Organopolymerization

DOI: 10.1002/anie.201406630

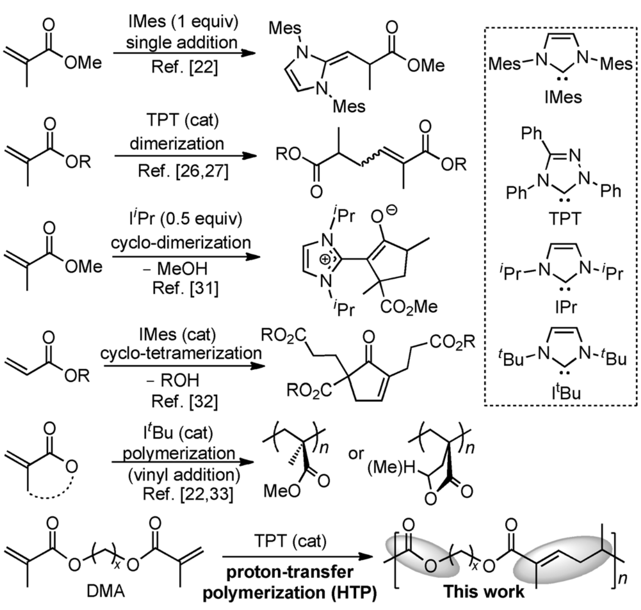
Proton-Transfer Polymerization (HTP): Converting Methacrylates to Polyesters by an N-Heterocyclic Carbene**

*Miao Hong and Eugene Y.-X. Chen**

Abstract: *A new polymerization termed proton (H)-transfer polymerization (HTP) has been developed to convert dimethacrylates to unsaturated polyesters. HTP is catalyzed by a selective N-heterocyclic carbene capable of promoting intermolecular Umpolung condensation through proton transfer and proceeds through the step-growth propagation cycles via enamine intermediates. The role of the added suitable phenol, which is critical for achieving an effective HTP, is twofold: shutting down the radically induced chain-growth addition polymerization under HTP conditions (typically at 80–120 °C) and facilitating proton transfer after each monomer enchainment. The resulting unsaturated polyesters have a high thermal stability and can be readily cross-linked to robust polyester materials.*

The field of organocatalysis[1] using inherently sustainable small-molecule organic compounds as efficient and selective catalysts has risen to prominence in synthesis and thrived over the last decade, thanks to its versatile synthetic utilities developed for the efficient "greener" synthesis of pharmaceuticals and fine chemicals[2] and biorefining products[3] as well as polymeric materials.[4] As an important class of organic catalysts, N-heterocyclic carbenes (NHCs)[5] have attracted ever increasing attention due to their unique reactivity and selectivity observed in many different types of organic reactions.[6] Hedrick and Waymouth[7] pioneered the utility of the NHC-mediated reactions in polymer synthesis.[8] The predominant NHC-mediated polymerization method is the ring-opening polymerization (ROP) of heterocyclic monomers, such as lactides,[9] lactones,[10] epoxides,[11] cyclic carbonates,[12] cyclic (carbo)siloxanes,[13] and *N*-carboxyl-anhydrides.[14] NHC-mediated step-growth polymerization has been reported as well.[15] NHCs have also been used as alternative nucleophilic catalysts[16] in the chain-growth polymerization of α,β-unsaturated esters such as methyl methacrylate (MMA), through the classic group-transfer polymerization (GTP) initiated by silyl ketene acetals.[17] In addition, such acrylic monomers can be rapidly polymerized by frustrated Lewis pairs consisting of bulky NHC bases, such as the Arduengo carbenes 1,3-di-*tert*-butylimidazolin-2-ylidene (I^{t}Bu) and 1,3-di-mesitylimidazolin-2-ylidene (IMes),[18] and the strongly acidic, sterically encumbered $Al(C_6F_5)_3$ via zwitterionic imidazolium enolaluminate intermediates.[19]

The exquisite selectivity of the structures of NHCs and substrates (specifically an important class of Michael acceptors, α,β-unsaturated esters or acrylic monomers) for the five types of reactions—single addition, dimerization, cyclodimerization, cyclotetramerization, and polymerization—is highlighted in Scheme 1. Fu et al.[20] reported the first intramolecular Umpolung of α,β-unsaturated esters carrying a ω-pendant leaving group to form β-alkylation/cyclization products, catalyzed by triazolylidene carbenes such as TPT (1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene).[21] With simple methacrylates, such as MMA, we found that IMes reacts with the substrate to form only the single-addition product, an enamine;[22] the formation of the enamine, or the deoxy-Breslow intermediate[23] analogous to the Breslow intermediate[24] involved in the benzoin condensation reaction,[25] was proposed to proceed through the initial conjugate addition of the IMes to MMA to form the corresponding enolate that undergoes proton transfer. Glorius[26] and Matsuoka[27] discovered that TPT, which was estimated to be 10^3 times less nucleophilic than IMes,[28] catalyzes the tail-to-tail dimerization (intermolecular Umpolung) of MMA and



Scheme 1. Highlighted known reaction pathways involved in the reaction of NHCs and acrylic monomers and the proposed new HTP to convert dimethacrylates to unsaturated polyesters.

