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Yuxi Zhao, Marion Rollet, Laurence Charles, Gabriel Canard, Didier Gimes, et al.. Switching from Single to Simultaneous Free-Radical and Anionic Polymerization with Enamine-Based Organic Electron Donors. *Angewandte Chemie International Edition*, 2021, 60 (35), pp.19389-19396. 10.1002/anie.202106733 . hal-03402294

**HAL Id: hal-03402294**

**<https://hal.science/hal-03402294>**

Submitted on 25 Oct 2021

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Polymerization Hot Paper

# Switching from Single to Simultaneous Free-Radical and Anionic Polymerization with Enamine-Based Organic Electron Donors

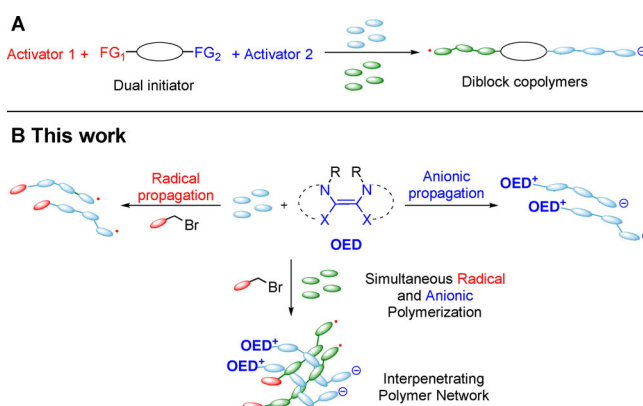
Yuxi Zhao, Marion Rollet, Laurence Charles, Gabriel Canard, Didier Gigmes, Patrice Vanelle, and Julie Broggi\*

**Abstract:** Although most monomers can polymerize through different propagation pathways, polymerization-initiating systems that can switch from one mode to another are rare. In this study, we demonstrate that enamine-based organic electron donors (OEDs) constitute the first systems able to initiate either free-radical or anionic polymerization under simple, mild, and safe conditions. While direct electron-transfer reduction of monomers by OEDs results in the initiation of anionic chain-growth polymerization, introduction of a competing oxidant with a higher reduction potential than the monomer switches the former anionic propagation to a clean radical-propagation process. The benefit of this dual-mode activator is highlighted in the synthesis of an interpenetrating polymer network through simultaneous initiation of radical and anionic propagation processes.

## Introduction

Although most monomers can polymerize through different propagation pathways (cationic, radical, anionic, etc.), rare are the polymerization initiating systems that can switch from one mode to another. Polymerization initiators are usually confined to one type of propagation: metallic reducing agents and peroxides for free radical polymerization (FRP), strong anions and alkali metals for anionic polymerization (AP), or Lewis acids and carbenium ion salts for cationic polymerization (CP).<sup>[1]</sup> Accordingly, simultaneous initiation of different propagating modes in a one-pot setup requires three-component systems mixing two types of activators, one for each propagation mode, with an additive.<sup>[2,3]</sup> Moreover, these dual-curing systems usually require external stimuli such as thermal or photo-activation. Lalevée and co-workers used copper complexes<sup>[4]</sup> or terphenyl photosensitizers<sup>[5]</sup> in combination with iodonium salts and additives for the dual cationic/radical photopolymerizations of interpenetrating polymer networks (IPN). Dual anionic/radical

polymerizations are rarer in the literature and generate diblock copolymers connected by a dual initiator (Scheme 1A). Dual initiators<sup>[6]</sup> feature two distinct functional groups (hydroxyl, bromoalkyl, nitroxide, etc.) activated by two different activators (e.g. organometallic compounds, metal catalysts, high temperature) for simultaneous ring-opening (ROP) and radical polymerizations.<sup>[7]</sup>



**Scheme 1.** (A) Previous work: Diblock copolymers connected by a dual initiator (FG = functional group). (B) This work: Switching from single to simultaneous free radical and anionic polymerizations. Preparation of interpenetrating polymer networks.

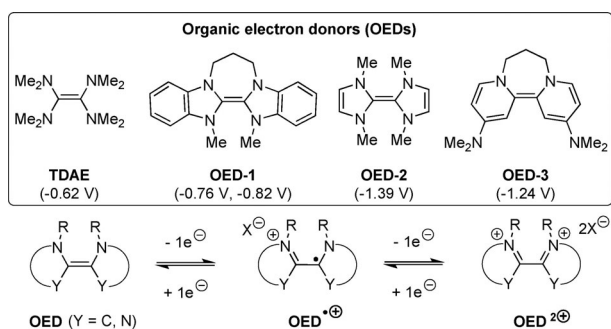
The concept of a single activator priming more than one type of polymerization had never been addressed to the best of our knowledge. Our aim was thus to develop a single initiating system capable of simultaneous radical and anionic polymerizations of two monomers without any external stimuli (Scheme 1B).

