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Organopolymerization

Conjugate-Addition Organopolymerization: Rapid Production of Acrylic Bioplastics by N-Heterocyclic Carbenes**

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Organocatalysis using N-heterocyclic carbenes (NHCs) has attracted growing interest because of its unique reactivity and selectivity in many different types of organic reactions.[1] The utility of NHC-mediated reactions has also been expanded to polymer synthesis,[2] predominantly through the ring-opening polymerization (ROP) of cyclic monomers such as cyclic esters,[3] epoxides,[4] cyclic siloxanes,[5] and N-carboxyl anhydrides.[6] NHC-catalyzed step-growth polymerization has been reported as well.[7] Polymerization of α,β-unsaturated esters (acrylics) such as methyl methacrylate (MMA) has also been recently realized through the classic group-transfer polymerization (GTP) initiated by silyl ketene acetals[8] using NHCs as alternative nucleophilic catalysts to activate the acetal initiator.[9] In addition, such acrylic monomers can be rapidly polymerized by frustrated Lewis pairs (FLPs) consisting of bulky NHC bases, such as the Arduengo carbenes 1,3-di-*tert*-butylimidazolin-2-ylidene (I*t*Bu) and 1,3-di-mesityl-butyl-imidazolin-2-ylidene (IMes),[10] and the strongly acidic, sterically encumbered, perfluoroaryl alane, via the proposed zwitterionic imidazolium enolaluminate intermediates.[11] When using such Arduengo NHCs alone, no MMA conversion was observed in either toluene[11] or THF.[9b] In contrast, the Enders triazolylidene carbene TPT (1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene),[12] which was estimated to be 10^3 times less nucleophilic than the imidazolylidene carbene (IMes),[13] catalyzes tail-to-tail dimerization (umpolung) of MMA and other methacrylate substrates, whereas the common imidazolylidene carbenes are ineffective.[14]

As can be seen clearly from the above overview, although the NHC-mediated ROP of cyclic monomers has been highly successful, the NHC-mediated conjugate-addition polymerization of functionalized alkenes such as acrylics still requires the use of a nucleophilic initiator in the case of GTP[9] or a Lewis acid catalyst in the case of the FLP polymerization.[11] To the best of our knowledge, efficient conjugate-addition polymerization of such monomers directly by NHCs (i.e., in the absence of any other initiator or catalyst components) has not been previously achieved.[15] Communicated herein is the first, rapid conjugate-addition polymerization of α,β-unsaturated esters by NHCs alone, with the most active catalyst achieving quantitative monomer conversion in less than one minute. Among the NHC catalysts investigated (Figure 1), the most nucleophilic NHC (I*t*Bu) directly polymerizes a large excess (e.g., 800 equiv) of renewable methylene butyrolactone monomers,[16] including naturally occurring α-methylene-γ-butyrolactone (MBL)[17] and plant biomass-derived γ-methyl-α-methylene-γ-butyrolactone (MMBL),[18] at room temperature into medium- or high-molecular-weight polymers in less than one minute, thus giving a high turnover frequency (TOF) of greater than $4.8\times10^4\ \text{h}^{-1}$. The rate of the polymerization is strongly affected by the relative nucleophilicity of the NHC catalysts employed herein (Figure 1), and there exists a remarkable selectivity of the NHC for substrate structures, thus leading to three different modes of reaction involving acrylics.

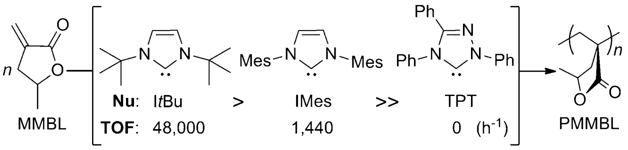

Figure 1. Rapid polymerization of the renewable MMBL by I*t*Bu in DMF at room temperature and correlation of the polymerization activity of NHCs with their relative nucleophilicity.