---

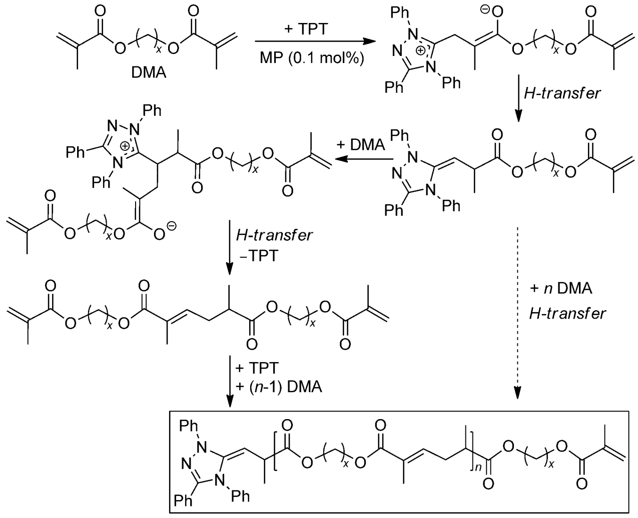
[*] Dr. M. Hong, Prof. Dr. E. Y.-X. Chen
Department of Chemistry, Colorado State University
Fort Collins, CO 80523-1872 (USA)
E-mail: Eugene.Chen@colostate.edu

[**] This work was supported by the U. S. National Science Foundation (NSF-1300267). We thank D. J. Liu for the preparation of TPT and TPT(OMe)H.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406630.

other methacrylates typically at 80 °C, whereas the common imidazolylidene carbenes are ineffective. Subsequently, analogous dimerization of methacrylonitrile[29] and styrenes[30] has also been recently realized by the Matsuoka and Glorius groups, respectively. Switching to I^{i}Pr (1,3-di-isopropylimidazolin-2-ylidene), Taton et al. recently found that MMA is cyclodimerized to an imidazolium enolate cyclodimer.[31] On the other hand, IMes catalyzes the cyclotetramerization of acrylates, as recently showed by Matsuoka.[32] Intriguingly, I^{t}Bu polymerizes MMA in dimethylformamide (DMF) at room temperature (RT) to produce PMMA with a M_n of 33.2 kg mol^{-1} and a polydispersity index ($Đ$) of 1.99.[22] We also revealed that the I^{t}Bu-mediated polymerization of a cyclic analogue of MMA, the biomass-derived γ-methyl-α-methylene-γ-butyrolactone (MMBL), is extremely rapid, converting quantitatively 1000–3000 equiv of MMBL in 1 min at RT to the corresponding bioplastics.[33] Buchmeiser et al. showed that MMA can also be polymerized by the CO_2-protected NHC latent precatalyst, I^{t}Bu-CO_2.[34]

It is clear from the above concise overview that although suitable NHCs such as I^{t}Bu can directly polymerize acrylic monomers, the polymerization proceeds through a chain-growth mechanism by conjugate addition, producing exclusively the vinyl-addition polymers, namely poly(meth)acrylates. We hypothesized that, if a dimethacrylate (DMA) monomer is treated with a selective NHC catalyst, such as TPT, that promotes intermolecular Umpolung condensation through the proposed step-growth propagation cycles, consisting of repeated [conjugate addition/proton transfer/NHC release] fundamental steps as outlined in Scheme 2, a new polymerization reaction termed proton (H)-transfer polymerization (HTP) could be established and its end product would be an unsaturated polyester (Scheme 1). Such resulting unsaturated polyesters are of scientific and technological interest for producing tailor-made polyester materials through postfunctionalization and cross-linking.[35] However, accomplishing this new polymerization requires effective strategies to meet two key challenges: shutting down the conventional chain-growth pathway through either NHC-mediated conjugate addition via the zwitterionic enolate intermediate or through radically induced vinyl-addition processes under HTP conditions (typically at 80–120 °C), and promoting effective proton transfer after each monomer enchainment. Reported herein is the first successful HTP that utilizes the NHC catalyst to directly polymerize dimethacrylates into unsaturated polyesters with M_w up to 28 kg mol^{-1}.



Scheme 2. Proposed possible mechanistic scenario for HTP of dimethacrylates to unsaturated polyesters.

Considering the observed exquisite selectivity of TPT towards methacrylates for tail-to-tail dimerization through intermolecular Umpolung[26,27] over chain-growth polymerization through conjugate addition (preferred by I^{t}Bu),[22,33] we initially investigated the reactivity of TPT towards a dimethacrylate, 1,4-butanediol dimethacrylate (BDMA). At RT, the reaction of TPT and BDMA (in various mole ratios) in toluene resulted in only enamine formation (i.e., the TPT–BDMA adduct or single-monomer addition product),[36] similar to the reaction of TPT with the monomethacrylate MMA.[33] However, unlike MMA, which is not polymerized by TPT in toluene or DMF at RT or 80 °C up to 24 h, heating a mixture of TPT and BDMA (20 equiv, 1.6 M in toluene) to 80 °C for 24 h yielded a mixture of polymer products. The product mixture (Figure S1b) can be separated by solvent fractionation with diethyl ether into two fractions: the insoluble white solid (60 wt %) and light yellow viscous oil (40 wt %). The solid was shown by NMR (Figure S1c) to be the vinyl-addition polymerization product, presumably due to thermally induced radical polymerization of one methacrylate double bond followed by some cross-linking through the other (which contributed to the poor solubility of the polymer). Switching the solvent to DMF and 1,4-dioxane (DOX) or lowering the temperature to 60 °C did not prevent the vinyl-addition polymer formation. More significantly, the ^{1}H NMR spectrum of the ether-soluble polymer (Figure S1d) indicated that it is an unsaturated polyester consisting of the unique [-C(Me)$^{1.83(s)}$=CH$^{6.69(t)}$–CH$_2^{2.51,2.30(m)}$–CH$^{2.60(m)}$-(Me)$^{1.18(d)}$-] linkage, clearly a result of the intermolecular Umpolung through proton transfer; these characteristic NMR features are consistent with the same structural motif observed in the MMA tail-to-tail coupling product.[26,27]

These initial results showed it is indeed possible to produce an unsaturated polyester from the dimethacrylate monomer by TPT. However, they also presented the challenge of developing a strategy to effectively shut down the vinyl-addition chain-growth pathway at a relatively high temperature (80 °C or higher), which is due to radically initiated processes, while maintaining the catalytic activity of TPT. After having screened several commonly used radical inhibitors, we arrived to 4-methoxyphenol (MP) and catechol (COL) that showed the ability to not only shut down the radically induced vinyl-addition polymerization but also to enhance the activity of the step-growth polymerization catalyzed by TPT. Hence, in the presence of 0.1 mol % (or 0.02 equiv relative to TPT) of MP or COL, the polymerization of BDMA by TPT (5 mol %) in toluene at 80 °C led to the exclusive formation of the unsaturated polyester PBDMA with $M_w = 17.6$ kg mol^{-1} and $Đ = 1.90$ (run 1, Table S1) or

