Chain-Growth Polymerization

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Polymerization Initiated by Organic Electron Donors

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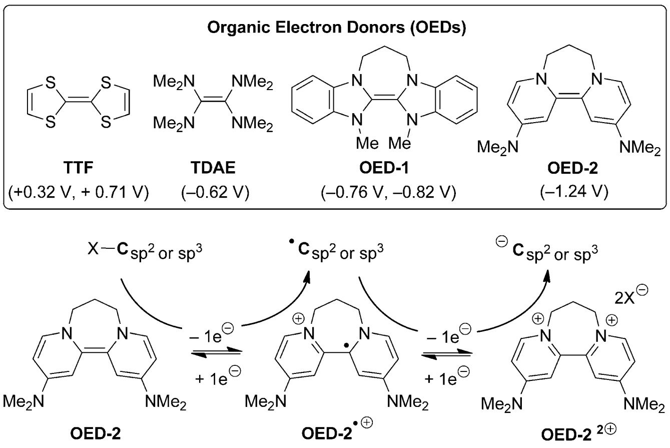
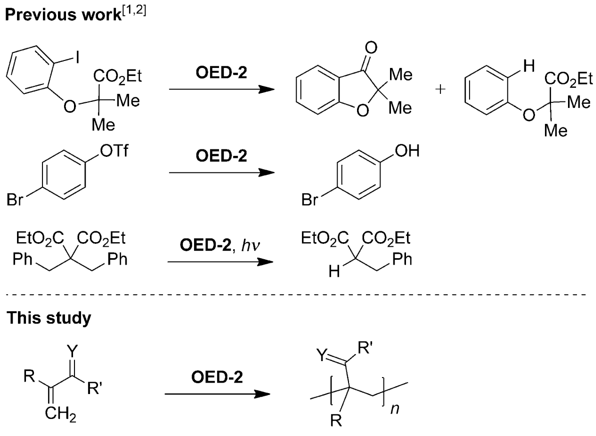
Abstract: *Polymerization reactions with organic electron donors (OED) as initiators are presented herein. The metal-free polymerization of various activated alkene and cyclic ester monomers was performed in short reaction times, under mild conditions, with small amounts of organic reducing agents, and without the need for co-initiators or activation by photochemical, electrochemical, or other methods. Hence, OED initiators enabled the development of an efficient, rapid, room-temperature process that meets the technical standards expected for industrial processes, such as energy savings, cost-effectiveness and safety. Mechanistic investigations support an electron-transfer initiation pathway that leads to the reduction of the monomer.*



Scheme 1. Selected OEDs with their redox potentials ($E_{1/2}$ vs. SCE) and redox equilibria of **OED-2**.



Scheme 2. Reduction of organic substrates by **OED-2**.

Reducing agents with totally neutral organic structures and exceptionally negative redox potentials have undergone astonishing advances and gained renewed interest (Scheme 1).[1] Strong organic electron donors (OEDs) are capable of single- or double-electron transfer to organic substrates under mild conditions, thus promoting bond formation through the generation of radical or anionic intermediates. Among others, Murphy and co-workers made major contributions by demonstrating the efficiency of OEDs in the reduction of challenging substrates, such as aryl halides and arenes, for which metallic reducing agents are usually used (Scheme 2).[1,2]

To further study the potential of OEDs, we decided to tackle the reduction of hitherto uninvestigated functional groups and explore unprecedented applications. We focused on the initiation of chain-growth polymerization by electron transfer. Typical redox initiating systems combine a reducing agent (metal) and a radical priming source.[3,4] Examples in which the monomer itself acts as one component of the redox pair are rare and generally use constraining alkali-metal systems.[5,6] In 1977, Tsuda and co-workers reported a case of free-radical polymerization through the formation of an electron-transfer complex between an amine and a vinyl monomer.[7] Considering that aminoethylene derivatives are more powerful reducers than amines,[1a] we believed that they could be remarkable initiators. We report herein the concept of chain-growth polymerization induced by spontaneous and intrinsic electron transfer between organic reducers and various monomers. As our OED system could lead to radical or anionic priming species, we also undertook mechanistic investigations to better understand the initiation and chain-propagation pathways.

