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Similarities and differences of epoxide, aldehyde and peroxide initiators for Cp$_2$TiCl-catalyzed styrene living radical polymerizations

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Abstract

Cp$_2$TiCl is the first example of a single electron transfer (SET) agent that both provides initiating radicals from three different types of functionalities (i.e. radical ring opening of epoxides and reduction of aldehydes and peroxides) and doubles as mediator for the living radical polymerization of styrene (St) by reversibly endcapping the growing polymer chains. An initiator (I) comparison was performed using 1,4-butanediol diglycidyl ether (BDE), benzaldehyde (BA) and benzoyl peroxide (BPO) as models. The investigation of the effect of reaction variables was carried out over a wide range of experimental conditions ([Cp$_2$TiCl$_2$]/[I] = 0.5/1–4/1; [Zn]/[Cp$_2$TiCl$_2$] = 0.5/1–3/1, [St]/[I] = 50/1–400/1 and T = 60–130 °C) to reveal living polymerization features such as a linear dependence of molecular weight on conversion and narrow molecular weight distribution (M_w/M_n) for each initiator class. However, progressively lower polydispersities and larger initiator efficiencies are obtained with increasing the [Cp$_2$TiCl$_2$]/[I] and [Zn]/[Cp$_2$TiCl$_2$] ratios and with decreasing temperature. Accordingly, optimum conditions correspond to [St]/[I]/[Cp$_2$TiCl$_2$]/[Zn] = [50–200]/[1]/[2–3]/[4–6] at 70–90 °C. By contrast to peroxides, aldehydes and the more reactive epoxides provide alcohol end groups useful in block or graft copolymers synthesis.
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1. Introduction

Over the last decade, living radical polymerization (LRP) has undergone notable development and has become one of the most capable and vigorous synthetic methods in modern polymer chemistry [1]. The ability of LRP to conveniently manipulate molecular weight (M_n) and polydispersity (M_w/M_n) has greatly benefited complex macromolecular synthesis. Accordingly, the broad applications of LRP have prompted extensive efforts in the development of novel initiators and catalytic systems. Detailed investigations have established that M_n and M_w/M_n can be controlled by the reversible termination of growing chains with persistent radicals [2] or degenerative transfer (DT) agents [3]. Mechanistically, LRP occurs by atom

transfer (ATRP), dissociation-combination (DC) or degenerative transfer (DT) [3] processes. While organo-catalyzed LRP is represented by nitroxides [4] (DC) and by iodine [5] or sulfur-based reversible addition-fragmentation transfer agents [6] (DT), catalytic systems based on *late* transition metal persistent [7] radicals have also proven very successful. Thus, ATRP is mediated by Cu, Ni, Fe, or Ru [1,3,8,9] halides, while organometallic [10] DC and DT LRP is catalyzed by Co [11] Te [12], Sb [13] and Mo [10] complexes.

Currently, aside from conventional applications in α-olefin coordination polymerizations [14] and organometallic reactions [15], increased attention is given to the radical organic chemistry of early transition metals (ETM) [16]. A representative example, the paramagnetic Cp$_2$Ti(III)Cl [17] complex, is inexpensively available from the reduction of Cp$_2$Ti(IV)Cl$_2$ with Zn [18]. The lime-green Cp$_2$TiCl is a very mild single electron transfer (SET) [19] agent and catalyzes a variety of radical reactions [20] including the radical

ring opening (RRO) of epoxides [21] and the reduction and pinacol coupling [22] of carbonyls [23].

We recently extended the use of Cp$_2$TiCl to polymer chemistry and introduced both epoxides [24a] and aldehydes [25] as novel classes of initiators for radical polymerizations. Moreover, the first examples of an ETM-catalyzed LRP was demonstrated for styrene (St) by initiation from epoxide RRO [24], aldehyde SET reduction [25] or redox reaction with peroxides [26]. Furthermore, Ti alkoxides generated in situ by epoxide RRO catalyze the living ring opening polymerization of cyclic esters [27]. These novel initiating methodologies have recently found applications in the Ti-catalyzed synthesis of mixed arm brush copolymers [28].

Interestingly, while the ligand effect was thoroughly investigated in ETM-catalyzed coordination polymerizations, little is known for radical processes. Thus, in our efforts to optimize Ti-LRP, the effect of ligands [24b–d], reducing agents [24e], solvents and additives [24f], as well as reagent ratios and temperature [24e,24f] was also investigated. This study has revealed the superiority of sandwich metallocenes over alkoxide and half-sandwich ligands, as well as the relatively weak influence of the Cp substituents. Gratifyingly, the most promising catalyst (Cp$_2$TiCl$_2$) was also the least expensive one [24g].

Current conventional LRP systems are still somewhat bounded by the restrictive choice of only activated halide and thermal or redox initiators which may limit chain end functionality [1]. Hence, a broader initiator and catalyst selection would greatly augment the synthetic ability of macromolecular chemistry. Epoxides and carbonyls are fundamental motifs in organic and polymer chemistry, can be easily synthesized and are commercially available with a wide structural variation. Moreover, they also provide easy access to alcohol polymer chain ends which can be further used in block or graft [27] copolymer synthesis.