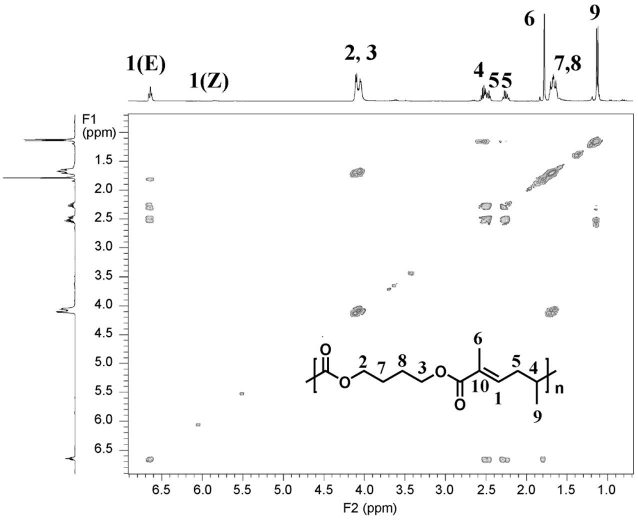


Figure 1. ^{1}H–^{1}H COSY NMR spectrum (CDCl$_3$) of PBDMA (run 1, Table S1).

$M_w = 10.9$ kg mol^{-1} and $Đ = 1.72$ (run 2), without formation of any detectable amount of the vinyl-addition polymer. The resulting structure of the unsaturated polyester ($E/Z = 96:4$), $-[(C{=}O)O-(CH_2)_4-O(C{=}O)-C(Me){=}CH-CH_2-CH(Me)]_n-$, was confirmed by ^{1}H–^{1}H COSY (Figure 1) and ^{1}H–^{13}C HMQC (Figure S2) NMR correlation spectra, the molecular weight (MW) by GPC (Figure S4), and the end groups by MALDI-TOF MS (Figures 2 and S16). Most notably, the NMR features of the polyester are the unique Umpolung linkage $-[C(Me^6){=}CH^1-(CH^5)_2-CH^4(Me^9)]-$ and the ester linkage $-[(C{=}O)O-(CH^2)_2-(CH^7)_2-(CH^8)_2-(CH^3)_2-O(C{=}O)]-$, the correct connectivity of which was clearly demonstrated by correlation of the peaks marked in Figure 1.

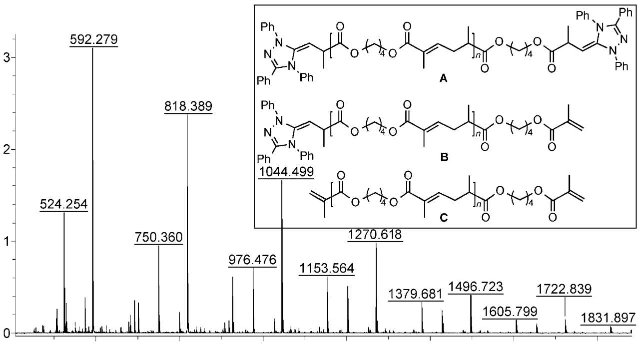


Figure 2. MALDI-TOF mass spectrum of a low MW PBDMA (run 9) and structures of polymer chain ends.

The present HTP was further explored under different conditions (solvent, time, and temperature). Switching the solvent from toluene to DOX lowered the conversion to 70.3% and the polymer M_w to 12.8 kg mol^{-1} (run 3). When DMF was used, the polymerization not only became more sluggish (run 4 versus 1) but also afforded a mixture of the polyester and the vinyl-addition polymer, thus exhibiting a bimodal molecular weight distribution (run 4). By fixing the solvent (toluene), the BDMA/TPT/MP ratio (35:1:0.035), and the temperature (80 °C), the polymerization was stopped at different times, from 6 h to 24 h (runs 5–8). The observed polymerization features (Figure S5)—including a small gradual increase of the MW with an increase in conversion, followed by a much larger increase in MW when approaching quantitative conversion, and the continued growth of the MW beyond quantitative monomer conversion (run 8 versus 7), whereas the MW distribution increases monotonically with conversion—are characteristic of condensation polymerization by a step-growth mechanism. Lastly, raising the temperature with a fixed BDMA/TPT/MP ratio of 100:1:0.1 and time (48 h) from 80 °C to 100 °C (runs 9, 14, and 10) enhanced the conversion and the polymer MW. Raising the temperature further to 110 °C brought about a significant increase in activity, achieving quantitative conversion in 24 h to produce PBDMA with a M_w of 27.3 kg mol^{-1} (run 11). However, the polymerization at an even higher temperature of 120 °C became uncontrolled and gelled in 3 h, producing PBDMA with a low MW, plus the vinyl-addition polymer (run 12).

