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Cp_2TiCl-catalyzed radical chemistry: living styrene polymerizations from epoxides, aldehydes, halides, and peroxides

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ABSTRACT

Four different Cp_2TiCl-activated radical sources (1,4-butanediol diglycidyl ether, benzaldehyde, (1-bromoethyl)benzene, and benzoyl peroxide) were investigated as initiators in the Cp_2TiCl-catalyzed living radical polymerization of styrene (St). The effect of reaction variables was investigated over a wide range of values ($[St]/[I]=50/1–400/1$, $[I]/[Cp_2TiCl_2]=1/0.5–1/4$, $[Cp_2TiCl_2]/[Zn]=1/0.5–1/3$ and $T=40–130$ °C). A linear dependence of molecular weight on conversion was observed for each initiator, but larger initiator efficiencies and lower polydispersities were obtained upon increasing $[Cp_2TiCl_2]$ and [Zn] and decreasing temperature. The optimum conditions are initiator dependent but broadly correspond to $[St]/[I]/[Cp_2TiCl_2]/[Zn]=[50–200]/[1]/[2–3]/[4–6]$ at 70–90 °C. The most robust initiators are aldehydes followed by peroxides, epoxides, and finally halides.

1. Introduction

Since their inception in the mid 90s, living radical polymerizations (LRPs) have undergone a remarkable development and have become one of the most capable and vigorous synthetic methods in modern polymer chemistry.[1] The ability of LRP to control molecular weight (M_n) and polydispersity (M_w/M_n or PDI) while requiring considerably more user-friendly reaction conditions versus water sensitive ionic and coordination polymerizations has greatly benefited the polymer synthesis toolbox and has substantially enabled complex macromolecular synthesis. Accordingly, such applications of LRP have motivated extensive efforts in the development of novel initiators and catalytic systems. It is currently accepted that the livingness of the polymerization (linear dependence of M_n on conversion, low M_w/M_n values, and the ability to synthesize block copolymers) is afforded 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. Catalyst-wise, organic derivatives such as nitroxides[4] and iodine[5] or sulfur-based transfer agents[6] mediate LRP via the DC and, respectively, DT mechanism, while organometallic[7] complexes based Co,[8] Te,[9] Sb,[10] and Mo[7] favor both DC and DT pathways. Finally, late transition metal halide persistent radicals[11] (Cu, Ni, Fe, or Ru,[1,3,12,13] etc.) have proven very successful in ATRP.

However, current LRP systems are still somewhat limited by the restrictive choice of only activated halide or thermal initiators, which may limit chain end functionality,[1] and in certain cases, by the range of monomers polymerizable by a given initiator/catalyst system. Thus, a broader initiator and catalyst selection would further enhance macromolecular synthesis. Epoxides and carbonyls are fundamental motifs in organic and polymer chemistry, and are commercially available with a wide structural variation. Moreover, they could provide alcohol polymer chain ends, useful in block or graft[31] copolymer synthesis. Yet, none of the current late transition metal catalyzed radical polymerizations has previously taken advantage of these possibilities.

While the applications of early transition metals (ETMs) in α-olefin coordination polymerizations[14] and organometallic reactions[15] have been established for a long time, the unique advantages offered by Ti radical chemistry have only recently been recognized, [16] and this area of research has since witnessed and effervescent and sustained growth.[17] Thus a representative example, the paramagnetic $Cp_2Ti(III)Cl$[18] complex, is inexpensively available from the reduction Zn of $Cp_2Ti(IV)Cl_2$.[19] The lime-green Cp_2TiCl is a very mild single electron transfer (SET)[20] agent, which catalyzes a variety of radical reactions[21] including the radical ring opening (RRO) of epoxides,[16] the reduction and pinacol coupling[22,23b] of aldehydes as well as halide abstraction not only from activated allylic,[23a] benzylic[23b] or α-haloester substrates[23c] typically used as initiators in ATRP polymerizations,[1] but also from inactivated glycosyl chlorides and bromides[24a–d] and olefinic iodoethers.[24e]

We have recently extended the use of Cp_2TiCl to polymer chemistry and introduced both epoxides[25] and aldehydes[26] as

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novel classes of initiators for radical polymerizations. The first examples of an ETM-catalyzed LRP were demonstrated for styrene (St) with initiation from epoxide RRO,[25] aldehyde SET reduction,[26] redox reactions with peroxides[27] as well as halide abstraction.[28] Similar protocols were developed for the LRP of isoprene.[29]

While the ligand effect was thoroughly investigated in ETM-catalyzed coordination polymerizations, it is less documented for radical processes.[30] Thus, in our efforts to optimize Ti-LRP, the effect of ligands,[25b–d] reducing agents,[25e] solvents and additives,[25f] as well as reagent ratios and temperature[25e,f] was also investigated. This study 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_2TiCl_2) was also the least expensive one.[25g]

Interestingly, the Cp_2ClTi-OR alkoxides generated in situ by epoxide RRO[31a] or aldehyde SET reduction[31b] were also found to catalyze the living ring opening polymerization of cyclic esters such as caprolactone. Moreover, these novel initiating methodologies were applied in the Cp_2ClTi-catalyzed synthesis of graft or mixed arm brush copolymers where epoxide groups along polymer chains (e.g. copolymers of glycidyl methacrylate,[32a–g] epoxidized polyisoprene copolymers,[32f,g] or epoxy-functionalized silica particles[32h]) were used as initiating sites for graft copolymerizations of both olefins and cyclic esters.[32i]