Cp$_2$TiCl is a unique catalyst as it provides the first example of both a SET agent and an LRP mediator, which can initiate from at least three different classes of oxygen containing functional groups and therefore, allows for initiator comparison to be made. We are describing herein the similarities and differences in the effect of the reaction variables on Cp$_2$TiCl-catalyzed styrene polymerizations from epoxides [24e,24f], aldehydes [25] and peroxides [26].

2. Experimental

2.1. Materials

Cp$_2$TiCl$_2$ (97% Acros) was recrystallized from CH$_2$Cl$_2$. Zn (nanosize powder, 99+%), 1,4-butanediol diglycidyl ether (BDE, 95%), benzaldehyde (BA, 99.5%) (all from Aldrich) were used as received. Benzoyl peroxide (BPO, Janssen Chimica; 75%) was recrystallized from MeOH. 1,4-Dioxane (99%, Fisher) was distilled from a blue Na/benzophenone. Styrene (St, 99+%, Fluka), was dried over CaH$_2$, filtered, and passed through an acidic Al$_2$O$_3$ column.

2.2. Techniques

^{1}H NMR (500 MHz) spectra were recorded on a Bruker DRX-500 at 24 °C in CDCl$_3$ (Aldrich; 1% v/v tetramethylsilane (TMS) as internal standard). GPC analyses were performed at 34 °C on a Waters 150-C Plus gel permeation chromatograph equipped with a Waters 410 differential refractometer, a Waters 2487 dual wavelength absorbance UV–Vis detector set at 254 nm, a Polymer Laboratories PL-ELS 1000 evaporative light scattering (ELS) detector and with a Jordi Gel DVB 105 Å, a PL Gel 104 Å, a Jordi Gel DVB 100 Å, and a Waters Ultrastyragel 500 Å column setup. Tetrahydrofuran (Fisher; 99.9% HPLC grade) was used as an eluent at a flow rate of 3 mL/min. Number-average (M_n) and weight-average molecular weights (M_w) were determined from calibration plots constructed with polystyrene standards.

2.3. Polymerizations

Cp$_2$TiCl$_2$ (86.9 mg, 0.35 mmol), Zn (45.6 mg, 0.70 mmol), CaH$_2$ (<10 mg as trace moisture scavenger) and dioxane (1 mL) were added to a 25-mL Schlenk tube. The tube was degassed by several freeze–pump–thaw cycles and was filled with Ar. The reduction occurred in under 5 min and was accompanied by the characteristic lime-green color of Cp$_2$TiCl. The tube was then cooled to −78 °C and St (1 mL, 8.7 mmol) and initiator (e.g. BA, 8.9 μl, 0.087 mmol) were injected and the mixture was re-degassed and was heated at 90 °C. Samples were taken under Ar using an airtight syringe and were used for conversion and M_n determination by NMR and, respectively, by GPC.

3. Results and discussion

The proposed polymerization mechanism is outlined in Scheme 1. Zn reduction of Cp$_2$Ti(IV)Cl$_2$ to Cp$_2$Ti(III)Cl is conveniently carried out in situ (Eq. (1)) and occurs readily at room temperature, as evidenced by a characteristic red to green color change. Injection of epoxide, aldehyde or peroxide into such green Cp$_2$TiCl solutions leads to the fast appearance of the yellow-orange color of the Ti(IV) alkoxide (Cp$_2$TiClOR), indicating the occurrence of corresponding SET reduction process. Three representative initiators (I) from each class, I = 1,4-butanediol diglycidyl ether (BDE), benzaldehyde (BA), and benzoyl peroxide (BPO) were chosen as models. The epoxide RRO proceeds with the formation of a mixture of reactive, constitutionally isomeric primary and secondary β-titanoxy radicals (Scheme 1, Eqs. (2) and (3)), where typically the secondary radical is favored, but both have the same thermodynamic stabilization as the corresponding alkyl radicals [29]. Similarly, aldehydes form reactive α-titanoxy radicals which also add readily to conventional monomers such as (meth)acrylates [21] and styrene [24]. In the case of peroxides (Scheme 1, Eqs. (5) and (6)), while both thermal
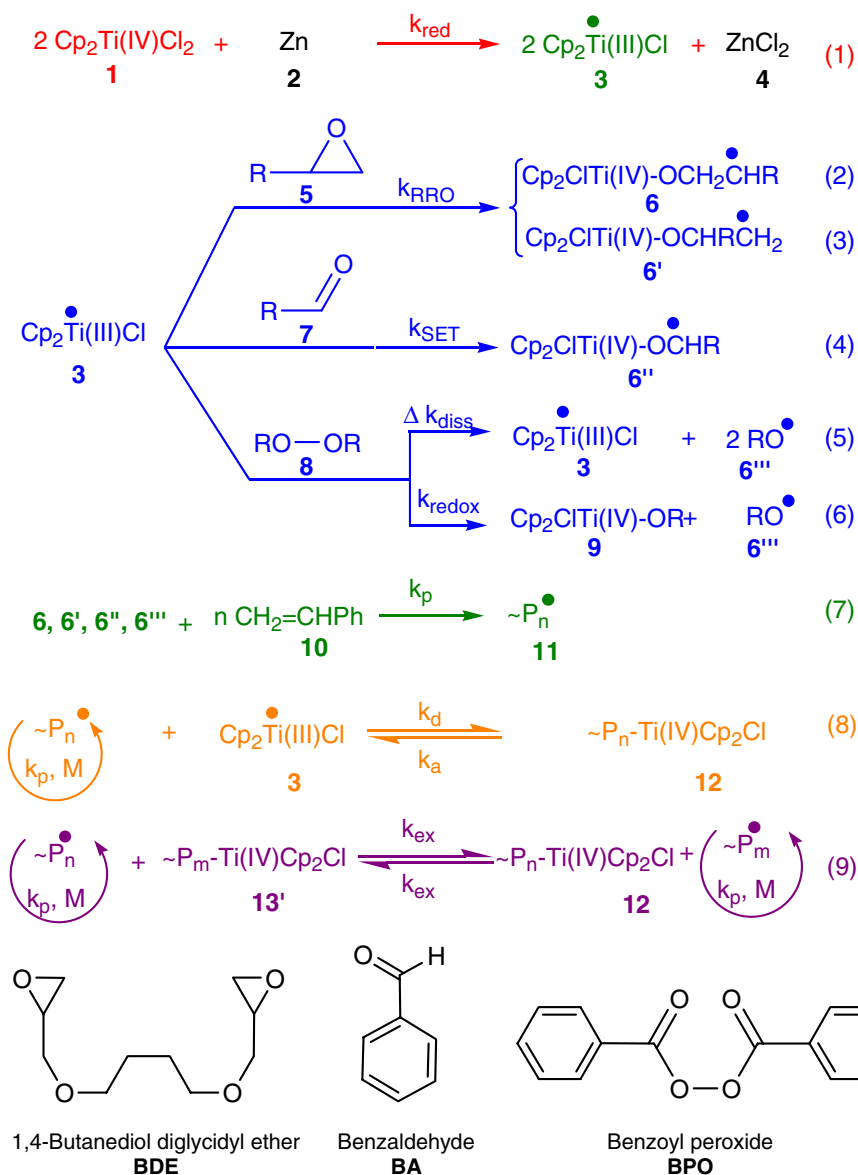
Scheme 1. Mechanism of the Cp_2TiCl-catalyzed LRP of styrene initiated from epoxides, aldehydes and peroxides.