We hypothesized that even though NHCs showed no activity in the polymerization of the most common acrylic monomer MMA in toluene or THF,[9b,11] they could directly polymerize renewable the monomers MBL and MMBL because such α-methylene-γ-butyrolactones exhibit greater reactivity in chain-growth polymerization than typical alkyl methacrylates (e.g., MMA) and this activity is attributable to the presence of both the nearly planar five-membered lactone ring (which provides resonance stabilization for the active species) and the higher energy exocyclic C=C double bond (as a result of the ring strain and the fixed *s-cis* conformation).[16] Indeed, with a monomer to initiator ([M]/[NHC]) ratio of 200, rather fast polymerization of MMBL by I*t*Bu (0.5 mol%) was observed even in toluene at room temperature, thus achieving 93 and 99% conversions in 30 minutes and 1 hour, respectively (entry 1, Table 1). The polymerization was heterogeneous, thereby producing poly-γ-methyl-α-methylene-γ-butyrolactone (PMMBL) with a number-average molecular weight (M_n) of $58.4\ \text{kg mol}^{-1}$ at 93% conversion, which is about three times higher than the calculated M_n. The less nucleophilic IMes showed noticeably lower activity (entry 2), whereas the least nucleophilic NHC of this series, TPT, exhibited the lowest activity (entry 3). The polymerization by I*t*Bu in THF was still heterogeneous and slower; it yielded PMMBL with a considerably lower M_n of $23.0\ \text{kg mol}^{-1}$ (polydispersity index, PDI = 1.69, entry 4). A similar trend

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Table 1: Selected results of polymerization by NHCs.[a]

Entry	Monomer	NHC	[M]/[NHC]	Solvent	T [°C]	t [min]	Conv.[b] [%]	TOF [h^{-1}]	M_n[c] [kg mol^{-1}]	PDI[c] (M_w/M_n)
1	MMBL	I*t*Bu	200	tol	RT	(30)60	(93)99	(372)198	(58.4)[d]	n.d.
2	MMBL	IMes	200	tol	RT	(60)1440	(84)98	(168)8	51.2[d]	n.d.
3	MMBL	TPT	200	tol	RT	(60)1440	(20)79	(40)7	38.9[d]	n.d.
4	MMBL	I*t*Bu	200	THF	RT	(60)1440	(79)100	(158)8	23.0	1.69
5	MMBL	IMes	200	THF	RT	(540)1440	(76)87	(17)7	29.4	1.54
6	MMBL	TPT	200	THF	RT	1440	0	0	–	–
7	MMBL	I*t*Bu	200	DMF	RT	1	100	12000	38.5	1.68
8	MMBL	I*t*Bu	400	DMF	RT	1	100	24000	69.0[e]	1.93
9	MMBL	I*t*Bu	800	DMF	RT	1	100	48000	84.7[e]	2.11
10	MMBL	IMes	200	DMF	RT	(1)1440	(12)100	(1440)8	17.8	1.46
11	MMBL	TPT	200	DMF	RT	1440	0	0	–	–
12	MMBL	I*t*Bu	200	DMF	0	60	100	200	40.6	1.66
13	MMBL	I*t*Bu	200	DMF	−60	600	>99	20	45.8	1.84
14	MMBL	I*t*Bu	200[f]	DMF	RT	1	100	12000	29.3[e]	1.78
15	MMBL	I*t*Bu	200[g]	DMF	RT	1	100	12000	19.1[e]	1.80
16	MBL	I*t*Bu	200	DMF	RT	(1)1440	(70)100	(8400)8	27.0[e]	1.59
17	MBL	IMes	200	DMF	RT	(300)1440	(89)100	(36)8	10.6	1.36
18	MBL	TPT	200	DMF	RT	1440	0	0	–	–
19	MMA	I*t*Bu	200	DMF	RT	(60)210	(68)87	(136)50	33.2	1.99
20	MMA	IMes	20	DMF	RT or 80	1440	<1	–	–	–
21	MMA	TPT	20	DMF	RT or 80	1440	<1	–	–	–
22	FMA	I*t*Bu	200	DMF	RT	(60)1440	(48)100	(96)8	14.7	1.94