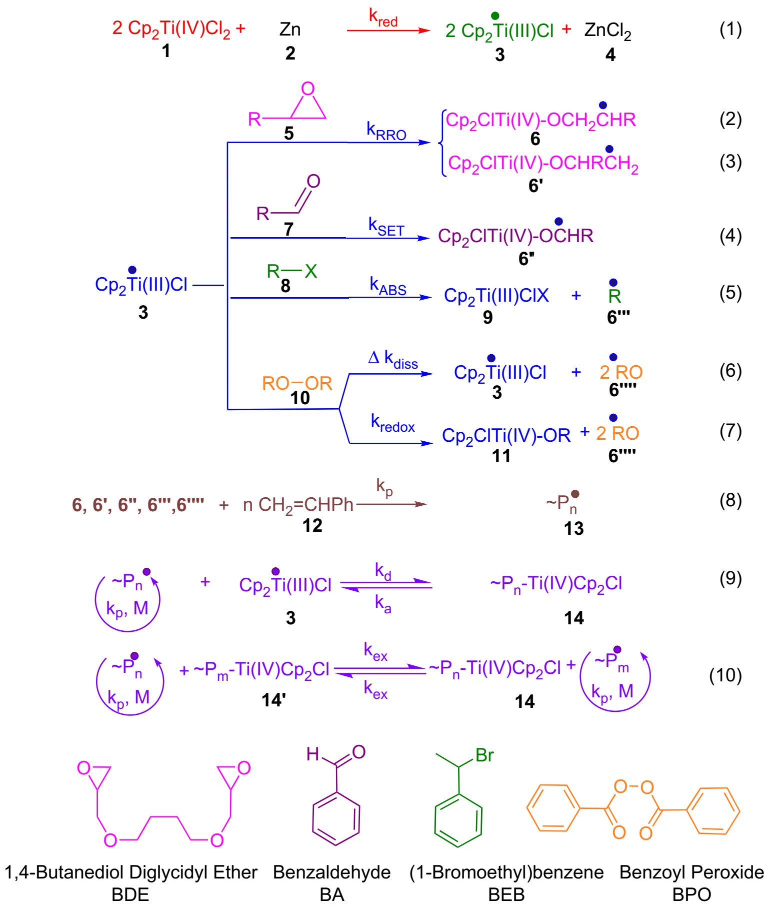
By contrast with other LRP reagents, Cp_2TiCl uniquely grants the first example of an SET agent doubling as an LRP mediator, which can initiate from four different types of functional groups, and thus allows for initiator comparisons to be made. We are thus describing herein the similarities and differences in the effect of the reaction parameters on Cp_2TiCl-catalyzed styrene living radical polymerizations initiated from epoxides,[25] aldehydes,[26] halides,[28] and peroxides.[27]

2. Results

The mechanism of Ti-mediated styrene LRP is presented in Scheme 1. The Zn reduction of $Cp_2Ti(IV)Cl_2$ to the $Cp_2Ti(III)Cl$ metalloradical (Eq. 1) is carried out in situ and proceeds readily in dioxane at room temperature, as indicated by a typical red to green color change. While the reduction occurs even with stoichiometric Zn, a small excess was typically employed to accelerate the process.

The strong affinity of this radical toward epoxides, aldehydes, halides or peroxides is evidenced by the rapid color change to yellow-orange upon injection of excess initiator into the green Cp_2TiCl solutions, indicating the occurrence of corresponding SET process.

Four representative initiators (I) from each class, I=1,4-butanediol diglycidyl ether (BDE), benzaldehyde (BA), (1-bromoethyl)benzene (BEB), and benzoyl peroxide (BPO) were selected as models. The epoxide RRO[17b,33] proceeds with the formation of a mixture of 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.[34] The addition of such radicals to double bonds is well documented.[17,17b,28,33] Similarly, aldehydes (Eq. 4) provide α-titanoxy radicals, which also add readily to styrene.[26] Halides (Eq. 5), especially activated ones (BEB), are also easily abstracted by Cp_2TiCl to generate a radical which mimics the styrene repeat unit and thus similarly to Cu-catalyzed



Scheme 1. Mechanism of the Cp_2TiCl-catalyzed styrene LRP initiated from epoxides, aldehydes, halides, and peroxides.

ATRP[1] will also initiate styrene. For peroxides (Eqs. 6 and 7), both the thermal decomposition and a redox reaction with Cp_2TiCl could supply radicals. However, the Ti redox reaction proceeding with the formation of a benzoyl radical and a Ti benzoate is faster than the thermal process.[27]

Once generated by the Ti activation of the initiator, the corresponding radicals subsequently add to styrene (Eq. 7) thereby starting the polymerization, which is mediated in a living fashion by reversible termination with a second equivalent of Cp_2TiCl via a combination of the DC and DT mechanisms (Eqs. 8 and 9). Since after initiation the polymerizations proceed in a similar fashion, one would expect them to be similarly influenced by the reaction variables. However, the nature of I affects the initiator efficiency (IE, the fraction of polymer chains initiated by one I molecule), which is closely related to the livingness of the polymerization. The similarities and differences are extracted by evaluating comparatively the effect of the reagent ratios ([St]/[I], $[I]/[Cp_2TiCl_2]$, and $[Cp_2TiCl_2]/[Zn]$) and temperature on St polymerizations initiated from BDE, BA, BEB, and BPO.

2.1. Effect of the [Initiator]/$[Cp_2TiCl_2]$ ratio

As described in Scheme 1, for all functional groups in the initiator, one Cp_2TiCl equivalent is required for the radical generation and a second one for polymerization control by reversible endcapping of the propagating growing chain. Thus an [I]/[Ti] ratio of at least 1/2 is necessary for a living process. This hypothesis is supported by the results presented in Figure 1 and Table 1. The experiments were carried out at 90 °C with a $[Cp_2TiCl_2]/[Zn]=1/2$, $[St]/[I]=100$ for BA, BEB, and BPO and 50 for BDE, and the [initiator group]/$[Cp_2TiCl_2]$ ratio was varied from 1/1 to 1/4. One should note that both BA and BEB are monofunctional, BDE is difunctional, while BPO may initiate either one or two chains by redox[27] or, respectively, thermal decomposition. Thus, although the comparison is made for different monomer/initiator group ratios, this does not influence the trend in the initiator/catalyst effect.