decomposition and a redox reaction with Ti could provide radicals, the kinetics of the Ti reaction are much faster than the thermal process [26]. The corresponding radicals subsequently add to styrene (Eq. (7)) initiating the polymerization which is mediated in a living fashion by reversible termination with a second equivalent of Cp_2TiCl via most likely a combination of the DC and DT mechanisms (Eqs. (8) and (9)). The effect of $[I]/[Cp_2TiCl_2]$, $[Cp_2TiCl_2]/[Zn]$, and $[St]/[Cp_2TiCl_2]$ ratios and of temperature on St polymerizations initiated from BDE, BA and BPO is presented in Figs. 1–4 and summarized in Tables 1–4.

3.1. Effect of $[Cp_2TiCl_2]/[Initiator]$ ratio

According to the mechanism in Scheme 1, for all three classes of initiators (I), one Cp_2TiCl equivalent is theoretically required for initiator generation and a second one for

polymerization control. This assumption is demonstrated by the results presented in Fig. 1 and Table 1. The experiments were carried out in dioxane at 90 °C with a $[Cp_2TiCl_2]/[Zn] = 1/2$ ratio while the $[Cp_2TiCl_2]/[initiator group]$ ratio was varied from 0.5/1 (BPO) to 4/1 (BA). One should note that BA is monofunctional, BDE is difunctional, while BPO may initiate one or two chains by redox [26] or thermal decomposition. Thus, although the data in Table 1 correspond to different monomer to initiator group ratios, this does not influence the trend in the initiator/catalyst effect.