The following studies uncovered the dual role of the added phenol (MP or COL): acting as the radical inhibitor to shut down the vinyl-addition chain-growth polymerization and enhancing the step-growth polymerization activity. The radical inhibition role was clearly shown above, whereas the activity enhancement role was demonstrated by the following set of experiments. For the BDMA polymerization by TPT at 80 °C without the phenol, the conversion was only 35.7% after 12 h (Figure S6a). In contrast, the conversion was enhanced significantly to 83.3% in the presence of COL (2 mol%) for only 3 h (Figure S6b). The polymerization in the presence of MP was even faster, achieving more than 99% conversion in 3 h (Figure S6c); the higher MW and higher $Đ$ polymer produced by MP relative to that by COL (run 1 versus 2) is due to this activity difference. This pronounced (> 10-fold) polymerization activity enhancement can be attributed to the facilitated proton transfer processes by the phenol (a Brønsted acid), a phenomenon that has also been observed in other NHC-mediated catalytic processes through NHC/Brønsted acid cooperative catalysis.[29,37] In comparison, aliphatic alcohols such as ^{i}PrOH and MeOH effected neither activity enhancement nor radical inhibition, thus producing a product mixture containing both the vinyl-addition polymer (21–25%) and the desired polyester in low yield (27–38%). TPT can form two different types of adducts with aliphatic and aromatic alcohols; with MeOH, TPT forms a stable TPT(OMe)H[21] which can release MeOH to regenerate TPT at 80 °C (Figure S7), whereas with MP, TPT forms a hydrogen-bonded adduct[38] TPT-HOAr (Figures S8–S11). Upon addition of 2 equiv of BDMA to this adduct, the peak at 8.83 ppm for the H-bonded proton (C··H–O) disappeared and the characteristic peaks attributed to the single-addition product (Figure S12b) emerged. It is noteworthy that the peaks corresponding to PBDMA did not show up at RT, which is consistent with the fact that nucleophilic addition of the enamine to the incoming monomer occurs only at higher temperature (≈ 80 °C or higher). Different from the hydrogen-bonded TPT-MP adduct, the TPT(OMe)H adduct is robust at RT and not reactive towards BDMA (Figure S7b). Hence, the added aliphatic alcohol such as MeOH can effectively trap the reactive TPT catalyst, thus suppressing its polymerization activity. However, the direct use of TPT-(OMe)H (1 mol %) for the polymerization of BDMA in the presence of MP (0.1 mol %) in toluene at 100 °C led to a similar polymerization performance compared to that by TPT, achieving quantitative conversion after 48 h to produce PBDMA with $M_w = 21.2$ kg mol^{-1} and $Đ = 1.80$ (versus PBDMA with $M_w = 24.1$ kg mol^{-1} and $Đ = 1.70$ by TPT under the same conditions). The practical significance of this result is that, thanks to the air/moisture stability of TPT(OMe)H, this polymerization can be more conveniently handled than that using the more sensitive TPT catalyst.[39]

Because the added phenol doubly benefits the step-growth polymerization for producing the desired polyester, we examined the influence of the amount of added MP on the polymerization behavior by fixing the BDMA/TPT ratio (100) and reaction conditions (toluene, 90 °C, 48 h), while varying the MP amount from 0.05 to 1 equiv (relative to TPT, runs 13–16). The results, summarized in Figure S13, showed that the polymerizations with only a small amount of MP (0.05 to 0.1 equiv) achieved a quantitative conversion, whereas a further increase in the MP amount to 0.5 or 1 equiv significantly reduced the conversion to only 67 % or 59 %, respectively. On the other hand, the MW of the resulting polymer initially increased on going from 0.05 to 0.1 equiv of MP and then decreased on further increasing the MP amount to 0.5 and 1 equiv. These results suggested that the polymerization activity (thus monomer conversion and polymer MW) is enhanced by the increased MP amount (0.05 to 0.1 equiv), due to the facilitated proton transfer processes (see above), but the higher amount of MP in the system significantly reduces the polymerization activity, due to trapping the active propagating species (the enamine) by MP. The latter reasoning was confirmed by the observed facile addition of MP across the polarized enamine double bond in adducts (enamine and bisenamine) formed between BDMA and TPT, as shown in Figure S14, thereby deactivating the propagating enamine species.

The generality of HTP was addressed by extending the monomer to other dimethacrylates, ethylene glycol dimethacrylate (EDMA) and 1,6-hexanediol dimethacrylate (HDMA), which should reveal the effect of the spacing between the two methacrylate moieties on polymerization. Indeed, the polymerization of EDMA by TPT (1 mol %) in an EDMA/TPT/MP ratio of 100:1:0.1 at 100 °C in toluene reached a quantitative conversion in 24 h to form the corresponding polyester PEDMA ($E/Z = 96{:}4$, Figure S3) with $M_w = 28.4$ kg mol^{-1} (run 17). In contrast, BDMA and HDMA polymerizations under the same conditions needed 48 h to reach quantitative conversion (runs 10 and 19). However, the polymerization of EDMA at a lower catalyst loading of 0.5 mol % at 100 °C became less controlled and gelled in 12 h with formation of the vinyl-addition polymer; this problem can be easily overcome by employing more MP (EDMA/TPT/MP = 200:1:0.4), thereby affording the homogeneous polyester with $M_w = 22.8$ kg mol^{-1} (run 18). HDMA, with a longer (six) methylene chain separating the two methacrylate moieties, is much less reactive, but the polyester PHDMA ($E/Z = 96{:}4$, Figure S3) with a M_w of 16.1 kg mol^{-1} can be achieved by raising the temperature to 110 °C and using COL as the radical inhibitor (run 20).

The proposed HTP's step-growth mechanism outlined in Scheme 2 predicts the presence of possible three types of chain structures (**A**, **B**, and **C**) carrying different end groups (Figure 2). Indeed, the analysis of a low MW polyester sample (run 9) by MALDI-TOF MS that also depicts linear plots of m/z values (y) versus the number of BDMA repeat units (x) for the observed three series of peaks (Figure S16) clearly showed that the polyester exhibits three types of chain ends: doubly and singularly TPT-capped methacrylate ends (**A**, $M_{end} = 820$; **B**, $M_{end} = 523$ g mol^{-1}) as well as methacrylate ends (**C**, $M_{end} = 226 + 23(Na^+)$ g mol^{-1}). These results are consistent with the results obtained from the control reactions between BDMA and TPT that yielded the bisadduct BDMA-(TPT)$_2$ (i.e., bisenamine **A**) for the 1 (BDMA):2 (TPT) reaction, or a mixture containing the bisadduct, the mono-adduct, and the unreacted monomer (i.e., a mixture of **A**, **B**, and **C**) for the 1:1 reaction (Figures S14 and S15).[36]

The thermal properties of the unsaturated polyesters obtained by TPT-mediated HTP were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) analyses, showing a decrease in the glass transition temperature (T_g) with an increase of the methylene unit (x) in the monomer structure: −51 °C for PEDMA ($x = 2$), −55 °C for PBDMA ($x = 4$), and −60 °C for PHDMA ($x = 6$) (Figure S17). No melting transitions were detected under current DSC conditions, contributable to the disruption of the polyester crystallization by the double bond segment on the main chain. TGA and derivative thermogravimetric analysis (DTG) curves of the polyesters (Figure S18) showed the high thermal stability of the polyesters that exhibited a sharp, one-step degradation profile with a high onset degradation temperature (T_d, defined by the temperatures of 5 % weight loss) of approximately 360 °C and a high maximum degradation temperature (T_{max}) of about 410 °C. In sharp contrast, the BDMA vinyl-addition polymer exhibited a three-step degradation profile with a T_{max} of only 247 °C for the first degradation step (Figure S19).