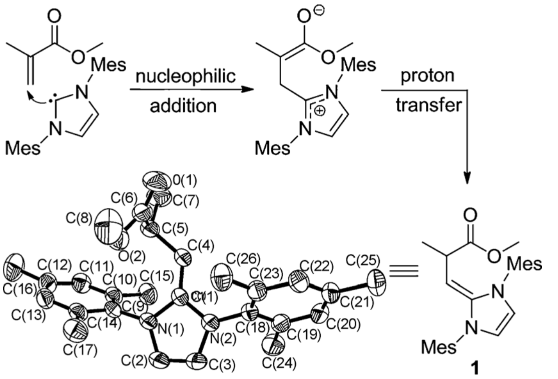
[a] Solvents: used 4.5 mL, except for the MMA polymerization where 8.0 mL solvent was used; RT (ca. 25 °C). [b] Conv. = % monomer conversion measured by ^{1}H NMR spectroscopy. [c] Number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) determined by GPC in DMF relative to PMMA standards. [d] The reaction was heterogeneous in toluene, thus giving the polymer that contained a small shoulder to the left of the peak (higher molecular weight). [e] Contained a small (ca. 1–2 %) high-molecular-weight tail to the peak. [f] In the presence of 10 equiv of 3-methyl-2-butanone (MBO). [g] In the presence of 50 equiv of MBO. THF = tetrahydrofuran), DMF = *N*,*N*-dimethylformamide, n.d. = not determined. Numbers in parentheses have the same meaning and units as those next to them.

was also observed for IMes (entry 5), and TPT showed no polymerization activity in THF after up to 24 hours (entry 6).

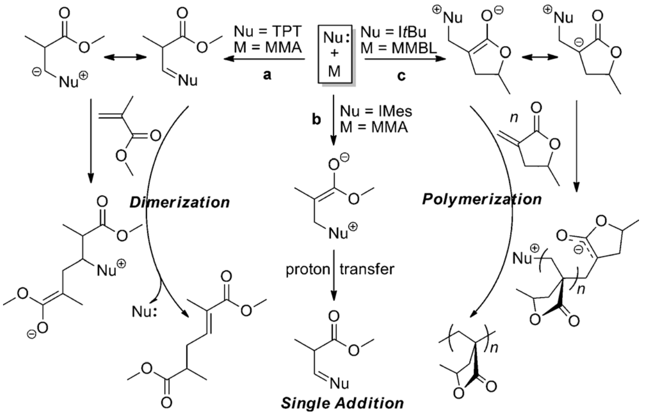
Remarkably, the homogeneous polymerization by I*t*Bu in the much more polar solvent DMF is *extremely rapid*. Thus, all 200, 400, or 800 equivalents of MMBL were rapidly polymerized in less than 1 minute (entries 7–9), thereby giving a high TOF of greater than 4.8×10^4 h^{-1} (entry 9). The M_n of the resulting PMMBL increased from 38.5 kg mol^{-1} to 69.0 kg mol^{-1} to 84.7 kg mol^{-1} as the [M]/[NHC] ratio increased from 200 to 400 to 800, respectively (entries 7–9), thus demonstrating the ability of the system to control M_n by adjusting the [M]/[NHC] ratio. As in the polymerization of MMBL mediated by metal- and metalloid-based catalysts or initiators,[16a–d] no ring-opening of the butyrolactone ring was observed; control runs using NHCs or NHC/Lewis acid pairs for the ROP of five-membered lactones (e.g., γ-butyrolactone and γ-valerolactone) also showed no polymerization activity. The use of IMes resulted in a considerable initial polymerization rate reduction by more than 30-fold, and the polymer M_n value at 100 % conversion was also lowered by more than twofold (entry 10 versus 9), and the least nucleophilic TPT in the series again exhibited no polymerization activity after up to 24 hours (entry 11). Lowering the temperature of the MMBL polymerization, run with I*t*Bu in DMF, from room temperature to either 0 or −60 °C decreased the TOF values (entries 12 and 13 versus 7). The PMMBL tacticity was not noticeably affected by the reaction temperature: *mm* = 20.6 % and 21.6 %; *mr* = 43.3 % and 43.8 % at 25 °C and −60 °C, respectively. Interestingly, an enolizable organic acid, 3-methyl-2-butanone (MBO), can be used to modulate the polymer M_n value. Thus, addition of 10 equivalents of MBO lowered the M_n by 24 % relative to the same run without MBO (29.3 kg mol^{-1} in entry 14 versus 38.5 kg mol^{-1} in entry 7), and 50 equivalents of MBO reduced the M_n by one half to 19.1 kg mol^{-1} (entry 15); in both cases, the high polymerization activity was maintained.