In all cases (except $[BPO]/[Ti]=1/1$) the reactions provide linear kinetics and linear dependence of M_n on conversion, indicating a living process (Fig. 1a). However, sub-stoichiometric amounts of Ti ($[I]/[Ti]<1/2$) generate poorly controlled polymerizations with broad molecular weight distribution ($M_w/M_n \sim 1.6$–2.1) and low initiator efficiency (IE ~ 0.1, Fig. 1b). This is the result of an insufficient amount of Cp_2TiCl available to control the propagating chains once most of it is consumed during radical generation. Conversely, upon increasing $[I]/[Cp_2TiCl_2]$ to 1/2 and higher, more Ti becomes available to trap propagating radicals. Thus, better living polymerization features such as lower PDIs (Fig. 1b) and higher IEs are observed. This is the joint result of the increase in the rate of initiation and of the reversible endcapping of growing chains by additional Cp_2TiCl. Simultaneously with the decrease in PDI to a reasonable value of about 1.2, a parallel trend is observed for the IE (Fig. 1b).

Thus, with increasing Cp_2TiCl concentration, IE increases noticeably from about 0.1 to about 0.5 for BPO (upper limit for redox initiation), to about 0.7 for BDE and BA and to about 1 for BEB. It is also apparent that these initiators undergo divergent behaviors at large excess catalyst. Thus, for both BA and BPO, which are less likely to undergo side reactions, a slight Ti excess (1/3) is beneficial but afterwards IE levels off in a plateau. By contrast, for epoxides, excess Ti decreases the IE via most likely deoxygenation.[21]

As this reaction is not possible for aldehydes, IE^{BA} increases with Cp_2TiCl concentration, also benefiting from the suppression of pinacol coupling with increasing persistent radical concentration.[2] For BEB, IE increases continuously with increasing the catalyst concentration. In this case, $Cp_2TiClBr$ formed in situ upon halide abstraction is reduced again by Zn to generate an additional equivalent of Cp_2TiCl, thus bringing the real BEB/Ti ratio up to 1/4. It is also possible that large excess of Ti may catalyze secondary initiation mechanisms. Interestingly, while an optimum [I]/[Ti] ratio appears to be 1/3 for BA, BEB, and BPO, the higher IE of BDE at the stoichiometric $[I]/[Ti]=1/2$ may also indicate that epoxide RRO is faster than the Ti reaction with the other functional groups.