While linear kinetics are observed in all cases, sub-stoichiometric amounts of Ti (less than 2/1) generate poorly controlled polymerizations with low initiator efficiency (IE ~ 0.1) and broad molecular weight distribution ($M_w/M_n \sim 1.6$–2.1, Fig. 1a). This is a consequence of the Ti-catalyzed free radical initiation, where not enough Cp_2TiCl is
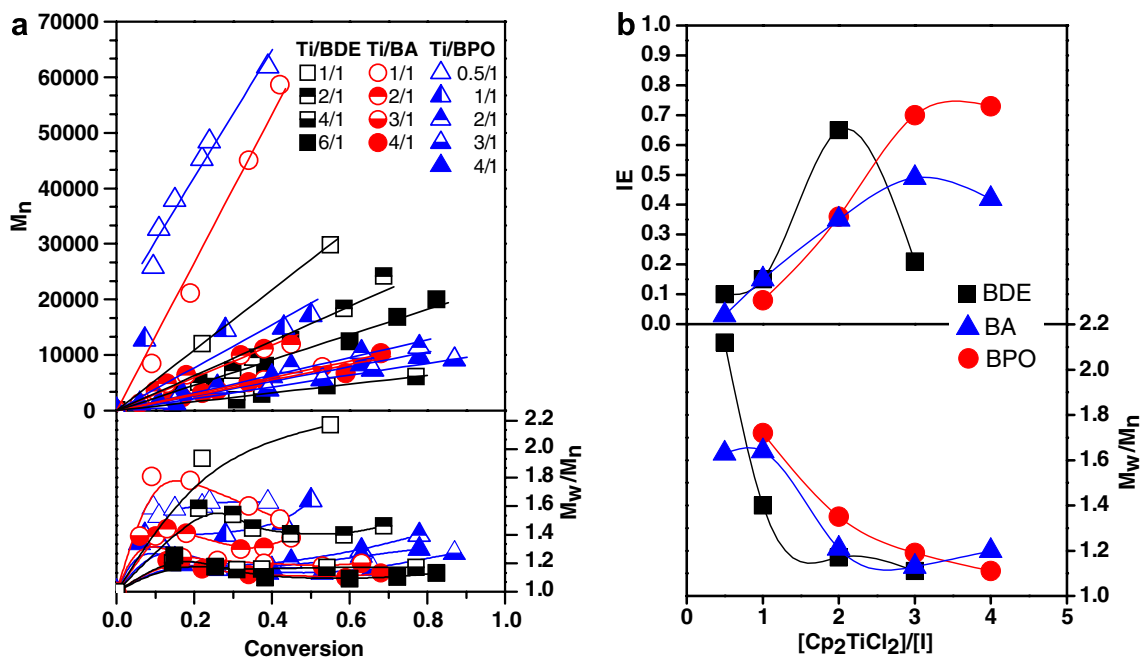
Fig. 1. Effect of the [I]/[Cp$_2$TiCl$_2$] ratio in the Cp$_2$TiCl-catalyzed styrene polymerizations initiated from BDE, BA and BPO: (a) dependence of the M_n and M_w/M_n on conversion. (b) Dependence of IE and of M_w/M_n at 50% conversion on [I]/[Cp$_2$TiCl$_2$]. [Cp$_2$TiCl$_2$]/[Zn] = 1/2, T = 90 °C, dioxane.
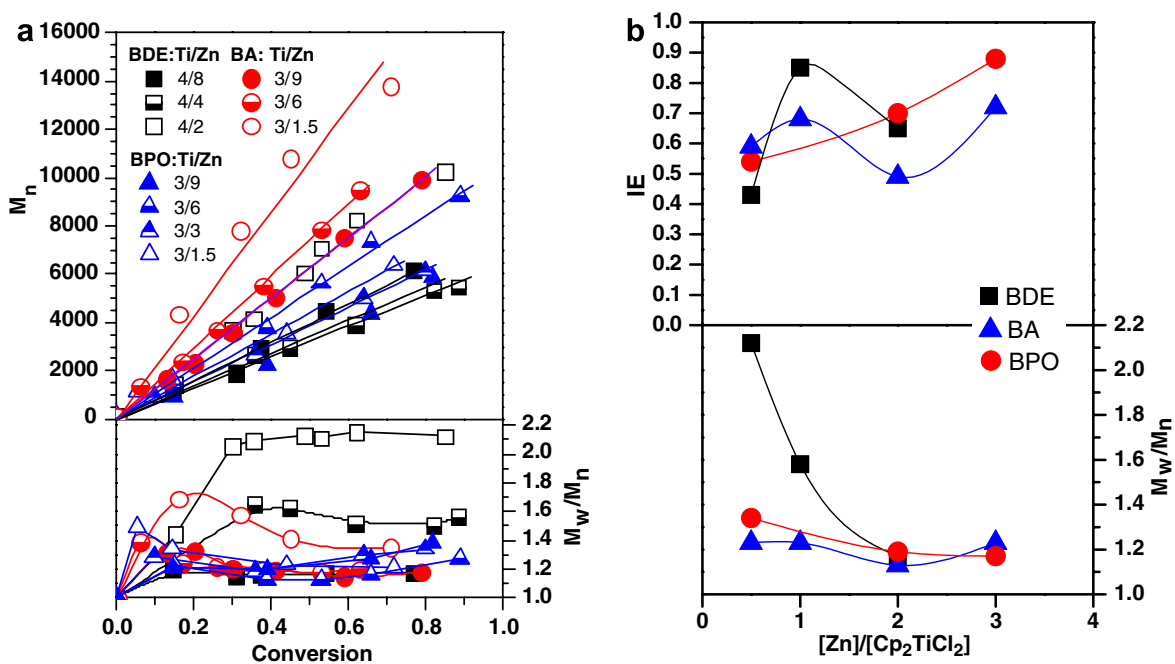

Fig. 2. Effect of the [Cp$_2$TiCl$_2$]/[Zn] ratio in Cp$_2$TiCl-catalyzed styrene polymerizations initiated from BDE, BA and BPO: (a) dependence of M_n and M_w/M_n on conversion. (b) Dependence of IE and of M_w/M_n at 50% conversion on [Cp$_2$TiCl$_2$]/[Zn]. [St]/[BA or BPO]/[Cp$_2$TiCl$_2$] = 100/1/3, [St]/[BDE]/[Cp$_2$TiCl$_2$] = 50/1/4; T = 90 °C, dioxane.

available to reversibly trap the growing chains. However, increasing the [Cp$_2$TiCl$_2$]/[I] ratio to 2/1 and higher leads to typical living polymerization features such as a linear dependence of M_n on conversion and low polydispersities (Fig. 1b). This is the combined result of the increase in the initiation rates and of the reversible trapping of growing chains by additional Cp$_2$TiCl.