Preliminary investigations into cross-linking of the resulting unsaturated polyesters examined two different approaches: in situ self-cross-linking (through chain-end double bonds) and ex situ copolymerization (through both chain-end and main-chain double bonds). In the first approach, the polymerization with a BDMA/TPT/MP ratio of 100:1:0.1 was first carried out at 100 °C for 48 h to produce a linear unsaturated polyester; the temperature was subsequently raised to 130 °C, and at this temperature MP loses the ability to prevent vinyl-addition polymerization by radical pathways, resulting in rapid cross-linking (gelation, Figure S20) between the methacrylate chain ends in different polyester chains. As shown in Figure S21, the self-cross-linked PBDMA exhibits an essentially identical FTIR spectrum to that before the cross-linking, except for the anticipated poor solubility. Accordingly, the T_g of −37 °C (Figure S22a) for the cross-linked polyester is noticeably higher than that of the uncross-linked PBDMA ($T_g = -55$ °C). Moreover, the cross-linked PBDMA displays a one-step degradation profile with $T_d = 345$ °C and $T_{max} = 415$ °C (Figure S23), the thermal degradation behavior of which is the same as PBDMA but differs from that of the vinyl-addition polymer (a three-step degradation profile). Intriguingly, a much more convenient self-crosslinking is achieved through microwave heating. Hence, heating the polymerization mixture consisting of BDMA/TPT(OMe)H/MP = 200:1:0.2 to 100 °C for 15 h in a microwave reactor achieved quantitative monomer conversion and afforded the cross-linked polyester gel that is essentially the same as that produced by the above two-stage thermal heating process, as confirmed by FTIR (Figure S21c), DSC (Figure S22b), and TGA/DTG (Figure S23). The ^{1}H NMR spectrum of the cross-linked PBDMA by microwave heating is also the same as that of PBDMA, except for its poor solubility due to cross-linking; it is also noteworthy that the resonances at 6.10 and 5.56 ppm, attributed to the retained double bond in the vinyl-addition polymer, were not observed, indicating that the cross-linking reaction under microwave heating occurred in the late stage of polymerization after all BDMA monomer was polymerized into polyester. In the second approach, the unsaturated polyester PBDMA was copolymerized with styrene (S) in different feed ratios (3:7 and 7:3 by weight) initiated by benzoyl peroxide (BPO). Thus, heating the mixture at 100 °C for 1 h formed a cross-linked gel (Figure S24). It is apparent from FTIR spectra (Figure S25) of the PBDMA/PS cross-linked polymers that new absorption bands attributed to the stretching vibration modes of PS at 3060, 3025, 1598, 1554, and 1494 cm^{-1} appeared and the intensity of such absorptions increased with increasing styrene in feed (Figure S25c versus S25b), while at the same time, the intensity of the absorption at 1648 cm^{-1}, attributed to the stretching vibration of the interior double bond (>C=CH-) of the starting unsaturated polyester, decreased accordingly, demonstrating the successful cross-linking between styrene and the interior double bonds of PBDMA.

In summary, we have developed a new polymerization termed HTP to convert commercially available dimethacrylates uniquely into unsaturated polyesters by an NHC catalyst that selectively promotes intermolecular Umpolung condensation through proton transfer. Several lines of experimental evidence obtained to date suggest that HTP proceeds through the step-growth propagation cycles consisting of repeated [conjugate addition/proton transfer/NHC release] fundamental steps. Keys to success in this development rest on the selectivity of the NHC for the proton-transfer pathway, following the zwitterionic enolate initially generated from the addition of the NHC to the monomer, to form the enamine propagating species, rather than continued conjugate additions which would produce the conventional chain-growth addition polymer (i.e., polymethacrylates), and the dual role of the added phenol that shuts down the radically induced vinyl-addition polymerization under HTP conditions (typically at 80–120 °C) and facilitates effective proton transfer after each monomer enchainment. The resulting unsaturated polyesters have a T_g between −51 °C and −60 °C and high thermal stability with a T_{max} of approximately 410 °C (versus 247 °C for the vinyl-addition polymer's first degradation step), and they can be readily cross-linked to robust polyester materials either by in situ self-cross-linking through chain-end double bonds or ex situ copolymerization through both chain-end and main-chain double bonds. HTP can also be conveniently executed using the air/moisture-stable alcohol adduct of an NHC such as TPT(OMe)H. The current HTP process is only achieved by the selective NHC (TPT) that can mediate the enamine formation/Umpolung coupling (through proton transfer) rather than the conjugate vinyl addition. As there is no loss of small molecules in HTP, this new polymerization method produces condensation polymers with quantitative atom efficiency. The well-known method of the metal (Ru, Mo)-mediated acyclic diene metathesis (ADMET), which is highly effective in the condensation polymerization of α,ω-dienes to yield unsaturated polymers, is not suitable for the homopolymerization of electron-deficient conjugated diolefins such as diacrylates and especially the more sterically demanding dimethacrylates.[40] Hence, we anticipate that HTP will open up new avenues in the synthesis of functional polymers, inaccessible by other polymerization methods, from multifunctional monomers, not just limited to di- or oligomethacrylates.