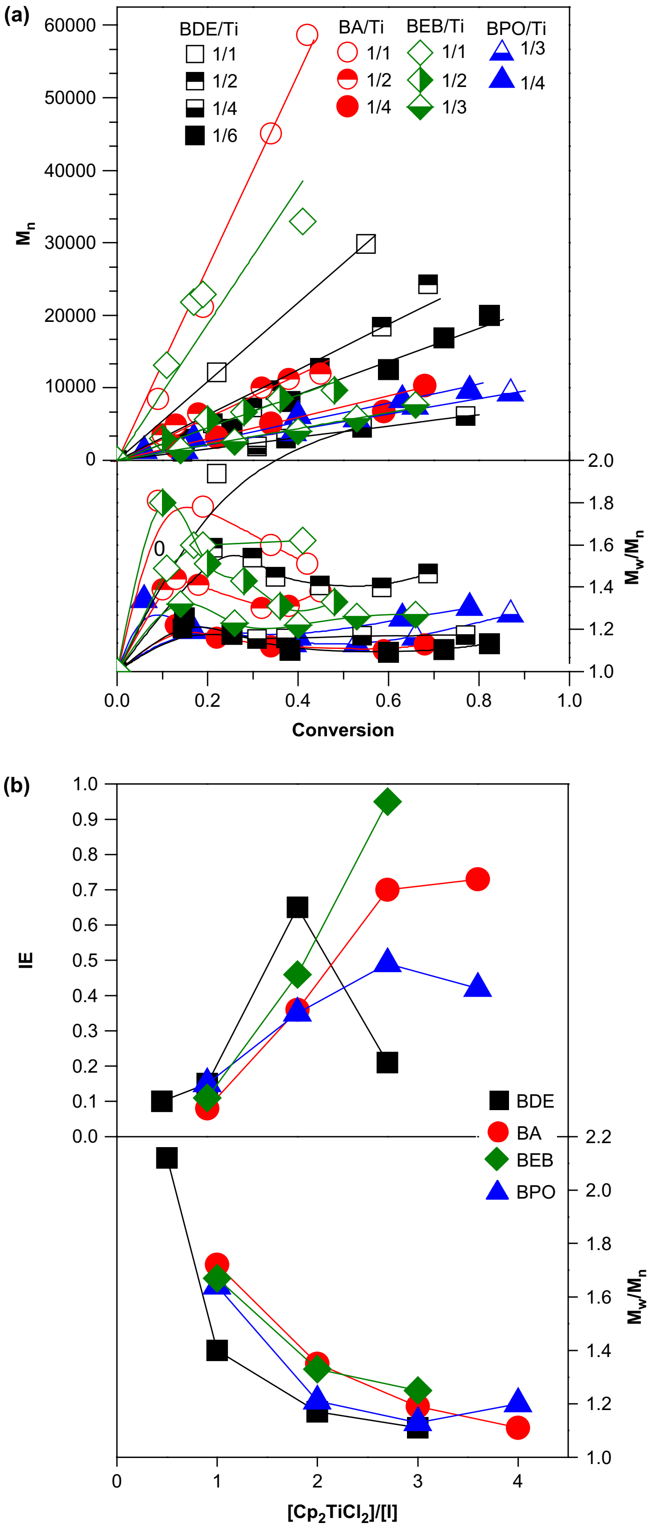


Figure 1. Effect of the $[I]/[Cp_2TiCl_2]$ ratio on the Cp_2TiCl-catalyzed styrene LRPs initiated from BDE, BA, BEB, and BPO. (a) Selected examples of the dependence of the M_n and M_w/M_n on conversion. (b) Dependence of IE and M_w/M_n at 50% conversion on $[I]/[Cp_2TiCl_2]$. $[St]/[I]=100$ (I=BA, BEB, BPO), $[St]/[BDE]=50$, $[Cp_2TiCl_2]/[Zn]=1/2$, dioxane, 90 °C.

Table 1
Effect of the [Initiator]/[Cp_2TiCl_2] ratios on Cp_2TiCl-catalyzed styrene LRPs initiated from epoxides, aldehydes, halides, and peroxides[a]

Exp	Initiator (I)	[St]/[I]/ [Cp_2TiCl_2]/[Zn]	M_n and M_w/M_n at 50%		IE	k_p^{app} (h^{-1})
1	BDE	50/1/1/2	27,200	2.12	0.10	1.33
2	BDE	50/1/2/4	15,600	1.40	0.15	0.16
3	BDE	50/1/4/8	3900	1.17	0.65	0.43
4	BDE	50/1/6/12	11,200	1.11	0.21	0.23
5	BA	100/1/1/2	68,357	1.72	0.08	0.08
6	BA	100/1/2/4	14,662	1.35	0.36	0.24
7	BA	100/1/3/6	7400	1.19	0.70	0.36
8	BA	100/1/4/8	7180	1.11	0.73	0.22
9	BEB	100/1/1/2	37,358	1.67	0.11	0.07
10	BEB	100/1/2/4	9781	1.33	0.46	0.16
11	BEB	100/1/3/6	5317	1.25	0.95	0.54
12	BPO	100/1/1/2	17,175	1.64	0.15	0.16
13	BPO	100/1/2/4	7959	1.21	0.35	0.28
14	BPO	100/1/3/6	5630	1.13	0.49	0.46
15	BPO	100/1/4/8	6800	1.20	0.42	0.27

[a] Dioxane, T=90 °C. Data from Refs. 25–28.

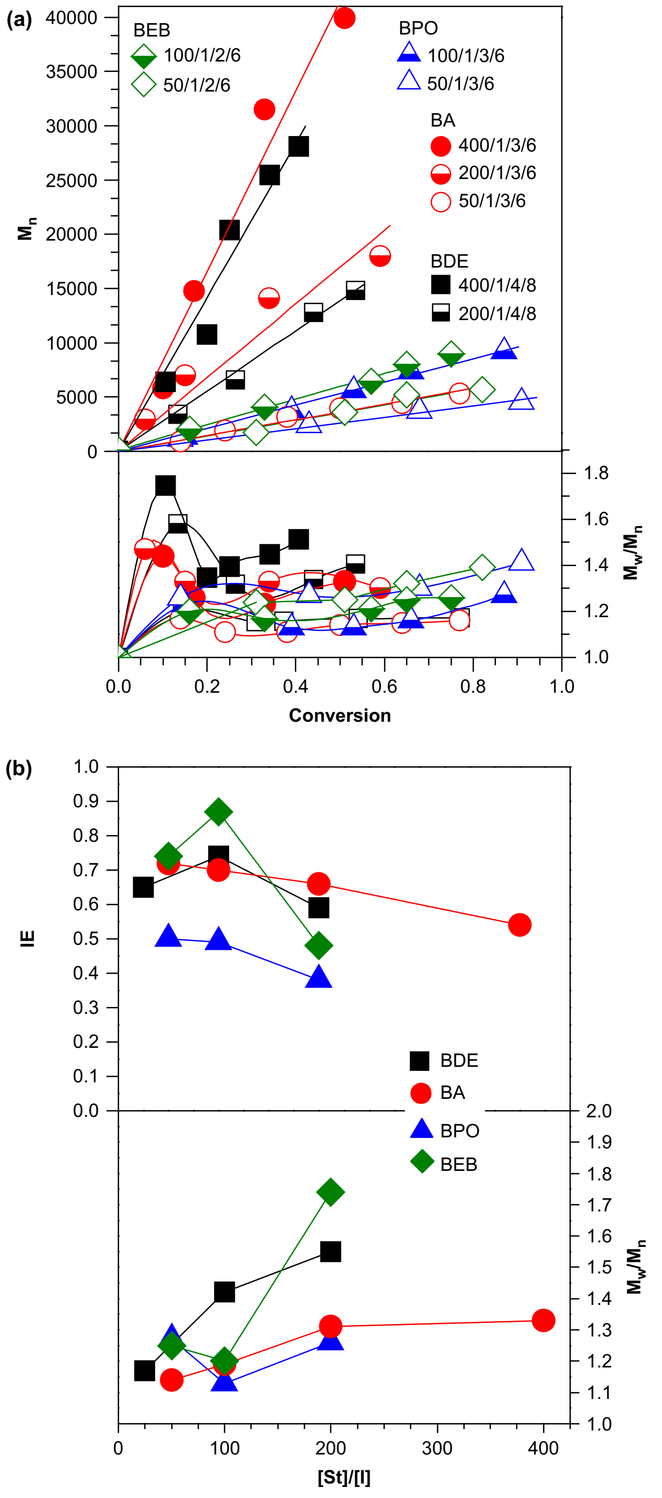


Figure 2. Effect of the [St]/[I] ratio on the Cp_2TiCl-catalyzed styrene LRP initiated from BDE, BA, BEB, and BPO. (a) Selected examples of the dependence of M_n and M_w/M_n on conversion; (b) dependence of IE and M_w/M_n at 50% conversion on [St]/[I]. Dioxane, 90 °C; [St]/[I]/[Cp_2TiCl_2]/[Zn] as indicated in the figure.