As the molecular weight distribution progressively narrows, a related trend is observed for the initiator efficiencies. Thus, with increasing Cp$_2$TiCl concentration, IE increases dramatically (Fig. 1b) from about 0.1 to about 0.7 for BDE and BA and to about 0.5 for BPO, which is the theoretical maximum for redox initiation. A slight Ti excess is beneficial for both peroxides and especially
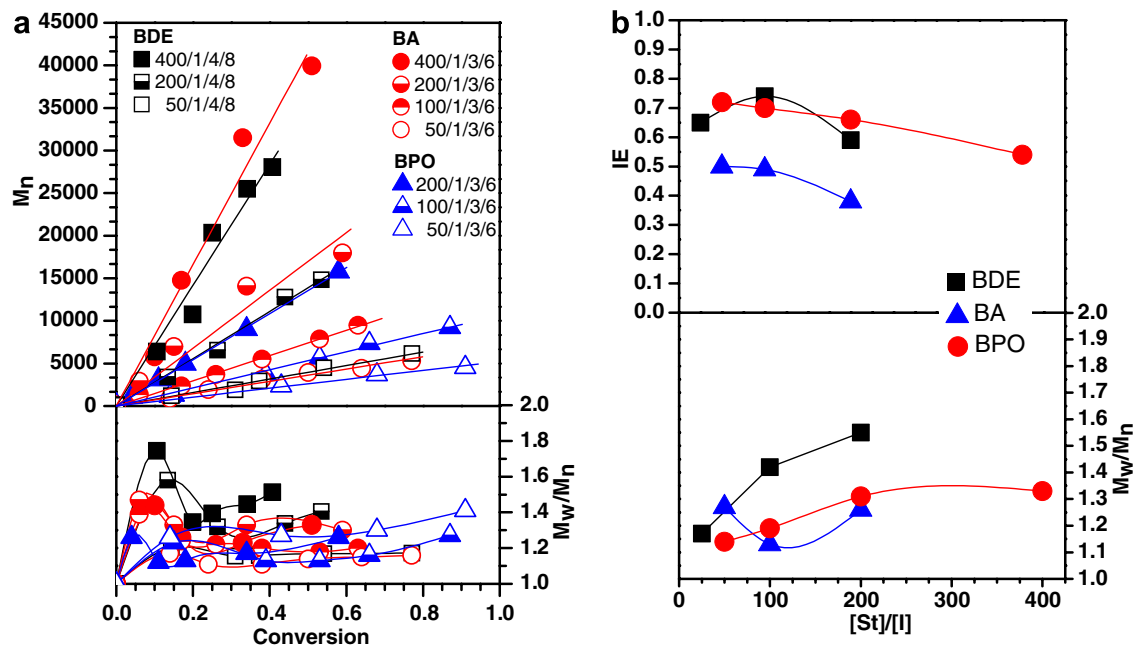
Fig. 3. Effect of the [St]/[I] ratio in the Cp$_2$TiCl-catalyzed styrene polymerization initiated from BDE, BA and BPO: (a) dependence of M_n and M_w/M_n on conversion. (b) Dependence of IE and of M_w/M_n at 50% conversion on [St]/[I]. $T = 90$ °C, dioxane.
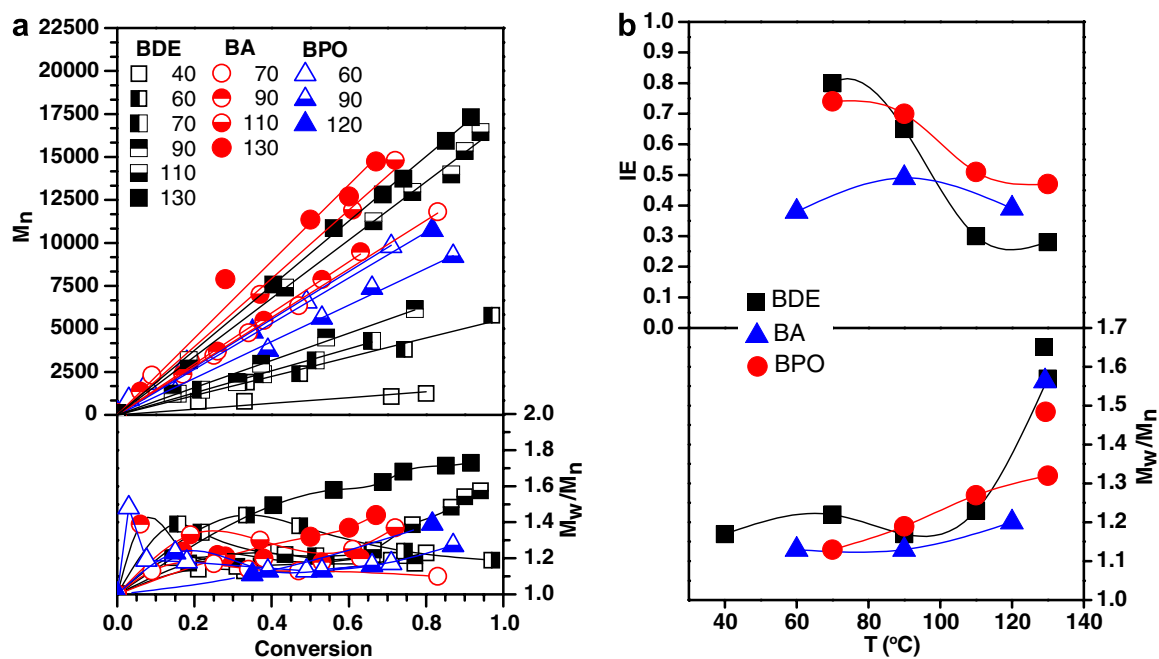