The polymerization process was first studied with ethyl methacrylate (EMA) as the monomer and various organic

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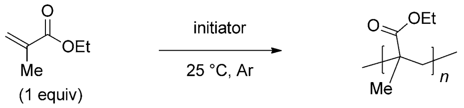
Table 1: Polymerization of EMA initiated by OEDs.[a]



Entry	Initiator (mol %)	Solvent	t	Conv. [%][b]	M_n	M_w	$Đ$
1	**TDAE** (10)	neat	24 h	0	–	–	–
2	**TTF** (10)	neat	24 h	0	–	–	–
3	**OED-1** (10)	DMF	24 h	0	–	–	–
4	**OED-1** (10)	DMF, 120 °C	2 h	99	oligomers		
5	**OED-2** (10)	neat	< 3 min	95	9900	13 100	1.33
6	**OED-2** (5)	neat	10 min	92	12 000	20 200	1.67
7	**OED-2** (2)	neat	4 h	95	28 000	161 000	5.76[c]
8	**OED-2** (1)	neat	24 h	25	ε	ε	ε
9	**OED-2** (5)	neat, 0 °C	3 h	95	17 300	44 800	2.55
10	**OED-2** (5)	neat, −30 °C	24 h	< 5	–	–	–
11	**OED-2** (5)	DMF	30 min	96	18 500	31 000	1.68
12	**OED-2** (5)	CH_3CN	24 h	30	$180 < M < 1800$		
13	**OED-2** (5)	THF	24 h	0[d]	–	–	–
14	**OED-2** (5)	C_6D_6	24 h	0[d]	–	–	–

[a] Reaction conditions: EMA (1 equiv), initiator (1–10 mol %), neat or solvent (1 M), 25 °C, Ar atmosphere. M_n and M_w values were determined by size-exclusion chromatography (SEC; eluent: THF, molar masses in PS-equivalent (g mol^{-1})). [b] Conversion was determined by ^{1}H NMR spectroscopy. [c] Multipopulated distribution. [d] Full conversion was reached upon evaporation of the solvent. DMF = N,N-dimethylformamide.

electron donors as initiators (Table 1). In the presence of the bispyridinylidene **OED-2** (10 mol %),[8] EMA was totally converted into the expected poly(ethyl methacrylate) (PEtMA) in less than 3 min (Table 1, entry 5). The weight-average molar mass (M_w) and the number-average molar mass (M_n) were 13 100 and 9900 g mol^{-1}, respectively, thus indicating a dispersity ($Đ$) of 1.33. The spontaneous and immediate initiation of the polymerization reaction was slightly exothermic (35 °C) and accompanied by a change of color (from dark purple to blood red) attributed to the formation of a stabilizing complex between the anionic propagating species and the oxidized form **OED-2**$^{2+}$. The experimental difficulties (side reactions, early chain termination) often encountered with ionic polymerizations of alkyl methacrylates were not experienced in this case.[3] Our simple methodology did not require particular precautions, such as special vessels and conditions, secure handling, or meticulous monomer and solvent purification. No solvent, additive, or activation by light or heating was necessary.

On the other hand, tetrakis(dimethylamino)ethylene (**TDAE**) and tetrathiafulvalene (**TTF**) were not able to initiate the polymerization reaction (Table 1, entries 1 and 2). Neither addition of a solvent nor thermal heating changed the outcome. The lower reduction potentials of these electron donors ($E_{1/2} = -0.62$ V and $E_{1/2} = +0.32$, $+0.71$ V, respectively) as compared to that of **OED-2** ($E_{1/2} = -1.24$ V) could explain their lack of reactivity (Scheme 1). This hypothesis was consistent with the results observed with the benzimidazole-based donor **OED-1**, which exhibits an intermediate redox potential ($E_{1/2} = -0.76$, -0.82 V):[9] At 25 °C, no reaction was observed, whereas at 120 °C, the electron transfer occurred but oligomers were recovered (Table 1, entries 3 and 4). The formation of radical species and chain-transfer reactions could explain the low molecular weights observed with **OED-1**. Unlike **OED-2**, which is able to initiate double-electron transfer reactions at room temperature to generate carbanions, **OED-1** is known as a single-electron-transfer reagent that enables the formation of radicals under thermal activation.[9,10]

The performance of **OED-2** was then compared at different loadings and in different solvents. Significantly, we found that the well-defined and solid form of **OED-2** allowed accurate control of the quantity of initiator introduced, thus enabling us to tune the length of the polymer chains. The number-average molar mass (M_n) increased (up to 28 000 g mol^{-1}) as the number of equivalents of the initiator decreased (Table 1, entries 5–7), thus indicating conventional controlled-polymerization behavior. The initiator loading could be decreased to 2 mol % without a change in the rate of conversion (95 %), though the reaction time increased to 4 h and led to a multipopulated distribution (Table 1, entry 7). Although the reaction was sluggish at −30 °C (Table 1, entry 10), polymerization proceeded at 0 °C with a good conversion of 95 % in 3 h and a higher M_n value (entry 9). A kinetic study of the polymerization revealed a process without an inhibition period and with a linear increase in the number-average molar mass (M_n) versus conversion (Figure 1). The observation of rapid priming and the linear growth of the polymer chain throughout the course of the reaction indicated a pseudocontrolled process, even if the polydispersities were quite large.