2.2. Effect of the degree of polymerization (DP=[St]/[Initiator])

Another requirement for a controlled polymerization process is the ability to manipulate M_n not only from conversion, but also from the monomer to initiator ratio. Thus, having established the required minimum [I]/[Ti]=1/2, the effect of [St]/[I] was further explored and is presented in Figure 2 and Table 2. A linear dependence of M_n on conversion is observed for all initiators over a wide range of ratios ([St]/[I]=50/1–400/1, Fig. 2a). Moreover, as required for a living polymerization, M_n scales directly with [St]/[I] while polymerization rates decrease with increasing M/I due to the reduction in the number of propagating chains.

As seen earlier, both BA and BEB are monofunctional, whereas BPO may initiate up to two polymer chains by thermal decomposition but only one[27] by the more likely redox reaction. While BDE is difunctional, it actually generates a single PSt chain consisting of two PSt chains of half the M_n and containing the BDE fragment in the middle. Thus, a fair comparison of these initiators for the same degree of polymerization e.g. DP=100 per initiator group corresponds to [St]/[BA]=[St]/[BEB]=[St]/[BPO]=100 and [St]/[BDE]=200. This normalization reveals that epoxides and aldehydes are relatively similar in IE (~0.7/group) while both halides (IE^{BEB}=0.9) and peroxides ($IE^{BPO,redox}$~0.5) initiate in an almost quantitative fashion.

At larger [St]/[I] ratios, IE appears to decrease for all initiators, but the effect is less pronounced for BDE and BA. The polydispersity increases with [St]/[I] especially for BDE and BEB. Larger degrees of polymerizations imply lower initiator and catalyst concentration, thus slower rates of initiation, which subsequently increase polydispersity. In addition, the BDE polymerizations were performed with stoichiometric amount of [epoxide group]/Cp_2TiCl=1/2 ratio while BA and BPO benefited from the slight [I]/[Ti]=1/3 excess, which may explain their weaker dependence on DP.

2.3. Effect of the amount of reducing agent: [Cp_2TiCl_2]/[Zn] ratio

The effect of Zn is presented in Figure 3 and Table 3. The polymerizations were carried out using a stoichiometric or slight excess of Ti over the initiating group ([I]/[Cp_2TiCl_2]=1/2 for BDE and BEB; 1/3 for BA and BPO) to ensure that enough Cp_2TiCl is available for polymerization control. It is readily apparent that the amount of Zn has a marked effect on the polymerizations from all initiators. Thus, while a linear dependence of M_n on conversion and linear kinetics, indicative of livingness are observed in all cases, increasing the amount of Zn from stoichiometric, ([Cp_2TiCl_2]/[Zn]=1/0.5) to excess ([Cp_2TiCl_2]/[Zn]=1/3), has a very strong influence on PDI, which decreases rapidly from about 2 to about 1.2–1.3 (Fig. 3b).

The trends in IE are less clear cut. Thus, only for aldehydes a clear and continuous increase in IE is observed (IE^{BA}=0.55–0.9) with increasing [Zn]. For the other initiators, IE appears to follow an

Table 2
Effect of [St]/[Initiator] ratios on Cp_2TiCl-catalyzed styrene LRPs initiated from epoxides, aldehydes, halides, and peroxides[a]

Exp	Initiator (I)	[St]/[I]/[Cp_2TiCl_2]/[Zn]	M_n and M_w/M_n at 50% conversion		IE	k_p^{app} (h^{-1})
1	BDE	50/1/4/8	3900	1.17	0.65	0.432
2	BDE	200/1/4/8	15,000	1.42	0.74	0.275
3	BDE	400/1/4/8	28,100	1.55	0.59	0.116
4	BA	50/1/3/6	3632	1.14	0.72	0.394
5	BA	100/1/3/6	7400	1.19	0.70	0.358
6	BA	200/1/3/6	15,890	1.31	0.66	0.241
7	BA	400/1/3/6	38,420	1.33	0.54	0.206
8	BEB	50/1/2/6	3520	1.25	0.74	0.638
9	BEB	100/1/2/6	5770	1.20	0.87	0.394
10	BEB	200/1/2/6	12,390[b]	1.74[b]	0.48	0.117
11	BPO	50/1/3/6	2370	1.27	0.5	0.647
12	BPO	100/1/3/6	5630	1.13	0.49	0.457
13	BPO	200/1/3/6	15,770	1.26	0.38	0.112

[a] Dioxane, $T=90$ °C. Data from Refs. 25–28.

[b] At 30% conversion.

odd–even dependence with larger values at [Ti]/[Zn]=1 or 3 and lower values at [Ti]/[Zn]=2 or 4. While the reason for this is unclear, all initiators provide however similar average values (IE=0.6–0.7). The overall effect of Zn on the polymerization is complex and can be explained by its involvement in the catalysis of both the initiation and the propagation steps. Accordingly, the trends in IE are derived from the specific interaction of Zn or $ZnCl_2$ with the respective initiators.