Fig. 4. Effect of temperature in the Cp$_2$TiCl-catalyzed styrene polymerization initiated from BDE, BA and BPO: (a) dependence of M_n and M_w/M_n on conversion. (b) Dependence of IE and of M_w/M_n at 50% conversion on temperature. [St]/[BA or BPO]/[Cp$_2$TiCl$_2$]/[Zn] = 100/1/3/6, [St]/[BDE]/[Cp$_2$TiCl$_2$]/[Zn] = 50/1/4/8; dioxane.

aldehydes where the IE increase towards as plateau. However, excess Ti may decrease the IE for epoxides via a deoxygenation [21] pathway.

The larger optimum [Cp$_2$TiCl$_2$]/[I] ratios used for BA and BPO reflect the fact that epoxide RRO is apparently faster than the Ti reduction of both aldehydes and peroxides. In addition, while large excess of Cp$_2$TiCl may lead to epoxide deoxygenation and lower IE, this reaction is not possible for

aldehydes, and thus IE^{BA} increases with Cp$_2$TiCl concentration also benefiting from the suppression of pinacol coupling with increasing persistent radical concentration [2].

3.2. Effect of the [Cp$_2$TiCl$_2$]/[Zn] ratio

The effect of Zn is presented in Fig. 2 and Table 2. The polymerizations were also carried out in dioxane at 90 °C,

Table 1

Effect of [Initiator]/[Cp$_2$TiCl$_2$] ratios in Cp$_2$TiCl-catalyzed styrene polymerizations initiated from epoxides, aldehydes and peroxides[a]

Experiment	Initiator (I)	[St]/[I]/[Cp$_2$TiCl$_2$]/[Zn]	M_n and M_w/M_n at 50%		IE	k_p^{app} (h^{-1})
1	BPO	100/1/0.5/1	61,953	1.63	0.03	0.017
2	BPO	100/1/1/2	17,175	1.64	0.15	0.155
3	BPO	100/1/2/4	7959	1.21	0.35	0.283
4	BPO	100/1/3/6	5630	1.13	0.49	0.457
5	BPO	100/1/4/8	6800	1.20	0.42	0.269
6	BA	100/1/1/2	68,357	1.72	0.08	0.079
7	BA	100/1/2/4	14,662	1.35	0.36	0.238
8	BA	100/1/3/6	7400	1.19	0.70	0.358
9	BA	100/1/4/8	7180	1.11	0.73	0.223
10	BDE	50/1/1/2	27,200	2.12	0.10	1.333
11	BDE	50/1/2/4	15,600	1.40	0.15	0.157
12	BDE	50/1/4/8	3900	1.17	0.65	0.432
13	BDE	50/1/6/12	11,200	1.11	0.21	0.234

[a] Data from Refs. [24e,25,26]; dioxane, $T = 90$ °C.

Table 2

Effect of [Cp$_2$TiCl$_2$]/[Zn] ratios in Cp$_2$TiCl-catalyzed styrene polymerizations initiated from epoxides, aldehydes and peroxides[a]

Experiment	Initiator (I)	[St]/[I]/[Cp$_2$TiCl$_2$]/[Zn]	M_n and M_w/M_n at 50%		IE	k_p^{app} (h^{-1})
1	BPO	100/1/3/9	3400	1.23	0.72	0.623
2	BPO	100/1/3/6	5630	1.13	0.49	0.457
3	BPO	100/1/3/3	3900	1.23	0.68	0.583
4	BPO	100/1/3/1.5	3570	1.23	0.59	0.333
5	BA	100/1/3/9	6266	1.17	0.88	0.392
6	BA	100/1/3/6	7400	1.19	0.70	0.358
7	BA	100/1/3/1.5	9692	1.34	0.54	0.139
8	BDE	50/1/4/8	3900	1.17	0.65	0.432
9	BDE	50/1/4/4	3200	1.58	0.85	0.176
10	BDE	50/1/4/2	6200	2.12	0.43	0.064

[a] Data from Refs. [24e,25,26]; dioxane, $T = 90$ °C.