We believed that organic electron donors (OEDs) containing an electron-rich enamine had this potential. Indeed, OEDs can form radical or anionic intermediates by the spontaneous stepwise transfer of one or two electrons to organic substrates under mild conditions (Scheme 2).<sup>[8]</sup> Thanks to their totally neutral organic structures and their large array of negative redox potentials, these reducers have attracted considerable attention in organic synthesis<sup>[9,10]</sup> and industrially-relevant research.<sup>[11,12]</sup> Among them, the bipyridinylidene **OED-3** is a very powerful two-electron donor with a high negative potential ( $E_{1/2} = -1.24$  V vs. SCE).<sup>[13]</sup> In the wake of our recent OED-promoted anionic process,<sup>[11]</sup> we now demonstrate that organic electron donors are also remarkable initiators for the radical polymerization of a large range of monomers; thereby making OED the first system

[\*] Dr. Y. Zhao, Dr. M. Rollet, Prof. L. Charles, Dr. D. Gigmes, Prof. P. Vanelle, Dr. J. Broggi  
Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire (ICR)  
13013 Marseille (France)  
E-mail: julie.broggi@univ-amu.fr

Dr. G. Canard  
Aix Marseille Univ, CNRS, Centre Interdisciplinaire de Nanoscience de Marseille (CINaM)  
13288 Marseille (France)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:  
<https://doi.org/10.1002/anie.202106733>.



**Scheme 2.** Redox equilibria and redox potential ( $E_{1/2}$  vs. SCE) of selected organic electron donors.

able to initiate either radical or anionic polymerizations under simple, mild and safe conditions. The benefit of this dual-mode activator is highlighted here in the synthesis of interpenetrating polymer networks through simultaneous initiation of radical and anionic propagation processes.

## Results and Discussion

Our group showed that direct electron-transfer reduction of monomers by **OED-3** resulted in the initiation of anionic chain-growth polymerizations (Scheme 1 B).<sup>[11]</sup> This remarkable metal-, peroxide- and oxidant-free one-component strategy spontaneously initiated the rapid anionic polymerization of a large variety of monomers at room temperature and with narrow dispersity. To now switch to an OED-promoted free radical polymerization process (FRP), our strategy was to introduce a competing oxidant with a higher reduction potential than the monomer. Selective single-electron transfer reduction of this oxidant would generate a radical initiator, that would add to the monomer to propagate the radical chain reaction. In addition to the benefit of a dual-mode activator, an OED-based system offers numerous advantages over classical initiators used in FRP (45% of the worldwide production of synthetic polymers).<sup>[14]</sup> Compared to the peroxide/activator (transition metals or amines) couple,<sup>[15]</sup> spontaneous electron-transfer from powerful OEDs to a large variety of radical initiators gives access to metal- and peroxide-free redox FRP strategies.

In our first study, direct reduction of ethyl methacrylate **EMA** by **OED-3** led to its anionic polymerization in 10 min with a number-average molar mass ( $M_n$ ) of 12000  $\text{g mol}^{-1}$ , and a dispersity ( $\mathcal{D}$ ) of 1.67 (Table 1, entry 1).<sup>[11]</sup> To switch to a radical propagation

process, ethyl  $\alpha$ -bromophenylacetate (**EBP**) was selected as competing oxidant for its higher reduction potential ( $E_{1/2} = -0.94$  V vs. SCE) compared to **EMA** ( $E_{1/2} = -2.53$  V vs. SCE). Since **OED-3** can reduce both the initiator and the monomer, the selectivity of **OED-3** for the initiator despite the large excess of monomer was crucial for a pure redox FRP process. Interestingly, in the presence of **EBP** as initiator ( $[I] = 10$  mol%), polymerization of **EMA** with **OED-3** as redox-active activator ( $[O] = 5$  mol%) also proceeded to full completion (Table 1, entry 2). Nevertheless, it took longer (90 min) and led to increased weight-average molar mass ( $M_w = 40000$   $\text{g mol}^{-1}$ ) and dispersity (2.43). The longer polymerization time and higher dispersity clearly indicated changes in the on-going mechanism, possibly due to a switch from an anionic to a radical process. The spontaneous and immediate initiation of the polymerization reaction caused low heat emission (35°C) and was accompanied by the instantaneous formation of a yellow solid in suspension in the solidifying liquid. This solid was also a new phenomenon not observed in our previous anionic strategy. Isolation of this yellow solid and full characterization confirmed the generation of the oxidized form of **OED-3** upon sequential loss of two electrons (Scheme 2), namely **OED-3<sup>2+</sup> 2Cl<sup>-</sup>** in 96% yield (see SI).<sup>[16]</sup>

We then performed an optimization of this redox-active system. The reduction ability of the OED significantly influenced the polymerization process. Replacing **OED-3** by other organic electron donors with lower reducing abilities, such as tetrakis(dimethylamino)ethylene (**TDAE**,  $E_{1/2} = -0.62$  V vs. SCE),<sup>[17]</sup> and *N,N'*-bridged dibenzimidazolinyldene (**OED-1**,  $E_{1/2} = -0.76, -0.82$  V vs. SCE),<sup>[18]</sup> resulted in less efficient polymerization processes with lower conversion rates (Table 1, entries 4–5, 34 or 74%, respectively). Compared to **TDAE**, the intermediate reduction potential of **OED-1** certainly afforded a better reduction rate of **EBP**, leading to a higher conversion rate. However, the propensity