Thus, the Lewis acidic $ZnCl_2$ formed in situ after Ti reduction assists the epoxide RRO process[35] and similarly, $ZnCl_2$ may also activate aldehydes. For BPO, a large Zn excess could form benzoyl radicals and, respectively, Zn benzoate, whereas for BEB, excess Zn may insert in the C–Br bond, thus competing with Ti abstraction. Conversely, the improvement in polydispersity may be the result of the organozinc-mediated catalysis of reversible termination step. Thus, Zn transmetalation of the Ti endcapped dormant chains ($\sim P_n$–Cp_2TiCl) regenerates Cp_2TiCl and transient dibenzyl-like organozinc species ($\sim P_{n2}Zn$), which homolyze liberating Zn(0) and the propagating radical, which adds more monomers until trapped again by Cp_2TiCl.[25] In addition, while excess Zn strongly accelerates the rate of the initial Cp_2TiCl_2 reduction, extra Zn and Cp_2TiCl may also contribute to stabilizing the polymerization against traces of oxygen.

2.4. Effect of temperature

The temperature effect was evaluated from 40 to 130 °C using [Cp_2TiCl_2]/[Zn]=1/2 and [I]/[Cp_2TiCl_2]=1/2–1/3 and is shown in Figure 4 and Table 4.

The linear dependence of M_n on conversion and the narrow M_n distributions (Fig. 4) 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, the temperature dependence of IE and PDI is also initiator dependent. Thus, IE decreases dramatically with temperature for I=BDE, BEB, and BA but is rather constant for BPO. This is the result of the increase in the rate of the initiator related side reactions (e.g. BDE deoxygenation, BA pinacol coupling, BEB dimerization). By contrast, for BPO, higher temperatures increase the amount of thermolysis-derived BPO radicals and probably compensate for BPO radicals lost as Ti benzoates. Thus, $IE^{BPO}\sim0.4$–0.5 and appears to be relatively constant.

Conversely, the polydispersity is rather constant with temperature in the 40–110 °C range for BDE and BPO, increases slightly with temperature for BA and much strongly for BEB as a consequence of the shift of the reversible dissociation equilibrium toward the active species, thus resulting in increased termination.

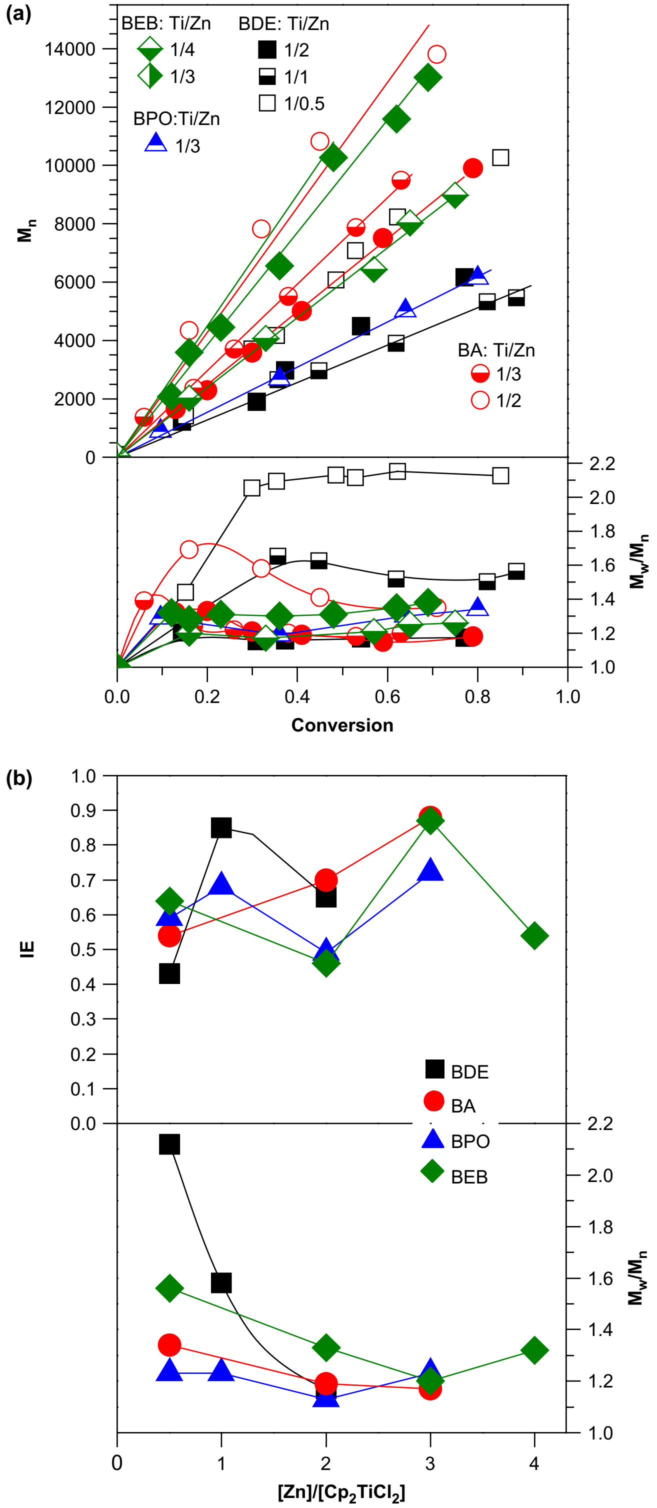


Figure 3. Effect of the [Cp_2TiCl_2]/[Zn] ratio on Cp_2TiCl-catalyzed styrene LRPs initiated from BDE, BA, BEB, and BPO. (a) Selected examples of the dependence of M_n and M_w/M_n on conversion. (b) Dependence of IE and M_w/M_n at 50% conversion on [Cp_2TiCl_2]/[Zn]. [St]/[BEB, BPO or BA]=100/1; [St]/[BDE]=50/1. [BEB]/[Ti]=1/2, [BPO or BA]/[Ti]=1/3, [BDE]/[Ti]=1/4, T=90 °C, dioxane.