Having achieved high activity for the polymerization of MMBL by I*t*Bu, we next examined five other conjugated acrylic monomers for their reactivity toward the present NHCs. The β-methyl derivative, β-methyl-α-methylene-γ-butyrolactone, can also be rapidly polymerized by I*t*Bu in DMF at room temperature. Likewise, the parent MBL was quickly polymerized by I*t*Bu in DMF at room tmeperature, thus achieving 70 % conversion in 1 minute (entry 16). A reactivity trend similar to that of the MMBL polymerization was observed for the MBL polymerization. Thus, substituting I*t*Bu by IMes resulted in a much less active polymerization (89 % conversion in 100 min; entry 17), and TPT exhibited no activity for MBL polymerization after up to 24 hours (entry 18). Interestingly, although I*t*Bu showed no activity for polymerization of MMA in toluene or THF at room tmeperature, good activity (68 % conversion in 1 h, TOF = 136 h^{-1}; entry 19) was observed for this polymerization in DMF. The PMMA produced at room temperature is a syndio-rich atactic material with *mm* = 4.7 %, *mr* = 39.6 %, and *rr* = 55.7 %. Not surprisingly, both IMes and TPT showed negligible activity for MMA polymerization in DMF (entries 20 and 21). Polymerization of the biomass-derived furfuryl methacrylate (FMA)[19] by I*t*Bu in DMF was also successful, thereby achieving 48 % monomer conversion in 1 hour (entry 22). The PFMA produced herein is also a syndio-biased atactic material with *mm* = 4.7 %, *mr* = 35.1 %, and *rr* = 60.2 %. In contrast, no polymerization was observed for *N*,*N*-dimethyl acrylamide at room temperature after up to 24 hours, presumably because of the higher basicity of the amide enolate arising from addition of the nucleophile, relative to that of the ester enolate.

To gain insight into the above-described polymerization behavior as a function of the NHC and monomer structures, we investigated stoichiometric reactions of NHCs and α,β-unsaturated ester substrates. As (M)MBL monomers are quickly polymerized by imidazolylidene carbenes, we tested the model reaction on MMA. The triazolylidene carbene TPT was found to undergo efficient dimerization (umpolung) of MMA, whereas other common imidazolylidene NHCs such as I*t*Bu and IMes are ineffective.[14] This intermolecular umpolung of MMA was proposed to proceed through the initial conjugate addition of TPT to MMA to form the corresponding ester enolate that undergoes proton transfer (tautomerization), thus affording an enamine intermediate similar to the Breslow intermediate in the benzoin reaction.[20] Addition of the enamine to another molecule of MMA leads to the tail-to-tail dimerization product, again via the ester enolate intermediate, which then undergoes proton transfer and release of TPT. This mechanism bears a close resemblance to the one proposed for the intramolecular umpolung of Michael acceptors catalyzed by NHCs.[21] We found that despite the fact that the imidazolylidene I*t*Bu did not react with MMA in toluene at room temperature (up to 3 days), another common NHC, IMes, reacted smoothly with MMA at room temperature to form the single-addition product enamine **1** (Scheme 1). Unlike the TPT-derived enamine intermediate involved in the dimerization of MMA, the enamine derived from IMes is stable, isolable, and nonreactive toward additional MMA, presumably because of the strong, irreversible binding of IMes with MMA. The enamine **1** has been characterized spectroscopically by NMR[22] analysis and structurally by X-ray diffraction analysis.[23] The molecular structure of **1** (Scheme 1) clearly displays a C=C double bond formed between C1 and C4 having a bond distance of 1.353(2) Å. This single-addition product resembles those enamines derived from the 1:1 addition of TPT to more highly (doubly) activated Michael acceptors.[12,24]



Scheme 1. Possible mechanism for the reaction between IMes and MMA and X-ray crystal structure of the resulting single-addition product enamine **1**. Hydrogen atoms have been omitted for clarity and ellipsoids drawn at 50 % probability. Selected bond lengths [Å]: C1–C4 1.353(2), C2–C3 1.316(2), C4–C5 1.508(2).



