meta ($\text{pK}_a = 2$ in water²⁵) on the pyridyl ring which can potentially interact with the hydroxyl end-group. NicAm did not show any sulfonate ending-groups, but similarly to NicAc, signals corresponding to chain ends different from the hydroxyl appeared at higher chemical shift. (Figure S12) The side-reaction between the catalyst and the chain end of the polyether has non-negligible consequences considering that the main application for these polyether polyols is the synthesis of polyurethanes, where the concentration of hydroxyl groups is a decisive parameter.

In a second step, the most promising mixtures were explored in different ratios, *i.e.* (1:1), (1:2) and (1:3), base to MSA, for catalyzing the self-condensation of HDO which involves, pyridine and TMG but also DMAP because of its high thermal stability and NicAc as the best bio-based option. ^1H NMR spectroscopy and TGA of the acid-base catalysts were performed for corroborating the formation of the complex and investigating their thermal behaviors. (Figures S13 to S20) The recorded ^1H NMR spectra of the (1:1) and (1:3) mixtures present the same characteristic signals as for the (1:2) mixtures for all bases. Only minor shifts of the signals can be identified depending on the acidity of the mixture (*i.e.* depending on the MSA load, 1, 2 or 3 eq.). As expected, the thermograms of the (1:1) and (1:3) complexes demonstrate a superior thermal stability compared to the lone bases. No significant change can be identified in the degradation profile between the three complexes for TMG and NicAc, while the DMAP:MSA (1:1), pyridine:MSA (1:1) and DMAP:MSA (1:3) clearly exhibit worse performances compared to their (1:2) counterparts. (Table S3)

These mixtures were also investigated as catalysts for the polymerization of polyHDO with the same parameters as previously, *i.e.* 72 h under vacuum following a temperature range of 130 °C (24 h), 160 °C (24 h) and 180 °C (24 h). The monomer conversion and the molecular weight were monitored through ^1H NMR spectroscopy. (Scheme 2) As a general observation for all catalysts, the stoichiometric mixture (1:1) is less efficient than the acidic mixtures (1:2) and (1:3) which could be expected as acid catalysts are reported for the condensation of alcohols.²⁶ (Figure 6) In equimolar mixtures, the acid proton is transferred to the base, and it is no longer available to catalyze the reaction. Therefore, an excess of acid seems necessary to efficiently catalyze the self-condensation of diols. However, pyridine:MSA (1:1) shows higher activity than DMAP- TMG- and NicAc:MSA (1:1), reaching 80% conversion after 72 h, compared to only 5%, 21% and 48% for DMAP, TMG and NicAc, respectively.

For all catalysts, no differences can be observed in terms of conversion between the ratios (1:2) and (1:3). (Figure 6a) For both DMAP and NicAc the most acidic mixture, (1:3), led to superior molecular weight after 72 h, from 1200 to 1600 g·mol⁻¹ for DMAP and from 1000 to 1600 g·mol⁻¹ for NicAc. (Figure 6b) Surprisingly, TMG:MSA (1:3) did not show any catalytic improvement compared to the (1:2) mixture, with a very similar conversion evolution and a final polyether of same molecular weight, *i.e.* 1600 g·mol⁻¹. (Table S4) This behavior is in good correlation with previous results obtained with TBD which is similar in structure and acidity ($\text{p}K_{\text{a}} = 26.1$ vs $\text{p}K_{\text{a}} = 13.2$ for TMG, in water²⁰), where the catalytic activity of the (1:3) mixture only slightly surpassed the one of the (1:2) at 180 °C.³ For the mixtures based on pyridine, same conversion is attained for both (1:3) and (1:2), but superior molecular weight is obtained for the mixture (1:2), *i.e.* 2800 g·mol⁻¹ vs 1400 g·mol⁻¹ for the mixture (1:3). Higher excess of MSA appears to favor the sulfonation of the ending group reaching 67% of sulfonate chain end while pyridine:MSA (1:3) is employed. (Figure S21) The same trend is observed for NicAc-based mixtures, where the amount of sulfonated ending-groups increased from 3% (1:2) to 17% (1:3), (Figure S22) whereas the quantity of MSA does not influence the sulfonation in the case of stronger bases such as DMAP and TMG, with only 3% of sulfonated chain end for both (1:2) and (1:3) DMAP mixtures, and 2% and 6% for TMG:MSA (1:2) and (1:3), respectively. (Figure S23 and S24) This observation is in good accordance with the relative basicity of each molecule, where a strong base is expected to form stronger interactions with the acid, preventing any reaction with the polyether's hydroxyl chain end.



Scheme 2. Self-condensation of 1,6-hexanediol into poly(1,6-hexanediol) catalyzed by an organic acid-base mixture.