Received: June 27, 2014
Revised: August 13, 2014

Keywords: N-heterocyclic carbenes · organocatalysis · polyesters · polymerization · polymers

---

[1] a) E. N. Jacobsen, D. W. C. MacMillan, Organocatalysis, special feature issue, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 20618–20619; b) C. Grondal, M. Jeanty, D. Enders, *Nat. Chem.* **2010**, *2*, 167–178; c) D. W. C. MacMillan, *Nature* **2008**, *455*, 304–308; d) Special edition issue *Asymmetric Organocatalysis* (Eds.: K. N. Houk, B. List), *Acc. Chem. Res.* **2004**, *37*, 487–631.

[2] Selected recent reviews: a) C. M. R. Volla, I. Atodiresei, M. Rueping, *Chem. Rev.* **2014**, *114*, 2390–2431; b) U. Scheffler, R. Mahrwald, *Chem. Eur. J.* **2013**, *19*, 14346–14396; c) R. C. Wende, P. R. Schreiner, *Green Chem.* **2012**, *14*, 1821–1849; d) T. Marcelli, H. Hiemstra, *Synthesis* **2010**, 1229–1279; e) D. Kampen, C. M. Reisnger, B. List, *Top. Curr. Chem.* **2010**, *291*, 1395–1356.

[3] A recent review: D. Liu, E. Y.-X. Chen, *Green Chem.* **2014**, *16*, 964–981.

[4] Selected recent reviews: a) C. Thomas, B. Bibal, *Green Chem.* **2014**, *16*, 1687–1699; b) K. Fuchise, Y. Chen, T. Satoh, T. Kakuchi, *Polym. Chem.* **2013**, *4*, 4278–4291; c) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2010**, *43*, 2093–2107; d) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, J. L. Hedrick, *Chem. Rev.* **2007**, *107*, 5813–5840.

[5] Selected recent reviews on NHCs: a) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723–6753; b) H. Mayr, S. Lakhdar, B. Maji, A. R. Ofial, *Beilstein J. Org. Chem.* **2012**, *8*, 1458–1478; c) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952; *Angew. Chem.* **2010**, *122*, 7094–7107; d) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; e) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; *Angew. Chem.* **2008**, *120*, 3166–3216; f) D. Bour-

issou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[6] Selected recent reviews on NHC-mediated organocatalysis: a) P. Chauhan, D. Enders, *Angew. Chem. Int. Ed.* **2014**, *53*, 1485–1487; *Angew. Chem.* **2014**, *126*, 1509–1511; b) J. Mahatthananchai, J. W. Bode, *Acc. Chem. Res.* **2014**, *47*, 696–707; c) S. J. Ryan, L. Candish, D. W. Lupton, *Chem. Soc. Rev.* **2013**, *42*, 4906–4917; d) X.-Y. Chen, S. Ye, *Org. Biomol. Chem.* **2013**, *11*, 7991–7998; e) S. De Sarkar, A. Biswas, R. C. Samanta, A. Studer, *Chem. Eur. J.* **2013**, *19*, 4664–4678; f) A. Grossmann, D. Enders, *Angew. Chem. Int. Ed.* **2012**, *51*, 314–325; *Angew. Chem.* **2012**, *124*, 320–332; g) X. Bugaut, F. Glorius, *Chem. Soc. Rev.* **2012**, *41*, 3511–3522; h) P.-C. Chiang, J. W. Bode in *Science of Synthesis: Asymmetric Organocatalysis* (Ed.: B. List), Georg Thieme, Stuttgart, **2012**, pp. 639–672; i) J. Izquierdo, G. E. Hutson, D. T. Cohen, K. A. Scheidt, *Angew. Chem. Int. Ed.* **2012**, *51*, 11686–11698; *Angew. Chem.* **2012**, *124*, 11854–11866; j) H. U. Vora, P. Wheeler, T. Rovis, *Adv. Synth. Catal.* **2012**, *354*, 1617–1639; k) A. T. Biju, N. Kuhl, F. Glorius, *Acc. Chem. Res.* **2011**, *44*, 1182–1195; l) J. L. Moore, T. Rovis, *Top. Curr. Chem.* **2010**, *291*, 77–144; m) V. Nair, S. Vellalath, B. P. Babu, *Chem. Soc. Rev.* **2008**, *37*, 2691–2698; n) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 2988–3000; *Angew. Chem.* **2007**, *119*, 3046–3058; o) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606–5655.

[7] a) G. W. Nyce, T. Glauser, E. F. Connor, A. Möck, R. M. Waymouth, J. L. Hedrick, *J. Am. Chem. Soc.* **2003**, *125*, 3046–3056; b) E. F. Connor, G. W. Nyce, M. Myers, A. Möck, J. L. Hedrick, *J. Am. Chem. Soc.* **2002**, *124*, 914–915; c) F. Nederberg, E. F. Connor, M. Möller, T. Glauser, J. L. Hedrick, *Angew. Chem. Int. Ed.* **2001**, *40*, 2712–2715; *Angew. Chem.* **2001**, *113*, 2784–2787.

[8] Selected recent reviews: a) H. A. Brown, R. M. Waymouth, *Acc. Chem. Res.* **2013**, *46*, 2585–2596; b) M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.* **2013**, *42*, 2142–2172.

[9] a) W. Jeong, E. J. Shin, D. A. Culkin, J. L. Hedrick, R. M. Waymouth, *J. Am. Chem. Soc.* **2009**, *131*, 4884–4891; b) D. A. Culkin, W. Jeong, S. Csihony, E. D. Gomez, N. P. Balsara, J. L. Hedrick, R. M. Waymouth, *Angew. Chem. Int. Ed.* **2007**, *46*, 2627–2630; *Angew. Chem.* **2007**, *119*, 2681–2684; c) A. P. Dove, H. Li, R. C. Pratt, B. G. G. Lohmeijer, D. A. Culkin, R. M. Waymouth, J. L. Hedrick, *Chem. Commun.* **2006**, 2881–2883; d) O. Coulembier, A. P. Dove, R. C. Pratt, A. C. Sentman, D. A. Culkin, L. Mespouille, P. Dubois, R. M. Waymouth, J. L. Hedrick, *Angew. Chem. Int. Ed.* **2005**, *44*, 4964–4968; *Angew. Chem.* **2005**, *117*, 5044–5048; e) S. Csihony, D. A. Culkin, A. C. Sentman, A. P. Dove, R. M. Waymouth, J. L. Hedrick, *J. Am. Chem. Soc.* **2005**, *127*, 9079–9084.