**Table 1:** Optimization of the free radical polymerization process initiated by EBP/OED redox system.

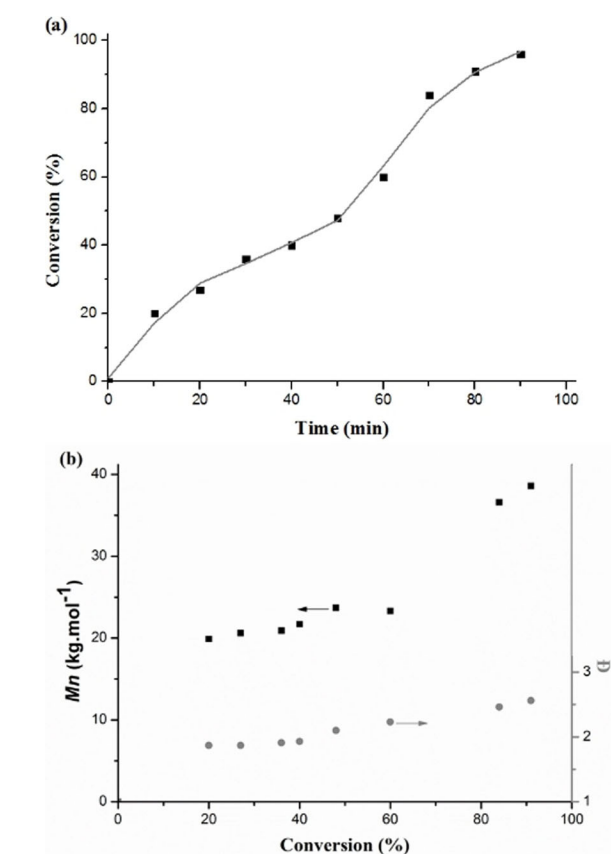
Entry	OED	[M] : [I] : [O]	Solvent	Time	Conv. (%)	$M_n$	$M_w$	$\mathcal{D}$
1	<b>OED-3</b>	100:-:5	neat	10 min	92	12 000	20 200	1.67
2	<b>OED-3</b>	100:10:5	neat	90 min	> 99	16 500	40 000	2.43
3	<b>OED-3</b>	100:5:5	neat	80 min	98	19 900	56 900	2.86
4	<b>TDAE</b>	100:5:5	neat	24 h	34	9 800	30 800	3.13
5	<b>OED-1</b> <sup>[a]</sup>	100:5:5	DMF(0.2 mL)	24 h	74	4 200	5 900	1.42
6	<b>OED-2</b> <sup>[a]</sup>	100:5:5	DMF(0.2 mL)	24 h	98	34 800	68 500	1.97
7	<b>OED-3</b>	100:5:2.5	neat	2 h	96	32 300	70 400	2.18
8	<b>OED-3</b>	100:2.5:5	neat	24 h	75	2 800	6 900	2.40
9	<b>OED-3</b>	100:2.5:2.5	neat	3 h	98	38 100	115 200	3.02
10	<b>OED-3</b>	100:0.5:0.5	neat	9 h	98	93 100	267 400	2.87
11 <sup>[b]</sup>	<b>OED-3</b>	100:0.5:0.5	neat	24 h	93	167 900	551 100	3.28

Reaction conditions: **EMA** (2 mmol, 1 equiv), **EBP** (0.5–10 mol%), **OED** (0.5–5 mol%), neat or DMF (10 M), 25°C, Ar. Conversion determined by <sup>1</sup>H NMR spectroscopy.  $M_n$ ,  $M_w$  and  $\mathcal{D}$  determined by size-exclusion chromatography SEC (eluent: THF, molar masses in PMMA-equivalent ( $\text{g mol}^{-1}$ )). [a] The OED was *in situ* prepared by deprotonation of the corresponding iminium salt with NaH in DMF (0.2 mL) (see SI). [b] **EMA** (8 mmol, 1 equiv). The reaction time was not optimized.



of the radical cation of **OED-1** (**OED-1<sup>+</sup>**) to trap alkyl radicals<sup>[19]</sup> probably accounted for the low molar mass of the polymer ( $M_w = 5900 \text{ g mol}^{-1}$ ), resulting from an early trapping of the propagating radical chain. Although the priming was not very effective, it is noteworthy that **TDAE** and **OED-1** were able to reduce **EBP** at room temperature to initiate the radical polymerization of **EMA**. In our previous anionic strategy, **TDAE** was not able to initiate the polymerization of the more challenging-to-reduce **EMA** monomer, while **OED-1** only promoted electron transfer to **EMA** under thermal activation ( $120^\circ\text{C}$ ).<sup>[11]</sup> On the other hand, bisimidazolinylidene **OED-2**,<sup>[20]</sup> which exhibits a similar redox potentials ( $E_{1/2} = -1.39 \text{ V vs. SCE}$ )<sup>[21]</sup> compared to **OED-3**, was also very effective in reducing **EBP**, enabling full conversion into **PEMA** with high  $M_n$  and  $M_w$  mass ( $34800$  and  $68500 \text{ g mol}^{-1}$ , respectively) and a dispersity of  $1.97$ , albeit in longer times (Table 1, entry 6).