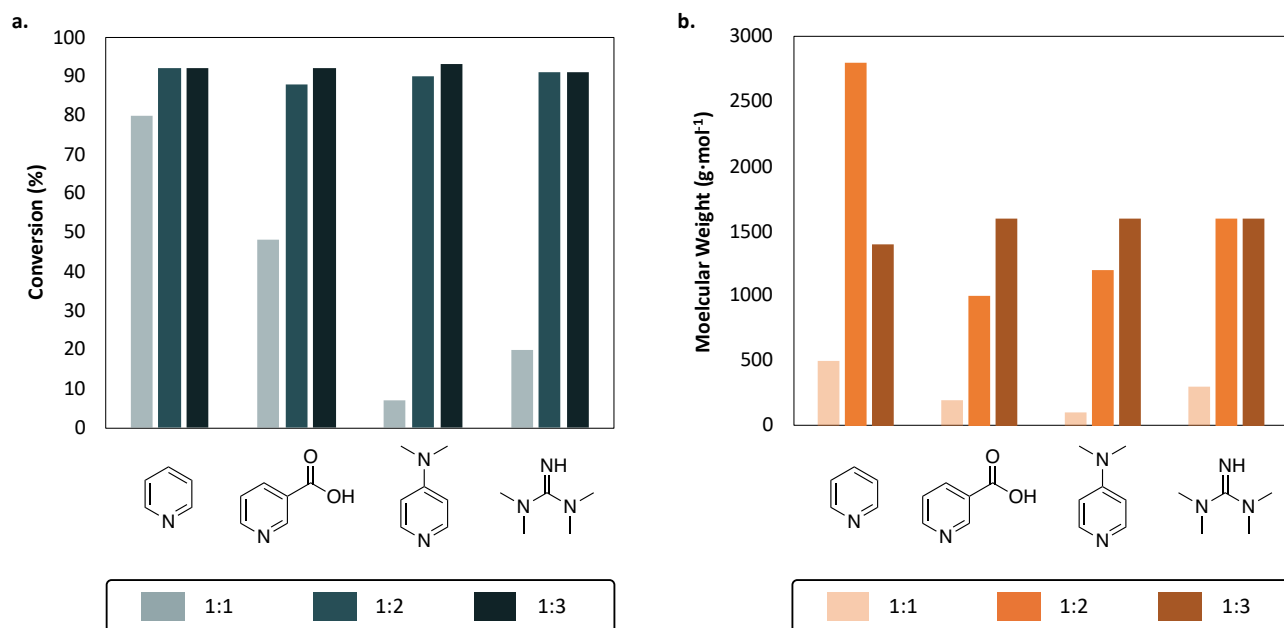


Figure 6. **a.** Monomer conversion and **b.** Molecular weight obtained from ^1H NMR spectroscopy (300 MHz, 293 K, CDCl_3), for the self-condensation of 1,6-hexanediol catalysed by base:MSA (1:1), (1:2), and (1:3) organocatalysts (0.05 eq.) after 72 h.

Conclusion

Overall, economical, and commercially available acid-base mixtures proved to be efficient in replacing TBD for the organocatalyzed self-condensation of HDO into the corresponding polyether. Thermal analysis revealed that each base mixed with MSA was forming a thermally stable complex under the reactions' conditions. Among these mixtures, pyridine:MSA (1:2) demonstrated the highest catalytic activity, but its use involved the formation of polyether polyols with sulfonate ending-groups. The less toxic and bio-sourced option based on Vitamin B3-derivative NicAc was also worth considering, but as pyridine, the presence of undesired ending-groups impedes its use as efficient catalyst. The guanidine superbase TMG remained the most promising alternative to TBD since its (1:2) mixture combined both good catalytic activity and an excellent thermal stability. This study also emphasized that a higher thermal stability was not correlated to an increased catalytic activity. Hereby, acid-base mixtures demonstrate their versatility and relevance for more economically competitive acid-base catalysts.

Experimental part

Materials

All reagents and solvents were purchased from Sigma-Aldrich, TCI Chemicals or Fisher and used as received without further purification. 1,6-hexanediol was dried in an oven at 60 °C overnight prior to use.

Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy. Spectra were recorded in a Bruker Avance DPX 300 at 300.16 MHz of resonance frequency. Deuterated DMSO ($\text{DMSO-}d_6$) was used as solvent at room temperature for catalysts' characterization. Deuterated CHCl_3 (CDCl_3) was used as solvent at room temperature for the polyethers. Data are reported as follows: chemical shift in parts per million (ppm), both integration and coupling constant in Hertz.

Thermogravimetric Analysis (TGA). The thermal stability was analyzed by a TGAQ500 (TA instrument) under nitrogen atmosphere. Samples of 10–30 mg were heated from 40 to 600 °C at a rate of 10 °C·min⁻¹.