Table 3

Effect of [M]/[Initiator] ratios in Cp$_2$TiCl-catalyzed styrene polymerizations initiated from epoxides, aldehydes and peroxides[a]

Experiment	Initiator (I)	[St]/[I]/[Cp$_2$TiCl$_2$]/[Zn]	M_n and M_w/M_n at 50%		IE	k_p^{app} (h^{-1})
1	BDE	50/1/4/8	3900	1.17	0.65	0.432
2	BA	50/1/3/6	3632	1.14	0.72	0.394
3	BPO	50/1/3/6	2371	1.27	0.5	0.647
4	BDE	200/1/4/8	15,000	1.42	0.74	0.275
5	BA	100/1/3/6	7400	1.19	0.70	0.358
6	BPO	100/1/3/6	5630	1.13	0.49	0.457
7	BDE	400/1/4/8	28,100	1.55	0.59	0.116
8	BA	200/1/3/6	15,890	1.31	0.66	0.241
9	BPO	200/1/3/6	15,775	1.26	0.38	0.112
10	BA	400/1/3/6	38,420	1.33	0.54	0.206

[a] Data from Refs. [24f,25,26]; dioxane, $T = 90$ °C.

but with a stoichiometric or larger [Cp$_2$TiCl$_2$]/[I] group ratio (2/1, BDE; 3/1 BA, BPO) such that enough Cp$_2$TiCl is available for polymerization control.

The reducing agent has a pronounced effect on polymerizations from all initiators. Thus, while a linear dependence of M_n on conversion and linear kinetics, indicative of a living process is observed in all cases, increasing the amount of Zn from stoichiometric, ([Cp$_2$TiCl$_2$]/[Zn] = 1/0.5) to excess ([Cp$_2$TiCl$_2$]/[Zn] = 1/3), has a very strong influence on polydispersity, which decreases rapidly from 2.2 to about 1.2 (Fig. 2b). The initiator efficiency also increases

with increasing Zn concentration especially for aldehydes, but is also pronounced for epoxides (Fig. 2b). This is due to the ZnCl$_2$-assisted RRO process [30] but it is likely that a similar ZnCl$_2$ activation is available for aldehydes as well. The trend is less clear for BPO, but it is possible that with large Zn excess, a redox reaction may also occur between BPO and Zn. The increase in IE also leads to a corresponding increase in the polymerization rate for all initiators.

The improvement in the polymerization is a result of the increase in the rate of Zn reduction of Cp$_2$TiCl$_2$, strongly

Table 4
Temperature effect in Cp_2TiCl-catalyzed styrene polymerizations initiated from epoxides, aldehydes and peroxides[a]

Experiment	Initiator (I)	[St]/[BA]/[Cp_2TiCl_2]/[Zn]	Temperature (°C)	M_n and M_w/M_n at 50% conversion		IE	k_p^{app} (h^{-1})
1	BDE	50/1/4/8	40	900	1.17	–	0.061
2	BPO	100/1/3/6	60	6560	1.13	0.38	0.161
4	BDE	50/1/4/8	70	3200	1.22	0.80	0.128
5	BA	100/1/3/6	70	7079	1.13	0.74	0.094
6	BDE	50/1/4/8	90	3900	1.17	0.65	0.432
7	BA	100/1/3/6	90	7400	1.19	0.70	0.358
8	BPO	100/1/3/6	90	5630	1.13	0.49	0.457
9	BDE	50/1/4/8	110	8200	1.23	0.30	0.770
10	BA	100/1/3/6	110	10,304	1.27	0.51	0.987
11	BPO	100/1/3/6	120	6700	1.20	0.39	0.688
12	BDE	50/1/4/8	130	9200	1.57	0.28	0.819
13	BA	100/1/3/6	130	11,166	1.32	0.47	1.313

[a] Data from Refs. [24e,25,26].

accelerated in the presence of excess heterogeneous reducing agent. Extra Zn and Cp_2TiCl may also be required to stabilize the polymerization against traces of oxygen. Moreover, it is also possible that Zn is involved in the catalysis of the reversible termination step by the transient formation of organozinc intermediates.

3.3. Effect of the [St]/[Initiator] ratio

The effect of [St]/[I] is presented in Fig. 3 and Table 3. The polymerizations were carried out in dioxane at 90 °C, with a stoichiometric or larger [Cp_2TiCl_2]/[I] group ratio and with excess Zn. A linear dependence of M_n on conversion, indicative of a living polymerization was observed over a wide range of ratios from [St]/[I] = 50/1 to 400/1 (Fig. 3a). As expected, M_n scales directly with M/I and the polymerization rates decrease with increasing M/I due to the reduction in the initiator concentration.

As noted earlier, BA is monofunctional, BDE is difunctional, but generates a single PSt chain consisting of two PSt chains of half the M_n, while BPO may initiate up to two chains by thermal decomposition but only one chain by a redox reaction, as previously observed [26]. Consequently, a fair comparison of the initiators for the same degree of polymerization, e.g. DP = 100 *per initiator group* corresponds to [St]/[BA] = 100, [St]/[BPO] = 100 (redox initiation) and [St]/[BDE] = 200. Such data normalization reveals that epoxides and aldehydes are quite similar in IE (~0.7/group) and that BPO initiation is almost quantitative (IE = 0.5) according to a redox process generating one benzoyl radical and one Ti benzoate. In addition, IE appears to decrease somewhat with increasing M/I for all initiators.

The PDI at median conversion increases slightly with DP, especially for BDE. This effect is most likely due to the decrease in the rate of initiation with the decrease in initiator and Ti concentration since only a stoichiometric amount of Cp_2TiCl is present for epoxides, but an excess is available for BA and BPO.