The ratio between the activator (**OED** [O]) and the initiator (**EBP** [I]) was also determinant and indicative of the on-going mechanism. Compared to a [I]:[O] ratio of 10:5 (entry 2), an equivalent amount of **EBP** and **OED-3** ([I]:[O] = 5:5) led to increased  $M_n$  and  $M_w$  ( $19900$  and  $56900 \text{ g mol}^{-1}$ , respectively), in line with a lower concentration of radical priming species (Table 1, entry 3). More interestingly, halving the concentration of **OED-3** ([O] =  $2.5 \text{ mol}\%$ ) increased  $M_n$  and  $M_w$  values by one-third ( $32300$  and  $70400 \text{ g mol}^{-1}$ , respectively) and lowered the dispersity  $\bar{D}$  to  $2.18$  (Entry 7). By contrast, halving the concentration of **EBP** ([I] =  $2.5 \text{ mol}\%$ ) rendered the initiation of polymerization ineffective and only led to the formation of a low- $M_w$  polymer (Entry 8). Considering that **OED-3** can sequentially transfer two electrons (Scheme 2), one molecule of **OED-3** should be sufficient to reduce two molecules of **EBP** (corresponding to a 1 to 1 ratio in terms of electron equivalents). Clean generation of two equivalents of corresponding benzyl radicals, when using **EBP** and **OED-3** in a [I]:[O] = 5:2.5 ratio, should logically promote the formation of a polymer with higher molar mass. On the other hand, using twice more **OED-3** in a [I]:[O] = 2.5:5 ratio (corresponding to a 2 to 1 ratio in terms of electron equivalents) might promote the over-reduction of **EBP** to benzyl anion species, deleterious for the initiation of FRP. These results also underline the crucial selectivity of **OED-3** for the initiator **EBP** despite the large excess of monomer **EMA**. Finally,  $M_n$  and  $M_w$  molar masses increased (up to  $93100$  and  $267400 \text{ g mol}^{-1}$ , respectively) as the number of equivalents of the redox initiating system decreased (Table 1, entries 9–10), indicative of a conventional initiator-dependent polymerization behavior. Loading of the redox initiating system could be decreased to  $0.5 \text{ mol}\%$  without any change in the rate of conversion ( $98\%$ ), albeit involving longer reaction times (Table 1, entry 10). A larger-scale polymerization was performed with the same efficiency, using only  $0.5 \text{ mol}\%$  of **OED-3** and **EBP** (Entry 11). The kinetic study of **EMA** polymerization, using a [M]:[I]:[O] = 100:5:2.5 molar ratio, revealed an immediate initiation and a linear progression of the conversion over time (Figure 1 A). A slight auto-acceleration of the polymerization rate was observed at 48% of conversion (50 min), along with a sharp increase in the  $M_n$  value (Figure 1 B). This pointed to



**Figure 1.** Kinetics of the polymerization of **EMA** with a molar ratio of [M]:[I]:[O] = 100:5:2.5 (a) Time evolution of the conversion. (b) Conversion determined by  $^1\text{H}$  NMR spectroscopy.  $M_n$  and  $\bar{D}$  values determined by SEC analysis (eluent: THF, molar masses in PMMA-equivalent ( $\text{g mol}^{-1}$ )). Sequence of 10 min intervals over 90 min.

a gel effect typically observed with radical bulk polymerizations.<sup>[22]</sup>

Interestingly, our OED-activated polymerization strategy was compatible with other types of initiators, unusual in typical redox FRP. Iodoarene, sulfone, sulfonamide, or triflate groups were reduced to initiate the polymerization of **EMA** (see SI, Table S2). Although initiation was less efficient than with **EBP**, these results underline the ability of **OED-3** to generate radical initiators from various types of oxidants. The **EBP/OED**-initiating system was also compatible with a large array of solvents (see SI, Table S3), from highly polar aprotic or protic solvents, like DMF or  $\text{H}_2\text{O}$ , to poorly polar solvents like  $\text{Et}_2\text{O}$ . Polymerization reached full conversion in DMF, DMA,  $\text{H}_2\text{O}$  and  $\text{Et}_2\text{O}$  with dispersities ( $\bar{D}$  2–4) of the same order of magnitude as that obtained under neat conditions. Particularly high- $M_w$  polymers were obtained in DMF and water (Table S3, entries 4 and 10,  $M_w = 128700$  and  $308600 \text{ g mol}^{-1}$ , respectively). Polymerization in protic solvents provided additional proof of a radical chain-growth propagation while, in our previous strategy,<sup>[11]</sup> water quenched the anionic propagation through proton-transfer termination.