Gel Permeation Chromatography (GPC). GPC measurements were performed in CHCl_3 on an Agilent 1260 Infinity II Multi-Detector SEC System fitted with RI, ultraviolet (UV, $\lambda = 309$ nm), and viscometer detectors. The polymers were eluted through an Agilent guard column (PLGel 5 μM , 50 × 7.5 mm) and two Agilent mixed-C columns (PLGel 5 μM , 300 × 7.5 mm) using CHCl_3 (buffered with 0.5% NEt_3) as the mobile phase (flow rate = 1 mL·min⁻¹, 40 °C). Number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity values ($D = M_w/M_n$) were determined using Agilent GPC software (vA.02.01) against a 15-point calibration curve ($M_p = 162 - 3,187,000 \text{ g} \cdot \text{mol}^{-1}$) based on poly(styrene) standards (Easivial PS- M/H, Agilent).

Synthesis of the catalysts

Catalysts were prepared following reported procedures³ by mixing MSA with DMAP, NMI, DBN, DBU, TMG, pyridine, NicAc or NicAm in the base to acid ratio (1:2): DMAP:MSA (0.207 g, 1.69 mmol of DMAP and 0.326 g, 3.39 mmol of MSA), NMI:MSA (0.139 g, 1.69 mmol of NMI and 0.326 g, 3.39 mmol of MSA), DBN:MSA (0.210 g, 1.69 mmol of DBN and 0.326 g, 3.39 mmol of MSA), DBU:MSA (0.258 g, 1.69 mmol of DBU and 0.326 g, 3.39 mmol of MSA), TMG:MSA (0.196 g, 1.69 mmol of TMG and 0.326 g, 3.39 mmol of MSA), pyridine:MSA (0.134 g, 1.69 mmol of pyridine and 0.326 g, 3.39 mmol of MSA), NicAc:MSA (0.209 g, 1.69 mmol of NicAc and 0.326 g, 3.39 mmol of MSA), NicAm:MSA (0.207 g, 1.69 mmol of NicAm and 0.326 g, 3.39 mmol of MSA). Mixtures in the ratios (1:1) and (1:3) were also prepared for certain bases. (1:1): DMAP:MSA (0.207 g, 1.69 mmol of DMAP and 0.163 g, 1.69 mmol of MSA), TMG:MSA (0.195 g, 1.69 mmol of TMG and 0.163 g, 1.69 mmol of MSA), pyridine:MSA (0.134 g, 1.69 mmol of pyridine and 0.163 g, 1.69 mmol of MSA), NicAc:MSA (0.209 g, 1.69 mmol of NicAc and 0.163 g, 1.69 mmol of MSA). (1:3): DMAP:MSA (0.207 g, 1.69 mmol of DMAP and 0.488 g, 5.08 mmol of MSA), TMG:MSA (0.195 g, 1.69 mmol of TMG and 0.488 g, 5.08 mmol of MSA), pyridine:MSA (0.134 g, 1.69 mmol of pyridine and 0.488 g, 5.08 mmol of MSA), NicAc:MSA (0.209 g, 1.69 mmol of NicAc and 0.488 g, 5.08 mmol of MSA). Afterward, the mixtures were thermally treated at 90 °C for 30 min under stirring until complete formation of a homogeneous and transparent medium as previously reported.³ At room temperature, all mixtures are white solids or color-less liquid. (Figure S7)

Self-condensation of 1,6-hexanediol catalyzed by base:acid mixtures

Each organocatalyzed self-condensation of 1,6-hexanediol was performed according to reported procedure.³ In a 25 mL Schlenk flask, 0.05 eq. (5 mol%) of the catalyst was mixed with 4 g of 1,6-hexanediol (33.9 mmol). Vacuum was first applied to the sealed reaction vessel for 30 min before immersion into a pre-heated oil bath at 130 °C – 160 °C – 180 °C for 72 h under magnetic stirring, varying the temperature every 24 h. The resulting polyether polyols were purified by dissolving in chloroform (10 mL) and precipitated in cold methanol (160 mL). The solution was centrifuged at 10 000 rpm for 5 min. The resulted polyethers were dried under vacuum at 65 °C for 24 h before characterization. All reactions were repeated two to five times for ensuring repeatability, the value in the tale is average, error for conversion = $\pm 1.5\%$

Computational details

All density functional theory (DFT) calculations were carried out using the Gaussian 16 suite of programs²⁷ and the ω B97XD functional²⁸ in conjunction with the 6-31+G(d,p) basis set for all atoms. To confirm that the optimized structures were minima on the potential energy surfaces, frequency calculations were carried out at the same level of theory and then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal vibrational corrections at $T = 298$ K. The electronic energy was refined by single-point energy calculations at the ω B97XD/6-311++G(2df,2p) level of theory.

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