3. Conclusions

Cp_2TiCl-activated, radical polymerization initiators such as epoxides, aldehydes, halides, and peroxides were comparatively evaluated by investigating the effect of reagent stoichiometry and temperature on initiator efficiency and polydispersity in the

Table 3
Effect of the [Cp_2TiCl_2]/[Zn] ratio on Cp_2TiCl-catalyzed styrene LRPs initiated from epoxides, aldehydes, halides, and peroxides[a]

Exp	Initiator (I)	[St]/[I]/[Cp_2TiCl_2]/[Zn]	M_n and M_w/M_n at 50%		IE	k_p^{app} (h^{-1})
1	BDE	50/1/4/2	6200	2.12	0.43	0.064
2	BDE	50/1/4/4	3200	1.58	0.85	0.176
3	BDE	50/1/4/8	3900	1.17	0.65	0.432
4	BA	100/1/3/1.5	9692	1.34	0.54	0.139
5	BA	100/1/3/6	7400	1.19	0.70	0.358
6	BA	100/1/3/9	6266	1.17	0.88	0.392
7	BEB	100/1/2/1	7677	1.56	0.64	0.444
8	BEB	100/1/2/4	9781	1.33	0.46	0.156
9	BEB	100/1/2/6	5770	1.20	0.87	0.394
10	BEB	100/1/2/8	10,492	1.32	0.54	0.108
11	BPO	100/1/3/1.5	3570	1.23	0.59	0.333
12	BPO	100/1/3/3	3900	1.23	0.68	0.583
13	BPO	100/1/3/6	5630	1.13	0.49	0.457
14	BPO	100/1/3/9	3400	1.23	0.72	0.623

[a] Dioxane, T=90 °C. Data from Refs. 25–28.

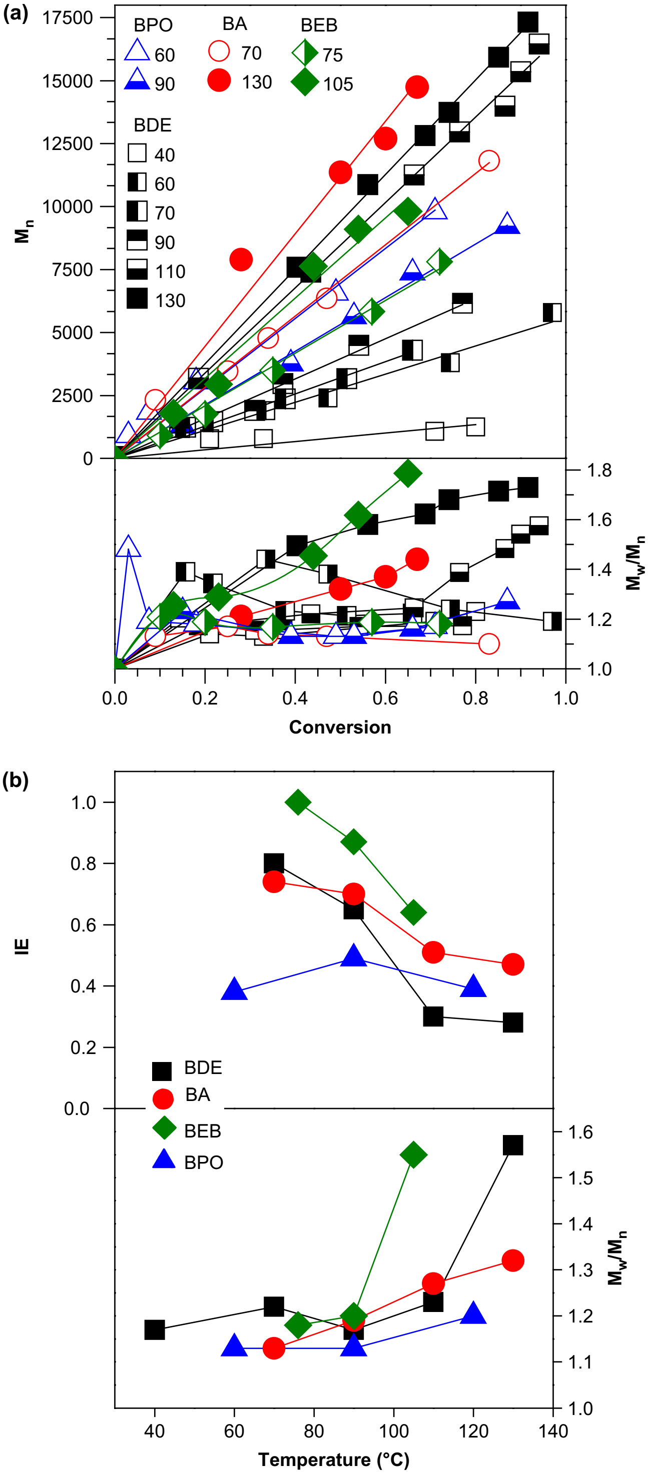


Figure 4. Effect of temperature on the Cp_2TiCl-catalyzed styrene LRPs initiated from BDE, BA, BEB, and BPO. (a) Selected examples of the dependence of M_n and M_w/M_n on conversion. (b) Dependence of IE and M_w/M_n at 50% conversion on temperature. [St]/[BDE]/[Cp_2TiCl_2]/[Zn]=50/1/4/8, [St]/[BEB]/[Cp_2TiCl_2]/[Zn]=100/1/2/6, [St]/[BA or BPO]/[Cp_2TiCl_2]/[Zn]=100/1/3/6, dioxane.

Cp_2TiCl-catalyzed living radical polymerizations of styrene. While living polymerization features such as a linear dependence of molecular weight on conversion and low polydispersity were obtained in most cases over a wide range of conditions, the comparison of the effect of the reaction variables carried out with BDE, BA, BEB, and BPO as model initiators revealed a set of initiator specific similarities and differences.