3.4. Effect of temperature

The temperature effect is presented in Fig. 4 and Table 4. The experiments were carried out with an optimum [Cp_2TiCl_2]/[Zn] = 1/2 and [I]/[Cp_2TiCl_2] = 1/2–1/3 ratios. As seen in Fig. 4, the linear dependence of M_n on conversion and the narrow M_n distributions demonstrate a living process over a wide temperature range ($T = 60$–130 °C), and as expected, the rate increases with temperature for all initiators. However, higher temperature also results in a slight increase in PDI for all initiators. This is most likely due to the increase in side reactions and to the shift of the reversible dissociation equilibrium towards the active species, resulting in increased termination. For BDE, the increase in PDI is also a consequence of the low degree of polymerization ([M]/[I] = 25 per epoxide vs. [M]/[I] = 100 for BA and BPO) which amplifies termination via the increase in the number of propagating radicals.

Higher temperature also results in decreased initiator efficiency for BA and especially BDE, where IE decreases from 0.7 to 0.8 at $T = 70$ °C to 0.3–0.5 at 130 °C as a result of loss of radicals to side reactions including BA pinacol coupling and BDE deoxygenation. By contrast, for BPO, higher temperatures increase the amount of thermolysis-derived BPO radicals and probably compensate for BPO radicals lost via side reactions with Ti. Thus, IE^{BPO} ~ 0.4–0.5 and appears to be relatively constant.

4. Conclusions

A comparative evaluation of epoxide, aldehyde and peroxide initiators for the Cp_2TiCl-catalyzed living radical polymerizations of styrene was performed by investigating the effect of reagent stoichiometry and temperature on initiator efficiency and polydispersity. The comparison of the effect of the reaction variables, carried out with BDE, BA and BPO as model initiators reveals living polymerization features such as a linear dependence of molecular weight on conversion in each initiator class over a wide range of

experimental conditions and a set of structure-derived similarities and differences, as outlined below.

[Cp$_2$TiCl$_2$]/[Initiator] ratio: For all initiators, substoichiometric reactions ([Cp$_2$TiCl$_2$]/[I] < 2/1) lead to uncontrolled polymerizations as not enough catalyst is available to reversible trap growing chains, whereas higher ratios provide progressively narrower polydispersities (M_w/M_n < 1.2). Increasing the catalyst amount from [Cp$_2$TiCl$_2$]/[I] = 0.5/1 to the optimum, stoichiometric 2/1 ratio, increases initiator efficiency from IE^{BDE,BA,BPO} ~ 0.1 to IE^{BDE,BA} ~ 0.7 and IE^{BPO} ~ 0.5 which is the maximum available for BPO redox initiation. However, while higher [Cp$_2$TiCl$_2$]/[I] = 3/1 ratios do not affect BA and BPO, they decrease IE^{BDE} to ~0.2 via epoxide deoxygenation. Thus, aldehydes and peroxides are more tolerant to excess Cp$_2$TiCl than epoxides. Conversely, epoxide SET-RRO is faster than aldehyde or peroxide SET reductions.

[Cp$_2$TiCl$_2$]/[Zn] ratio: In all cases, [Cp$_2$TiCl$_2$]/[Zn] ratios from 1/0.5 to 1/3 provide a linear dependence of M_n on conversion. Excess Zn has a strong effect on reducing polydispersity to below 1.2 for all initiators. While IE and polymerization rate are increased for BDE and BA it remains relatively unchanged for BPO. The improvement in polymerization with increasing Zn concentration is the combined result of faster Cp$_2$TiCl$_2$ reduction, and ZnCl$_2$-assisted initiation from epoxide and aldehyde as well as possible Zn involvement in the catalysis of the reversible termination.

[St]/[I] ratio: M_n shows a linear dependence on conversion and scales directly with [St]/[I] in all cases with [St]/[I] = 50/1–400/1. PDI increases somewhat for BDE, and while the IE decreases slightly with [St]/[I], epoxides and aldehydes have similar IE values (0.7) and the redox BPO initiation is almost quantitative (IE^{BPO} = 0.5).

Temperature: A linear dependence of M_n on conversion and linear kinetics were observed throughout the 60–130 °C range, but higher temperature decreases IE^{BA} and especially IE^{BDE} from 0.7–0.8 at T = 70 °C to 0.3–0.5 at 130 °C due to side reactions. By contrast, IE^{BPO} ~ 0.4–0.5 appears relatively constant vs. temperature.

Therefore, progressively narrower molecular weight distributions (M_w/M_n ~ 1.2) and larger initiator efficiencies are obtained with increasing the [Cp$_2$TiCl$_2$]/[I], [Zn]/[Cp$_2$TiCl$_2$] ratios and with decreasing temperature. Accordingly, optimum conditions which maximize IE and minimize PDI for such polymerizations would qualitatively correspond to reagent ratios of [St]/[I]/[Cp$_2$TiCl$_2$]/[Zn] = (50–200)/1/(2–3)/(4–6) at 70–90 °C. Overall, while peroxides are good initiators, they typically do not provide functional chain ends. By contrast, both epoxides and aldehydes allow access to Cp$_2$TiCl–O–PSt or HO–PSt end groups which can be further utilized in the synthesis of block copolymers. Moreover, while aldehydes seem to have fewer side reactions, epoxides are more reactive, require less Cp$_2$TiCl$_2$ for fast initiation and are more readily accessible on polymer backbones where they can be used to initiate the Ti-catalyzed synthesis of graft copolymers.

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