[10] a) H. A. Brown, S. Xiong, G. Medvedev, Y. A. Chang, M. M. Abu-Omar, J. M. Caruthers, R. M. Waymouth, *Macromolecules* **2014**, *47*, 2955–2963; b) E. J. Shin, H. A. Brown, S. Gonzalez, W. Jeong, J. L. Hedrick, R. M. Waymouth, *Angew. Chem. Int. Ed.* **2011**, *50*, 6388–6391; *Angew. Chem.* **2011**, *123*, 6512–6515; c) T. K. Sen, S. Ch. Sau, A. Mukherjee, A. Modak, S. K. Mandal, D. Koley, *Chem. Commun.* **2011**, *47*, 11972–11974; d) N. E. Kamber, W. Jeong, S. Gonzalez, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2009**, *42*, 1634–1639; e) W. Jeong, J. L. Hedrick, R. M. Waymouth, *J. Am. Chem. Soc.* **2007**, *129*, 8414–8415.

[11] a) J. Raynaud, C. Absalon, Y. Gnanou, D. Taton, *Macromolecules* **2010**, *43*, 2814–2823; b) J. Raynaud, W. N. Ottou, Y. Gnanou, D. Taton, *Chem. Commun.* **2010**, *46*, 3203–3205; c) J. Raynaud, C. Absalon, Y. Gnanou, D. Taton, *J. Am. Chem. Soc.* **2009**, *131*, 3201–3209.

[12] F. Nederberg, B. G. G. Lohmeijer, F. Leibfarth, R. C. Pratt, J. Choi, A. P. Dove, R. M. Waymouth, J. L. Hedrick, *Biomacromolecules* **2007**, *8*, 153–160.

[13] a) H. A. Brown, Y. A. Chang, R. M. Waymouth, *J. Am. Chem. Soc.* **2013**, *135*, 18738–18941; b) M. Rodriguez, S. Marrot, T. Kato, S. Stérin, E. Fleury, A. Baceiredo, *J. Organomet. Chem.* **2007**, *692*, 705–708; c) B. G. G. Lohmeijer, G. Dubois, F. Leibfarth, R. C. Pratt, F. Nederberg, A. Nelson, R. M. Waymouth, C. Wade, J. L. Hedrick, *Org. Lett.* **2006**, *8*, 4683–4686.

[14] a) L. Guo, S. H. Lahasky, K. Ghale, D. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 9163–9171; b) L. Guo, D. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 18072–18074.

[15] a) O. Coutelier, M. El Ezzi, M. Destarac, F. Bonnette, T. Kato, A. Baceiredo, G. Sivasankarapillai, Y. Gnanou, D. Taton, *Polym. Chem.* **2012**, *3*, 605–608; b) J. Pinaud, K. Vijayakrishna, D. Taton, Y. Gnanou, *Macromolecules* **2009**, *42*, 4932–4936; c) G. W. Nyce, J. A. Lamboy, E. F. Connor, R. M. Waymouth, J. L. Hedrick, *Org. Lett.* **2002**, *4*, 3587–3590.

[16] a) J. Raynaud, N. Liu, M. Fèvre, Y. Gnanou, D. Taton, *Polym. Chem.* **2011**, *2*, 1706–1712; b) J. Raynaud, N. Liu, Y. Gnanou, D. Taton, *Macromolecules* **2010**, *43*, 8853–8861; c) J. Raynaud, Y. Gnanou, D. Taton, *Macromolecules* **2009**, *42*, 5996–6005; d) J. Raynaud, A. Ciolino, A. Baceiredo, M. Destarac, F. Bonnette, T. Kato, Y. Gnanou, D. Taton, *Angew. Chem. Int. Ed.* **2008**, *47*, 5390–5393; *Angew. Chem.* **2008**, *120*, 5470–5473; e) M. D. Scholten, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2008**, *41*, 7399–7404.

[17] a) O. W. Webster, *Adv. Polym. Sci.* **2004**, *167*, 1–34; b) D. Y. Sogah, W. R. Hertler, O. W. Webster, G. M. Cohen, *Macromolecules* **1987**, *20*, 1473–1488; c) O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, T. V. RajanBabu, *J. Am. Chem. Soc.* **1983**, *105*, 5706–5708.

[18] a) A. J. Arduengo III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 6641–6649; b) A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.

[19] a) E. Y.-X. Chen, *Top. Curr. Chem.* **2013**, *334*, 239–260; b) Y. Zhang, G. M. Miyake, M. G. John, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, *Dalton Trans.* **2012**, *41*, 9119–9134; c) Y. Zhang, G. M. Miyake, E. Y.-X. Chen, *Angew. Chem. Int. Ed.* **2010**, *49*, 10158–10162; *Angew. Chem.* **2010**, *122*, 10356–10360.

[20] C. Fischer, S. W. Smith, D. A. Powell, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 1472–1473.

[21] a) D. Enders, K. Breuer, U. Kallfass, T. Balensiefer, *Synthesis* **2003**, 1292–1295; b) D. Enders, K. Breuer, J. H. Teles, K. Ebel, *J. Prakt. Chem.* **1997**, *339*, 397–399; c) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem. Int. Ed. Engl* **1995**, *34*, 1021–1023; *Angew. Chem.* **1995**, *107*, 1119–1122.

[22] Y. Zhang, E. Y.-X. Chen, *Angew. Chem. Int. Ed.* **2012**, *51*, 2465–2469; *Angew. Chem.* **2012**, *124*, 2515–2519.