To prove the applicability of this self-initiating free-radical polymerization strategy, a scope of diverse functional monomers was investigated using the [M]:[I]:[O] = 100:5:2.5 molar ratio (Table 2). Our all-organic **EBP/OED**-initiating



**Table 2:** Scope of the free radical polymerization initiated by EBP/OED-3 redox system.

Monomer (1 equiv.)	EBP (5 mol%) OED-3 (2.5 mol%) 25°C, Ar	Polymer	Conv. (%)	$M_n$	$M_w$	$\bar{D}$
	2 h		96	32 300	70 400	2.18
	1.5 h		90	18 400	52 000	2.82
	4.5 h		98	31 100	51 800	1.66
	2.5 h		96	38 200	112 800	2.95
	6.5 h		93	9 700	21 200	2.19 <sup>[a]</sup>
	20 min		>99	13 800	16 800	1.21 <sup>[a]</sup>
	1 h		96	3 300	5 400	1.66
	24 h		95	3 000	4 300	1.41

Monomer (1 equiv.)	EBP (5 mol%) OED-3 (2.5 mol%) 25°C, Ar	Polymer	Conv. (%)	$M_n$	$M_w$	$\bar{D}$
	3 h		99 <sup>[b]</sup>	-	-	-
	1.6 h		99	Oligomers		
	24 h		70	1 700	3 800	2.17
	24 h		52	7 400	16 600	2.25
SR348C	3 min	P-SR348C	Hard	nd	nd	nd
Bis-GMA	10 min	P-Bis-GMA	Hard	nd	nd	nd
	24 h <sup>[c]</sup>		0	-	-	-
	2 h <sup>[d]</sup>	PEMA-PMMA	99	23 800	63 800	2.68
	3 h <sup>[d]</sup>	PEMA-PBA	99	26 700	65 200	2.44
	3 h <sup>[d]</sup>	PEMA-PAN	98	13 000	48 000	3.68 <sup>[a]</sup>

SR348C Sartomer®

Bis-GMA

Reaction conditions: Monomer (2 mmol, 1 equiv), **EBP** (5 mol%), **OED-3** (2.5 mol%), neat, 25°C, Ar. Conversion determined by <sup>1</sup>H NMR.  $M_n$ ,  $M_w$  and  $\bar{D}$  determined by size-exclusion chromatography SEC (eluent: THF ([a] DMF), molar masses in PMMA-equivalent (g mol<sup>-1</sup>)). [b] Reticulation reaction occurred to give a gel. [c] DMF (0.2 mL) acted as the solvent to dissolve the D,L-lactide. [d] **EMA** (1 mmol, 1 equiv), monomer 2 (1 mmol, 1 equiv).

system was efficient in generating a large array of polymers with high added value. It enabled smooth and fast polymerization of acrylates, acrylonitriles and acrylamide with full conversion in the corresponding high molar-mass polymers and with dispersities of 2–2.5 on average. Only less activated *tert*-butyl-2-(trifluoromethyl)acrylate and styrene gave lower conversion rates of 70 and 52 %, respectively. It is noteworthy that, in our anionic strategy,<sup>[11]</sup> styrene could not be polymerized because its overly uphill reduction potential ( $E_{1/2} < -3.1$  V vs. SCE) exceeded the reducing ability of **OED-3**. By contrast, while the anionic strategy permitted the ring-opening polymerization of D,L-lactide,<sup>[11]</sup> the radical **EBP/OED-3** initiating system did naturally not allow it. Additionally, our **EBP/OED**-initiating system was efficient in the polymerization of key components of dental resins, such as ethoxylated bisphenol A dimethacrylate (**SR348C**, Sartomer®) and bisphenol A-glycidyl methacrylate (**bis-GMA**) (Table 2). It exhibited outstanding initiating properties in the polymerization of **SR348C** and **bis-GMA**, affording the corresponding hard polymers in 3 min (gel time = 43 seconds) and 10 min, respectively. The **EBP/OED-3** initiating system also allowed the preparation of random copolymers by simultaneous polymerization of two monomers (Table 2). Polymerization

of mixtures of **EMA** and methyl methacrylate **MMA**, butyl acrylate **BA** or acrylonitrile **AN** produced high- $M_w$  random copolymers in the same range of efficiency and conditions as for corresponding homopolymers.