The rate of the chain-growth polymerization was also strongly influenced by the solvent. The reaction only took

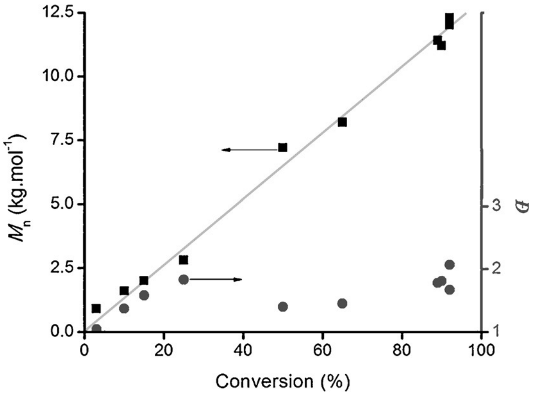
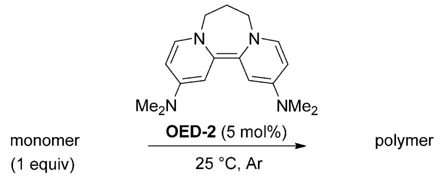
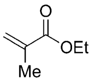
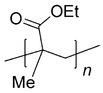
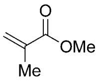
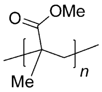
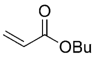
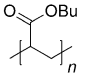
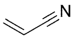
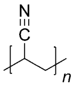
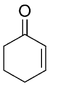
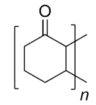
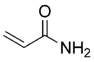
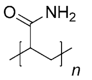
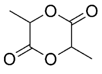
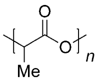
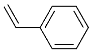
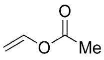


Figure 1. Kinetics of the polymerization of EMA with **OED-2** (5 mol %); sequence of 1 min intervals over 10 min. M_n values determined by SEC analysis (eluent: THF, molar masses in PS-equivalent (g mol^{-1})). Conversion determined by ^{1}H NMR spectroscopy.

place in highly polar aprotic solvents, and the conversion rate increased with the polarity of the solvent. In DMF (1 M), the molecular weight was higher than without a solvent, for a similar conversion rate (96 %) and reaction time (30 min) (Table 1, entry 11). On the other hand, the polymerization was very slow and led only to oligomers in acetonitrile, and did not proceed at all in tetrahydrofuran or [D$_6$]benzene (Table 1, entries 12–14). Surprisingly, complete removal of the solvent, by evaporation after 24 h, led to full conversion into the expected polymer in few minutes. Solvents can dramatically affect polymerization rates owing to preferential solvation interactions with either the initiator or the propagating species.[3] Equivalent reduction-potential values (ca. −1.25 V) were observed for **OED-2** in DMF, THF, and CH_3CN and suggest that EMA is reduced equally in these solvents.[11] Hence, the lack of reactivity in THF is unlikely to be a problem of electron-transfer initiation but rather of propagation. In ionic polymerization, increased solvent polarity favors the formation of solvent-separated ion pairs, which are more reactive than the tight ion pairs that predominate in solvents of low polarity.[3] We thus attributed the lack of reactivity in THF to the blocking of chain propagation by a solvent cage effect on the complex formed between the anionic intermediate and **OED-2**$^{2+}$. This particularity offers the interesting concept of a latent chain-propagation system that could be activated upon evaporation of the solvent.