Scheme 2. Possible mechanistic scenarios for the observed selectivity: three types of reactions involving α,β-unsaturated esters.

Possible mechanistic scenarios for the remarkable above-described selectivity of the NHC structure for each of the three types of reactions involving α,β-unsaturated esters, including single addition, dimerization, and polymerization, are outlined in Scheme 2. On the basis of the results available to date,[14] it appears that dimerization (path a, Scheme 2) is unique to the triazolylidene carbene TPT, the least nucleophilic NHC in the series, and to linear (meth)acrylates, as we found no dimerization for methylene butyrolactones with a fixed *s-cis* conformation. In contrast, the more nucleophilic IMes reacts with methacrylates such as MMA in toluene to selectively afford the single-addition product (path b, Scheme 2), but the most nucleophilic NHC in the series, I*t*Bu, does not react with MMA in the same solvent. Instead, I*t*Bu rapidly polymerizes methylene butyrolactones (path c, Scheme 2), especially MMBL in DMF, and also polymerizes methacrylates (e.g., MMA and FMA) in DMF. The polymerization scenario is proposed to proceed through reiterative 1,4-conjugate addition of the propagating ester enolate to the incoming monomer (path c), following the well-established conjugate-addition mechanism for the controlled anionic polymerization of acrylics using discrete or in situ generated metal ester enolates.[25] Preliminary studies on the resulting polymer structure by MALDI-TOF MS analysis of low-molecular-weight MMBL oligomers produced by NHCs in toluene showed that neither initiating nor terminating end groups were present in the major fraction of the oligomers,[22] which is indicative of a cyclic polymer structure. This possible structure is reminiscent of the cyclic poly(lactide) produced by the NHC-initiated zwitterionic ROP of lactide.[2,3] The origin of such a structure for the current conjugate-addition polymers can be rationalized by a mode involving chain termination through the back-biting of the growing ester enolate onto the electrophilic carbon directly bonded to the nucleophile, accompanied by elimination of the nucleophile. More extensive studies are needed to verify this possible cyclic polymer structure generated from the current polymerization system.

In conclusion, we have developed a rapid organopolymerization of acrylic monomers at room temperature through the proposed conjugate-addition propagation cycle mediated by NHCs alone (with no any other initiating or catalyzing components). This polymerization is especially effective for the biomass-derived renewable methylene butyrolactones such as MMBL, thus quantitatively converting the monomer into the corresponding bioplastics in typically less than 1 minute. This polymerization pathway also adds a new mode of reactivity to the NHC-mediated reactions involving Michael acceptors, α,β-unsaturated esters, that is, dimerization (intra- and intermolecular umpolung) and single addition (although the previously reported single addition applied to doubly activated Michael acceptors). Also noteworthy is the apparent correlation between the activity of polymerization and the nucleophilicity of NHCs employed in this study, with the most nucleophilic I*t*Bu in the series exhibiting the highest activity, the less nucleophilic IMes displaying much lower activity, and the least nucleophilic TPT often showing no activity at all. Intriguingly, there exists a remarkable selectivity of the NHC for the substrate structures, thus leading to three different reaction modes involving acrylic substrates: IMes selectively forms the single-addition product with methacrylates (MMA); TPT promotes dimerization of methacrylates (MMA); and I*t*Bu mediates rapid polymerization of methylene butyrolactones (MBL, MMBL). It is tempting to suggest that such selectivity rests on the relative reversibility of NHC binding with substrates (in the case of single addition versus dimerization) and the relative propensity for tautomerization of the ester enolate intermediate generated by addition of the nucleophile versus subsequent conjugate addition to the monomer (in the case of dimerization versus polymerization). Additional studies to address such mechanistic aspects are currently underway.

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