Throughout this study, a number of aspects pointed an on-going free radical mechanism. To confirm the initiation and propagation pathway of this **EBP/OED-3**-promoted polymerization process, several experiments were conducted (Table 3). In addition to the formation of the oxidized form **OED-3**<sup>2+</sup>, further evidence supporting an initiation through electron transfer mechanism was obtained from adding commonly used inhibitors. Inhibition of the **EMA** polymerization was observed in the presence of the radical trap 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**), the competitive electron acceptor *para*-dinitrobenzene (**p-DNB**), or when the reaction was carried out in air (Table 3, entries 1–5). Moreover, the lack of reactivity of the structurally related 4-(dimethylamino)pyridine (**DMAP**) excluded the involvement of the nonbonded nitrogen electron pairs of **OED-3** as one-electron-transfer or nucleophilic reagents (Table 3, entry 6). Instead, **DMAP** reacted with **EBP** to form a quaternary amine salt through nucleophilic substitution of the bromide atom (see SI). Replacing **OED-3** with typical radical poly-

**Table 3:** Mechanistic investigation of the radical polymerization process.

Entry	Activator	Conditions	Time	Conv. (%)	$M_n$	$M_w$	$\bar{D}$
1	OED-3	neat, TEMPO (5 mol%)	24 h	27	2 400	3 900	1.66
2	OED-3	neat	10 min	37	nd	nd	nd
		then TEMPO (5 mol%)	24 h	44	10 300	24 400	2.37
3	OED-3	neat, <i>p</i> -DNB (5 mol%)	24 h	66	9 500	18 400	1.94
4	OED-3	DMF (0.2 mL), air	24 h	0	–	–	–
5	OED-3	DMF (0.2 mL)	10 min	41	nd	nd	nd
		then under air	24 h	52	5 600	14 000	2.49
6	DMAP	neat	24 h	0	–	–	–
7	BPO	neat	24 h	52	82 800	174 500	2.11
8	AIBN	neat	24 h	84	116 700	239 400	2.05

Reaction conditions: **EMA** (2 mmol, 1 equiv), **EBP** (5 mol%), **Activator** (5 mol%), 25°C, Ar. Conversion determined by  $^1\text{H}$  NMR.  $M_n$ ,  $M_w$  and  $\bar{D}$  determined by size-exclusion chromatography SEC (eluent: THF, molar masses in PMMA-equivalent ( $\text{g mol}^{-1}$ )).

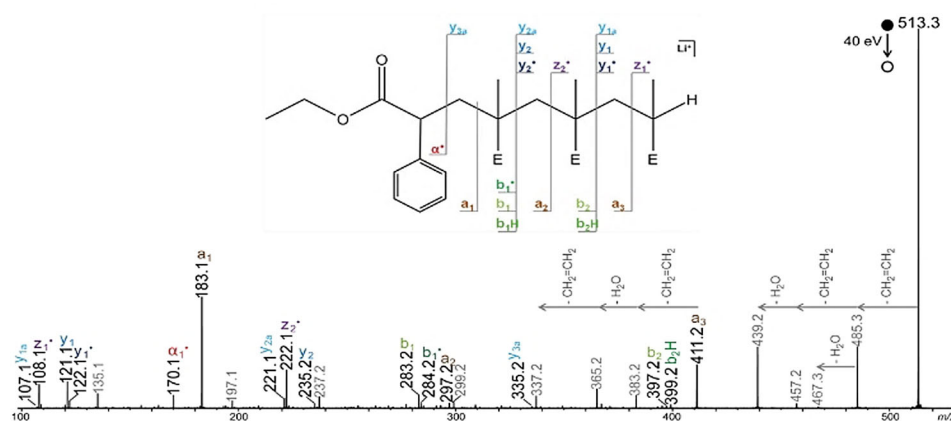
merization initiators such as benzoyl peroxide (**BPO**) or azobisisobutyronitrile (**AIBN**) decreased monomer conversion (52 and 84%, respectively in 24 h, Table 3, entries 7–8).

Evidence supporting the addition of the benzyl radical on **EMA** and subsequent radical propagation was obtained by mass spectrometry. Under electrospray ionization (ESI) in the positive ion mode, the mass spectra of the poly(**EMA**) oligomer exhibited a main polymeric distribution with peaks spaced by 114.1 Da, the mass of **EMA** repeating unit, and end-groups with residual mass of 50 Da (see SI, Figure S4). Tandem mass spectrometry (MS/MS) experiments combined with accurate mass measurements of fragments confirmed the end-groups of these poly(**EMA**) chains as ethyl 2-phenyl acetate as the  $\alpha$  termination and H as the  $\omega$  one (Figure 2). The absence of **PEMA** with ethyl 2-phenylacetate as both chain ends in these mass spectra shows that radical coupling of two propagating radical chains did not occur. Furthermore, overlaying both refractive index RI and UV (254 and 365 nm) signals obtained from the SEC analysis of the oligomer also

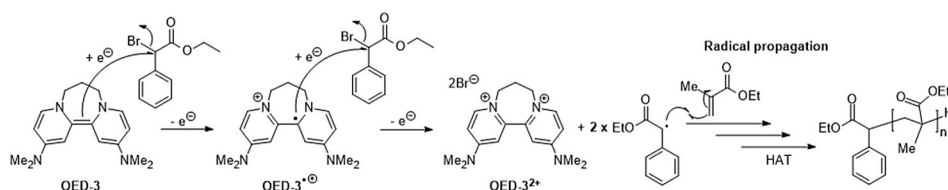
agitation by a radical trap (Table 3, entries 2 and 5) or polymerization in protic solvents (Table S3, entries 9–10) all provided good proof of the formation of the benzyl radical priming species and subsequent radical chain-growth propagation.