[23] Selected recent work on the structural characterization and property of the deoxy-Breslow intermediate: a) Ref. [22]; b) B. Maji, M. Horn, H. Mayr, *Angew. Chem. Int. Ed.* **2012**, *51*, 6231–6235; *Angew. Chem.* **2012**, *124*, 6335–6339; c) C. E. I. Knappke, A. J. Arduengo III, H. Jiao, J.-M. Neudörfl, J. A. von Wangelin, *Synthesis* **2011**, 3784–3795; d) C. E. I. Knappke, J.-M. Neudörfl, J. A. von Wangelin, *Org. Biomol. Chem.* **2010**, *8*, 1695–1705.

[24] Selected recent work on the structural characterization and property of the Breslow intermediate: a) A. Berkessel, V. R. Yatham, S. Elfert, J.-M. Neudörfl, *Angew. Chem. Int. Ed.* **2013**, *52*, 11158–11162; *Angew. Chem.* **2013**, *125*, 11364–11369; b) B. Maji, H. Mayr, *Angew. Chem. Int. Ed.* **2013**, *52*, 11163–11167; *Angew. Chem.* **2013**, *125*, 11370–11374; c) A. Berkessel, S. Elfert, V. R. Yatham, J.-M. Neudörfl, N. E. Schlörer, J. H. Teles, *Angew. Chem. Int. Ed.* **2012**, *51*, 12370–12374; *Angew. Chem.*

2012, *124*, 12537 – 12541; d) D. A. DiRocco, K. M. Oberg, T. Rovis, *J. Am. Chem. Soc.* **2012**, *134*, 6143 – 6145; e) B. Maji, H. Mayr, *Angew. Chem. Int. Ed.* **2012**, *51*, 10408 – 10412; *Angew. Chem.* **2012**, *124*, 10554 – 10558; f) A. Berkessel, S. Elfert, K. Etzenbach-Effers, J. H. Teles, *Angew. Chem. Int. Ed.* **2010**, *49*, 7120 – 7124; *Angew. Chem.* **2010**, *122*, 7275 – 7279.

[25] R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719 – 3726.

[26] A. T. Biju, M. Padmanaban, N. E. Wurz, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 8412 – 8415; *Angew. Chem.* **2011**, *123*, 8562 – 8565.

[27] a) T. Kato, Y. Ota, S.-I. Matsuoka, K. Takagi, M. Suzuki, *J. Org. Chem.* **2013**, *78*, 8739 – 8747; b) S.-I. Matsuoka, Y. Ota, A. Washio, A. Katada, K. Ichioka, K. Takagi, M. Suzuki, *Org. Lett.* **2011**, *13*, 3722 – 3725.

[28] B. Maji, M. Breugst, H. Mayr, *Angew. Chem. Int. Ed.* **2011**, *50*, 6915 – 6919; *Angew. Chem.* **2011**, *123*, 7047 – 7052.

[29] T. Kato, S.-I. Matsuoka, M. Suzuki, *J. Org. Chem.* **2014**, *79*, 4484 – 4491.

[30] M. Schedler, N. E. Wurz, C. G. Daniliuc, F. Glorius, *Org. Lett.* **2014**, *16*, 3134 – 3137.

[31] W. Nzahou Ottou, D. Bourichon, J. Vignolle, A. L. Wirotius, F. Robert, Y. Landais, M. M. Sotiropoulos, K. Miqueu, D. Taton, *Chem. Eur. J.* **2014**, *20*, 3989 – 3997.

[32] S.-I. Matsuoka, S. Namera, A. Washio, K. Takagi, M. Suzuki, *Org. Lett.* **2013**, *15*, 5916 – 5919.

[33] Y. Zhang, M. Schmitt, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 17925 – 17942.

[34] S. Naumann, F. G. Schmidt, R. Schowner, W. Frey, M. R. Buchmeiser, *Polym. Chem.* **2013**, *4*, 2731 – 2740.

[35] a) K. G. Johnson, L. S. Yang in *Preparation, Properties and Applications of Unsaturated Polyester* in *Modern Polyesters* (Eds.: J. Scheirs, T. E. Long), Wiley, Chichester, **2003**, pp. 699 – 713; b) H. V. Boenig, *Unsaturated Polyesters: Structure and Properties*, Elsevier, Amsterdam, **1964**.

[36] See the Supporting Information for details.

[37] a) Z. Fu, H. Sun, S. Chen, B. Tiwari, G. Li, Y. R. Chi, *Chem. Commun.* **2013**, *49*, 261 – 263; b) X. Zhao, D. A. DiRocco, T. Rovis, *J. Am. Chem. Soc.* **2011**, *133*, 12466 – 12469; c) D. A. DiRocco, T. Rovis, *J. Am. Chem. Soc.* **2011**, *133*, 10402 – 10405.

[38] For examples of the structurally characterized IMes-alcohol and IMes-phenol complexes through H-bonding, see: a) M. Movassaghi, M. A. Schmidt, *Org. Lett.* **2005**, *7*, 2453 – 2456; b) J. A. Cowan, J. A. C. Clyburne, M. G. Davidson, R. L. W. Harris, J. A. K. Howard, P. Kupper, M. A. Leech, S. P. Richards, *Angew. Chem. Int. Ed.* **2002**, *41*, 1432 – 1434; *Angew. Chem.* **2002**, *114*, 1490 – 1492.

[39] For a review on protected NHCs in organo- and polymerization catalysis, see: S. Naumann, M. R. Buchmeiser, *Catal. Sci. Technol.* **2014**, *4*, 2466 – 2479.

[40] Selected examples and reviews: a) L. Ding, M. Xu, J. Wang, Y. Kiao, J. Qiu, *Polymer* **2014**, *55*, 1681—1687; b) M. D. Schulz, K. B. Wagener, *ACS Macro Lett.* **2012**, *1*, 449—451; c) K. L. Opper, K. B. Wagener, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 821—831; d) H. Mutlu, L. M. de Espinosa, M. A. R. Meier, *Chem. Soc. Rev.* **2011**, *40*, 1404—1445; e) A. K. Chatterjee, T.-L. Choi, D. P. Sanders, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 11360 – 11370.