Table 2: Scope of the polymerization initiated by **OED-2**.[a]



Monomer	Solvent	*t*	Polymer	Conv. [%][b]	M_n	M_w	Đ
	neat	10 min		92	12 000	20 200	1.67
	neat	1 min		95	13 200	17 200	1.30
	neat	<1 min		>99	1700	6000	3.59
	DMF (1 M)	2 h[c]		>99	5600	8600	1.52
	neat	<1 min		>99	5000	9200	1.84[d]
	neat	<1 min		>99	15 800	22 900	1.45[d]
	DMF (1 M)	24 h[c]		97	1400	2000	1.42[e]
 D,L-lactide	DMF (1 M)	3 h		>99	2100	3150	1.50
S=C=S	DMF (1 M)	2 h[c]	−S−C(S)−S−	>99	21 200	35 600	1.68[d]
	neat	24 h		0	–	–	–
	neat	24 h		0	–	–	–

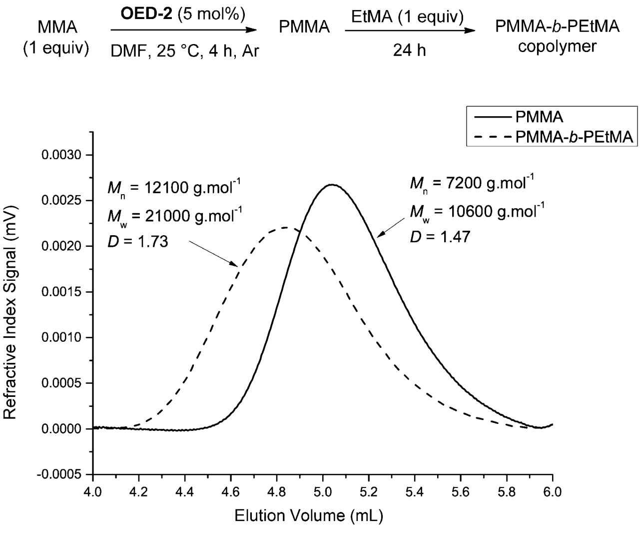
[a] Reaction conditions: monomer (1 equiv), **OED-2** (5 mol %), neat or DMF (1 M), 25 °C, Ar atmosphere. M_n and M_w values were determined by SEC analysis (eluent: THF, molar masses in PS-equivalent (g mol^{-1})). [b] Conversion was determined by ^{1}H NMR spectroscopy. [c] The reaction time was not optimized. [d] M_n and M_w values were determined by SEC analysis (eluent: DMF, molar masses in PMMA-equivalent(g mol^{-1})). [e] M_n and M_w values were determined by SEC analysis (eluent: H_2O/MeOH, molar masses in POE-equivalent (g mol^{-1})).

To further investigate the versatility of our system, we examined the polymerization of a range of monomers with the initiator **OED-2** (5 mol %; Table 2). Acrylates and acrylonitrile polymerized smoothly. Full conversion was observed by ^{1}H NMR spectroscopy after a few minutes. The cyclic α,β-unsaturated ketone, cyclohexenone, was converted into the corresponding polymer in less than 1 min with high M_w and M_n values. The high dispersity ($Đ = 3.59$) of fast-polymerizing poly(butyl acrylate) could be decreased to 1.5 under more dilute conditions. In the synthesis of poly(acrylamide), the polymer precipitated upon its formation in DMF; the reaction was therefore continued for 24 h, and the conversion (97 %) was determined after drying the crude product. Ring-opening polymerization of D,L-lactide was also possible, although it required a longer reaction time to reach total conversion and led to a relatively low M_n value. Usually prepared under photolysis or high pressure,[12] a carbon disulfide polymer (an important class of organic conductors) was smoothly obtained with high molar masses from liquid carbon disulfide (CS_2).

Thus, the organic reducer **OED-2** was able to initiate the polymerization of a lactone and diverse alkenes bearing activating substituents. Unfortunately, less activated alkenes, such as styrene or vinyl acetate, could not be polymerized. The reduction potentials of methyl and ethyl methacrylate were measured at −2.45 and −2.53 V versus the saturated calomel electrode (SCE) in DMF,[11] that is, in the range of redox potentials that the effective reducing power of **OED-2** can reportedly attain.[13] In contrast, at potentials up to −3.1 V versus SCE, no reduction wave was observed for styrene and vinyl acetate by cyclic voltammetry. The inability of **OED-2** to reduce these monomers certainly explains the absence of polymerization.

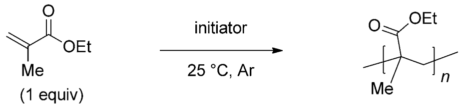
To evaluate the nonterminating character of the propagating anion stabilized by **OED-2**$^{2+}$, we explored the synthesis of well-defined block copolymers by the sequential addition of monomers. After the complete consumption of methyl methacrylate (MMA) to form PMMA, a second monomer (EtMA) added to the stirred reaction mixture also polymerized quantitatively (Scheme 3). The blood-red color, characteristic of propagating anions, persisted until the solution was exposed to air. ^{1}H NMR and SEC analysis confirmed the formation of a PMMA-*b*-PEtMA copolymer, as indicated by increased molecular weights as compared to those of the PMMA homopolymer.