These mechanistic considerations suggest the following mechanism for free radical polymerizations initiated by the redox-active **EBP/OED-3** system (Scheme 3). Unlike the previously reported **OED-3**-promoted direct reduction of the monomer,<sup>[11]</sup> introducing a competing oxidant like ethyl  $\alpha$ -bromophenylacetate **EBP** allows the formation of benzyl radical priming species, through selective single-electron transfer reduction. Sequential transfers of two electrons from one equivalent of **OED-3** generate two equivalents of corresponding benzyl radicals, along with the oxidized form **OED-3<sup>2+</sup>**. The benzyl radical is then capable of addition to the monomer, to propagate the radical chain reaction. Note that initiation of the polymerization by addition of the radical cation form **OED-3<sup>+</sup>** to the monomer was not observed by mass spectrometry analysis. Hydrogen-atom abstraction terminates this polymerization process.

The skills of **OED-3** as an efficient and rapid dual-mode activator were then exploited in the synthesis of interpenetrating polymer networks (IPN)<sup>[2]</sup> through simultaneous initiation of radical and anionic propagation processes. Addition of an excess of **OED-3** with respect to the competing oxidant (**EBP**) can on one hand initiate the radical polymerization of monomer 1 by SET to **EBP** and addition of the benzyl radical; on the other hand, the remaining OED can simultaneously



**Figure 2.** ESI-MS/MS of the  $[\text{P}_3 + \text{Li}]^+$  ion at  $m/z$  513.3. All fragments are consistent with the proposed end-groups shown in the inset dissociation Scheme (where E stands for  $(\text{CO})\text{OEt}$ ) and supported by accurate mass measurements (See SI, Figure S5). Fragments in grey contain either none of both chain terminations and are hence useless for end-group analysis.



**Scheme 3.** Proposed mechanism for free radical polymerizations initiated by **EBP/OED-3** redox system.

induce anionic polymerization through reduction of monomer 2. Simultaneous chain-growth polymerizations of monomers 1 and 2 thus lead to interpenetration of the two homopolymers in a one-pot setup. To demonstrate the feasibility of this strategy, we first selected styrene and D,L-lactide as monomer 1 and 2, respectively, based on the fact that: the styrene could be homopolymerized only by the **EBP/OED-3** radical initiating system to give polystyrene **PS** with 52% conversions (Table 4, entry 4), but could not be directly reduced by the anionic initiating system **OED-3** (Entry 3).<sup>[23]</sup> On the other hand, D,L-lactide could not be polymerized by the **EBP/OED-3** radical initiating system (Entry 2), but was efficiently polymerized (>99%) through ring-opening homopolymerization by **OED-3** (Entry 1). An equimolar mixture of styrene and D,L-lactide was first treated with only **OED-3** (10 mol %). After 24 h, a polylactide **PLA** homopolymer was formed, but no polymerization of styrene was observed (Table 4, entry 5). This result demonstrated that the ROP of D,L-lactide initiated by **OED-3** was unaffected by the presence of styrene and, more importantly, established that **OED-3** was still unable to promote the polymerization of styrene under these conditions. Subsequently, we examined the concomitant radical and anionic polymerization of styrene and D,L-lactide by simply adding **EBP** (5 mol %) as precursor of the radical species and excess **OED-3** (10 mol %)

hexane excluded the formation of co-polymers. Formation of porous materials from this IPN through selective dissolution of the polystyrene or etching of the polylactide (with a diluted aqueous base solution) could pave the way to various applications<sup>[24]</sup> (nanolithographic masks,<sup>[25]</sup> separation membranes,<sup>[26]</sup> templates for nanoparticle growth,<sup>[27]</sup> etc). Similarly, the concomitant radical polymerization of **SR348c**, **bis-GMA** or the methoxy PEG methacrylate **PEGMA**, and anionic polymerization of D,L-lactide efficiently produced the mixture of corresponding homopolymers (Entries 8, 10 and 12). Finally, concomitant radical and anionic polymerization of styrene and  $\epsilon$ -caprolactone gave the corresponding IPN (Entry 14).

## Conclusion

In conclusion, having established that organic electron donors are remarkable initiators for anionic chain-growth polymerizations, we now demonstrate that they can also be successfully used for the initiation of radical chain-growth polymerizations. Introduction of a competing oxidant, with a higher reduction potential than the monomer, switches the former anionic propagation to a clean radical propagation process. Our light-, metal- and peroxide-free redox initiator/OED system was applied to the

radical polymerization of a large variety of monomers of high industrial interest. In addition, simultaneous radical and anionic polymerization of several monomers was performed in a one-pot set-up to prepare interpenetrating polymer networks, using a slight excess of reducer **OED-3** with respect to the oxidant **EBP**. To our knowledge, this is the first example of a dual-mode activator promoting the reduction of different sources to generate either a radical or an anionic propagating species. These results highlight the versatility of OEDs as polymerization initiators and open new horizons for the development of macromolecular architectures through dual chain-growth modes. As **OED-3** spontaneously initiates the polymerizations of monomers, it cannot be stored in the monomer mixture.