For all initiators, sub-stoichiometric Ti ([I]/[Cp_2TiCl_2]<1/2) generates uncontrolled polymerizations as not enough catalyst is available for the reversible trapping of the growing chains. Conversely, higher [Cp_2TiCl_2] provides progressively narrower polydispersities (M_w/M_n<1.2). Thus, increasing [I]/[Cp_2TiCl_2] from 1/0.5 to the theoretical minimum of 1/2 increases initiator efficiency from IE∼0.1 to IE∼0.4–0.6 for all initiators. However, while higher [I]/[Cp_2TiCl_2] ratios (1/3, 1/4) continue to increase and eventually plateau $IE^{BA,BEB,BPO}$, they decrease IE^{BDE} to ∼0.2 via epoxide deoxygenation. Thus, the more reactive epoxides are also more sensitive to excess Cp_2TiCl than the other initiators.

M_n scales well with [St]/[I] for all initiators from [St]/[I]=50/1–400/1 and shows a linear dependence on conversion. An optimum degree of polymerization (DP) is about 50–100 where all initiators are the most efficient and almost quantitative (BPO, BEB). Larger DPs however lead to decrease in IE especially for BEB, which drops from IE^{BEB}=∼0.9 to 0.5 whereas for the other initiators the IE decrease by only about 0.2. The polydispersity is relatively constant for BA and BPO (1.2–1.3) but increases up to 1.6–1.8 for BDE and BEB.

A linear dependence of M_n on conversion is also observed upon varying the [Cp_2TiCl_2]/[Zn] ratios from 1/0.5 to 1/3. The IE follows an apparent odd–even dependence on [Cp_2TiCl_2]/[Zn] for BDE, BA, and BPO but increases continuously for BA. Excess Zn is clearly required to provide low polydispersity (<1.2) for all initiators. This results from the faster Cp_2TiCl_2 reduction, Zn and $ZnCl_2$-assisted initiation from BPO and BEB and, respectively, BDE and BA as well as potential Zn catalysis of the reversible termination.

The IE is relatively temperature independent of BPO (IE^{BPO}∼0.4–0.5) but decreases continuously with temperature for BDE (∼0.75 to ∼0.3), BA (∼0.75 to ∼0.5), and BEB (∼0.9 to ∼0.6) in the 60–130 °C range. Similarly, PDI is relatively low (∼1.2) up to ∼100 to 110 °C for all initiators but as a consequence of initiator specific side reactions and increased irreversible chain termination increases strongly at higher temperatures (110–130 °C) for BDE and especially BEB.

It is thus apparent that while the polymerizations are sensitive to the initiator structure, larger initiator efficiencies and narrower polydispersity (M_w/M_n∼1.2) are obtained when using excess Cp_2TiCl over the initiator and of Zn over Cp_2TiCl_2 and with decreasing temperature. Therefore, optimum conditions, which minimize PDI and maximize IE are [St]/[I]/[Cp_2TiCl_2]/[Zn]=(50–200)/1/(2–3)/(4–6) at 70–90 °C. However, they are also initiator dependent. Generally, peroxides are good initiators, but do not typically provide functional chain ends. Halides appear to be the most sensitive to the variation in the reaction parameters and their optimum conditions are in a narrower interval. Finally, both

Table 4
Effect of temperature on Cp_2TiCl-catalyzed styrene LRPs initiated from epoxides, aldehydes, halides, and peroxides[a]

Exp	Initiator (I)	$[St]/[BA]/[Cp_2TiCl_2]/[Zn]$	Temp (°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	BDE	50/1/4/8	70	3200	1.22	0.80	0.128
3	BDE	50/1/4/8	90	3900	1.17	0.65	0.432
4	BDE	50/1/4/8	110	8200	1.23	0.30	0.770
5	BDE	50/1/4/8	130	9200	1.57	0.28	0.819
6	BA	100/1/3/6	70	7079	1.13	0.74	0.094
7	BA	100/1/3/6	90	7400	1.19	0.70	0.358
8	BA	100/1/3/6	110	10,304	1.27	0.51	0.987
9	BA	100/1/3/6	130	11,166	1.32	0.47	1.313
10	BEB	100/1/2/6	60	3986	1.19	1.31	0.151
11	BEB	100/1/2/6	75	5104	1.18	1.00	0.158
12	BEB	100/1/2/6	90	5770	1.20	0.87	0.394
13	BEB	100/1/2/6	105	8496	1.55	0.64	0.526
14	BPO	100/1/3/6	60	6560	1.13	0.38	0.161
15	BPO	100/1/3/6	90	5630	1.13	0.49	0.457
16	BPO	100/1/3/6	120	6700	1.20	0.39	0.688

[a] Dioxane. Data from Refs. 25–28.

epoxides and aldehydes remain synthetically the most useful. Thus, epoxides may provide faster initiation and are more readily accessible on polymer backbones for the Ti-catalyzed synthesis of block and graft copolymers. However, aldehydes not only also allow access to the same PSt–OH functional chain ends but also seem to be the least affected by the reaction conditions and thus the most robust initiator in the series.

4. Experimental section

4.1. Materials

Cp_2TiCl_2 (97% Acros) was recrystallized from CH_2Cl_2. Zn (nanosize powder, 99%+), 1,4-butanediol diglycidyl ether (BDE, 95%), benzaldehyde (BA, 99.5%), and (1-bromoethyl)benzene (BEB, 97%) (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 solution. Styrene (St, 99%+, Fluka) was dried over CaH_2, filtered, and passed through an acidic Al_2O_3 column.

4.2. Techniques

^1H 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.

4.3. Polymerizations

Cp_2TiCl_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 less than 5 min and was accompanied by the characteristic lime-green color of Cp_2TiCl. 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.

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