We carried out several experiments to gain insight into the mechanism of polymerization initiated by **OED-2**. First, we focused on the initiation mode, since organic electron donors can act as a nucleophile, a base, or a reducing agent.[14] Initiation by attack of the nucleophilic double bond of **OED-2** on the monomer would involve the incorporation of the reducer as an end group of the polymer chain. However, no characteristic proton signal of **OED-2** was observed in the ^{1}H NMR spectrum of the purified polymer PEtMA.[11] Moreover, no polymerization in the presence of other electron-rich tetraminoethylenes, such as **TDAE**, was observed (Table 1, entry 1). Although not reported for **OED-2**, another possible source of a nucleophilic initiator comes from the existence in solution of an equilibrium between aminoethylenes and the corresponding carbenes.[15] N-Heterocyclic carbenes (NHCs), such as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), are well-known organocatalysts in polymer synthesis.[16] However, co-initiators are usually required to avoid the formation of the nonreactive single-addition product.[17] Under our reaction conditions, IMes-mediated polymerization of EMA gave small oligomers ($200 < M < 3400$) with a low conversion rate of 27% (Table 3, entry 9). NHC-initiated polymerization reactions are quenched by adding carbon disulfide to irreversibly trap the NHC within a zwitterionic NHC–CS_2 adduct.[18] In our case, the polymerization of CS_2 by **OED-2** (Table 2) irrefutably excluded the intervention of a carbene intermediate.



Scheme 3. Synthesis of PMMA and its block copolymer PMMA-b-PEtMA and resulting SEC traces.

Table 3: Mechanistic considerations for the polymerization of EMA.[a]

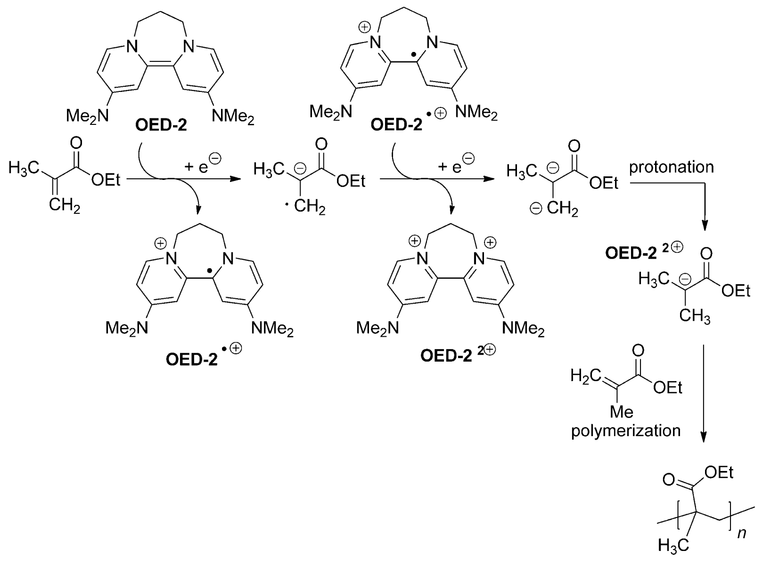


Entry	Initiator (mol%)	Conditions	t [h]	Conv. [%][b]	M_n	M_w	Đ
1	**OED-2** (5)	DMF, O_2	24	0	–	–	–
2	**OED-2** (5)	DMF, $CuCl_2$ (10 mol%)	24	0	–	–	–
3	**OED-2** (5)	DMF, *p*-DNB (10 mol%)	24	0	–	–	–
4	**OED-2** (5)	DMF, TEMPO (10 mol%)	0.5	99	6200	11 200	1.81
5	**OED-2** (5)	DMF, TEMPO (1 equiv)	0.5	99	8300	13 300	1.60
6	**OED-2** (5)	H_2O (degassed)	24	0	–	–	–
7	**OED-2** (5)	EtOH	24	0	–	–	–
8	DMAP (10)	neat	24	0	–	–	–
9	IMes (10)	neat	24	27	$200 < M < 3400$		

[a] Reaction conditions: EMA (1 equiv), **OED-2** (5 mol%), solvent (1 M), 25 °C, Ar atmosphere. M_n and M_w values were determined by SEC analysis (eluent: THF, molar masses in PS-equivalent ($g\,mol^{-1}$)). [b] Conversion was determined by ^{1}H NMR spectroscopy.