**Table 4:** Simultaneous polymerization of mechanistically distinct monomers.

Entry	Monomer 1 + Monomer 2		EBP OED-3		Time	Poly(M1) + Poly(M2)	
	Monomer 1 (equiv)	Monomer 2 (equiv)	[OED-3] (mol %)	[EBP] (mol %)		Poly(M1)	Poly(M2)
1	–	D,L-lactide (1)	5	–	3 h	–	PLA (>99)
2	–	D,L-lactide (1)	2.5	5	24 h	–	PLA (0)
3	Styrene (1)	–	5	–	24 h	PS (0)	–
4	Styrene (1)	–	2.5	5	24 h	PS (52)	–
5	Styrene (1)	D,L-lactide (1)	10	–	24 h	PS (0)	PLA (>99)
6	Styrene (1)	D,L-lactide (1)	10	5	24 h	PS (50)	PLA (82)
7	PEGMA (1)	D,L-lactide (1)	10	–	24 h	P-PEGMA (0)	PLA (>99)
8	PEGMA (1)	D,L-lactide (1)	10	5	24 h	P-PEGMA (96)	PLA (>99)
9	SR348C (1)	D,L-lactide (1)	10	–	24 h	P-SR348C (0)	PLA (>99)
10	SR348C (1)	D,L-lactide (1)	10	5	0.5 h	P-SR348C (Hard)	PLA (>99)
11	Bis-GMA (1)	D,L-lactide (1)	10	–	24 h	P-Bis-GMA (0)	PLA (>99)
12	Bis-GMA (1)	D,L-lactide (1)	10	5	0.5 h	P-Bis-GMA (Hard)	PLA (>99)
13 <sup>[a]</sup>	Styrene (1)	$\epsilon$ -Caprolactone (1)	10	–	24 h	PS (0)	PCL (>99)
14 <sup>[a]</sup>	Styrene (1)	$\epsilon$ -Caprolactone (1)	10	5	24 h	PS (50)	PCL (>99)

Reaction conditions: Monomer 1 (1 mmol, 1 equiv), Monomer 2 (1 mmol, 1 equiv), **OED-3** (2.5–10 mmol %), **EBP** (0–5 mol %), DMF (0.2 mL), 25 °C, Ar. Conversions were determined by <sup>1</sup>H NMR. [a] Under neat condition.



Hence, just like the air-stable precursors that we developed for organic synthesis applications,<sup>[10]</sup> our future works will focus on latent forms for the long-term storage of monomer mixtures.

## Acknowledgements

The Ministère de l'Enseignement Supérieur et de la Recherche is gratefully acknowledged for the JCJC ANR grant "iPOD" (17-CE07-000101). Aix Marseille Université (AMU) and the Centre National de la Recherche Scientifique (CNRS) are also acknowledged for financial support. Y.Z. is grateful for Ph.D. fellowships from the China Scholarship Council (CSC). We thank Ivoclar Vivadent SAS for providing **SR348C** and **bis-GMA** monomers and Dr. J. Morris for fruitful discussions.

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** dual-mode activator · interpenetrating polymer networks · organic electron donors · simultaneous polymerization

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Manuscript received: May 19, 2021  
Revised manuscript received: June 18, 2021  
Accepted manuscript online: June 22, 2021  
Version of record online: ■ ■ ■ ■ ■ ■ ■ ■ ■ ■

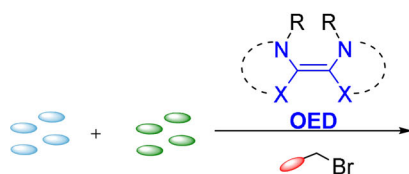
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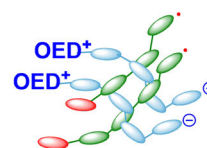
## Polymerization

Y. Zhao, M. Rollet, L. Charles, G. Canard,  
D. Gigmes, P. Vanelle,  
J. Broggi\*      

Switching from Single to Simultaneous  
Free-Radical and Anionic Polymerization  
with Enamine-Based Organic Electron  
Donors



Organic electron donors (OEDs) act as dual-mode activators priming concomitant radical and anionic polymerizations to prepare interpenetrating polymer networks. OEDs can simultaneously reduce an oxidant to initiate a radical propagation and reduce a monomer to



Interpenetrating  
Polymer Network

initiate an anionic propagation. These light-, metal-, and peroxide-free redox systems open new horizons for the development of macromolecular architectures through dual chain-growth modes.