Since **OED-2** contains nonbonded electron pairs on its nitrogen atoms, it is in principle sensitive to protons. We postulated that if **OED-2** behaved like a basic amine in catalyzing the polymerization, similar results should be obtained with structurally related 4-(dimethylamino)pyridine (DMAP). In the presence of a nucleophilic initiator, such as an alcohol, DMAP is able to catalyze polymerization processes, such as the ring-opening polymerization of L-lactide.[19] Under our alcohol-free conditions, DMAP did not catalyze the polymerization of EMA (Table 3, entry 8) or the polymerization of the D,L-lactide (not in the table). It was also observed that the polymerization process initiated by **OED-2** was inhibited by the addition of ethanol (Table 3, entry 7). We could thus reasonably discount the basic properties of **OED-2** and affirm that the activation of the monomer did not imply the formation of a hydrogen bond.

The documented performance of **OED-2** as a powerful electron donor in organic synthesis[1,8] suggests that the initiation of the polymerization was induced by electron transfer. As previously stated, the reactivity of the monomers, which varied according to their reduction potential, and the restriction to highly polar aprotic solvents both support this hypothesis. A change of color, as observed during the reaction, is also typical in electron-transfer reactions and corresponds to the formation of the donor–acceptor charge-transfer complex. Moreover, **OED-2**$^{2+}$ derivatives were observed by ^{1}H NMR spectroscopy at the end of the reaction. Oxygen (O_2), copper(II) chloride ($CuCl_2$), or *para*-dinitrobenzene (*p*-DNB) are commonly used as inhibitors in the study of electron-transfer mechanisms.[20] Under our reaction conditions, the polymerization was totally inhibited by $CuCl_2$, *p*-DNB, or O_2 (Table 3, entries 1–3). The inhibition took place regardless of when addition occurred, that is, at the outset or after stirring for 5 min (the reaction stopped at 65 % conversion). These results provide good evidence for a chain-initiation pathway through electron transfer.



Scheme 4. Proposed polymerization mechanism with the initiator **OED-2**.[22]

We next examined the pathway of the chain propagation. The cyclic voltammogram of **OED-2** exhibits a single two-electron redox wave,[11] and the **OED-2**-promoted formation of principally anionic intermediates has been observed on many occasions.[8] To confirm the predominance of anionic over radical chain propagation, we conducted the polymerization of EMA in protic solvents. The addition of ethanol or degassed water[21] at the outset or after stirring for 3 min inhibited the reaction by quenching the anionic chain propagation through proton-transfer termination (Table 3, entries 6 and 7). In contrast, the use of a large excess of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical trap did not inhibit the polymerization process (Table 3, entries 4 and 5). Finally, unlike certain monomers that can polymerize either by radical or anionic pathways, D,L-lactide is known to polymerize only by anionic chain propagation.

These mechanistic considerations support the hypothesis of the transfer of electrons from the organic donor **OED-2** to the monomer, thus leading to its reduction (Scheme 4). The generated anionic intermediate could then initiate the polymerization through anionic chain propagation. Even though several indicators pointed to the anionic pathway, competing processes cannot be totally excluded and could explain the modest dispersities observed. We are currently investigating the structures of the initiating and terminating fragments incorporated into the polymer chains by mass and NMR spectroscopy.

In conclusion, we have report herein the first chain-growth polymerization with small amounts of organic reducing agents as initiators. The metal-free polymerization of various activated alkene and cyclic ester monomers was performed in short times and under mild conditions, thus providing the expected polymers with good polydispersities and without the need for co-initiators or external activation. Organic electron donors are remarkable polymerization initiators, as they enable the development of efficient, simple, room-temperature processes that meet the technical standards of energy savings, cost-effectiveness and safety. Their high functional-group tolerance makes them fully compatible with the synthesis of a large range of polymers and biopolymers of wide industrial importance. Our mechanistic considerations support both initiation through electron transfer and anionic chain propagation. Moreover, these results open new horizons for OEDs, never previously used in the reduction of alkene or lactone functional groups or in intermolecular processes.

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[22] This mechanistic proposal was inspired by that in Ref. [6b] for polymerization initiated by metal-mediated electron transfer.

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