Cp_2TiCl-Catalyzed SET Reduction of Aldehydes: A New Initiating Protocol for Living Radical Polymerization

Alexandru D. Asandei* and Yanhui Chen

Institute of Materials Science, Polymer Program and Department of Chemistry, University of Connecticut, 97 North Eagleville Rd., Storrs, Connecticut 06269-3136

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ABSTRACT: The Cp_2TiCl-catalyzed SET reduction of aliphatic, α,β-conjugated, and aromatic aldehydes generates reactive α-titanoxy radicals which add readily to styrene and initiate a radical polymerization. The linear dependence of molecular weight on conversion in conjunction with the relatively narrow molecular weight distributions and linear kinetics support the living character of the process which is mediated by the reversible termination of the growing chains with Cp_2TiCl. Investigations of the reaction variables reveal a living polymerization in all cases, but with progressively narrower molecular weight distributions ($M_w/M_n \sim 1.2$) and larger initiator efficiencies (0.7−0.9) with increasing the Cp_2TiCl_2/aldehyde, aldehyde/styrene, and Zn/Cp_2TiCl_2 ratios at 70−90 °C for a wide variety of aldehyde structures. Aldehydes are thus introduced as a new class of initiators for living radical polymerizations and may also provide novel avenues for the synthesis of block and graft copolymers.

Introduction

Over the past decade, living radical polymerization (LRP) has undergone remarkable progress and has become one of the most efficient and robust synthetic methods in modern polymer chemistry.[1] The precise synthesis of complex macromolecular structures has greatly benefited from the ability of LRP to control molecular weight and polydispersity. Accordingly, the extensive applications of LRP have incited 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. ATRP is catalyzed by late transition metal (Cu, Ru, Ni, Fe, Mo, etc.)[1,3,4] halides in conjunction with ligands and additives. The DC mechanism is mediated by organic (nitroxides)[5] or organometallic (Co, Mo)[6] persistent radicals, while DT employs sulfur-based reversible addition−fragmentation transfer (RAFT)[7] agents as well as iodine,[8] Te,[9a] and Sb[9b] derivatives.

Currently, in addition to applications in α-olefin coordination polymerizations[10] and organometallic reactions,[11] there is increased interest in the radical organic chemistry of early transition metals.[12] One of the most successful examples, the paramagnetic $Cp_2Ti(III)Cl$[13] complex, is inexpensively available from the reduction of $Cp_2Ti(IV)Cl_2$ with Zn.[14] The lime-green Cp_2TiCl is a very mild one-electron-transfer agent which catalyzes a variety of radical reactions,[15] including the radical ring-opening (RRO) of epoxides[16] and the single electron transfer (SET)[17] reduction of carbonyls to carbon-centered radicals which subsequently dimerize to the corresponding 1,2-diols (i.e., pinacol coupling).[18] This reaction can occur enantioselectively[19] even under aqueous conditions[20] and proceeds readily with aromatic, α,β-unsaturated, and aliphatic aldehydes.[18−22]

We have recently extended the use of Cp_2TiCl to polymer chemistry and demonstrated the first examples of an early transition metal catalyzed organometallic[6c] living radical polymerization of styrene initiated by epoxide RRO[23a] or by peroxides.[23b] The effects of ligands,[23c−e] reducing agents,[23f] solvents and additives[23g] as well as reagent ratios and temperature were 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_2TiCl_2) was also the least expensive one.[23h] Furthermore, Ti alkoxides generated in situ by epoxide RRO catalyze the living ring-opening polymerization of cyclic esters.[23i]

Typical LRP initiators are based either on redox systems involving late transition metal complexes and activated alkyl halides or on thermal initiators.[1] Hence, a wider assortment of initiator functionalities and the availability of multifunctional catalysts would greatly augment the synthetic ability of macromolecular chemistry. Aldehydes are known to initiate the cationic polymerization of vinyl ethers[24a] and the aldol group transfer polymerization of silyl vinyl ethers.[24b] While ketyl radicals derived from ketone reductions with SmI_2[25a] and Bu_3SnH[25b] or constitutionally isomeric acyl radicals obtained by H abstraction from aldehydes[26] add to double bonds, no applications in radical polymerizations were ever reported. Moreover, aldehydes are typically used as chain transfer agents.[27] Conversely, the Ce,[28a] Cu,[28b] or Mn[28b] catalyzed oxidation of β-CH_2 groups of ketones, the aldehyde H-transfer to acrylates,[29] or the photolysis and sensitizing effect[27a,30] of aromatic ketones can be employed in initiating radical polymerizations. Polymers derived from pinacol radical polycondensations are also available.[31] As aldehydes generate ketyl radicals via their Cp_2TiCl-catalyzed SET reduction, it is reasonable to assume that such radicals should add to the double bonds of vinyl monomers. However, this reaction was never applied to the initiation of a radical chain polymerization. We have thus decided to explore the scope and limitations of this novel initiating methodology, and we are describing herein the Cp_2TiCl-catalyzed living radical polymerization of styrene initiated by SET reduction from a series of 15 aromatic, α,β-unsaturated, and aliphatic aldehydes.

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* Corresponding author: Ph 860-486-9062; Fax 860-486-4745; e-mail asandei@ims.uconn.edu.

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Experimental Section

Materials. Benzaldehyde (BA, 99.5%), 3,4,5-trimethoxybenzaldehyde (TMBA, 98%), 4-benzyloxybenzaldehyde (4-BBA, 95%), 4-hydroxybenzaldehyde (4-HBA, 96%), terephthaldicaboxaldehyde (TDCA, 99%), 2-nitrobenzaldehyde (2-NBA, 98%), 4-nitrobenzaldehyde (4-NBA, 98%), and 5-norbornene-2-carboxaldehdye (5-NCA, 95%) (all from Aldrich), 4-chlorobenzaldehyde (4-CBA, 98.5%) and 2-methoxybenzaldehyde (2-MBA, 98%) (Janssen Chimica), 2-thiophenecarboxaldehyde (TCA, 98%) and α-methylcinnamaldehyde (MCA, 98%), (Acros), *n*-butyraldehyde (BTA, 98%) and citral (CT, 98%) (Chem Service), Zn (nanosize activated powder >99%, Aldrich), and 2-methyl-3-(2-furyl) propenal (MFP, Avocado Research, 97%) were all used as received. Bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2, Acros, 97%) was recrystallized from methylene chloride. Styrene (Aldrich, 99+%) was dried over calcium hydride overnight and passed through a basic Al_2O_3 chromatographic column. 1,4-Dioxane (Fisher, 99.7%) was distilled over Na/benzophenone.

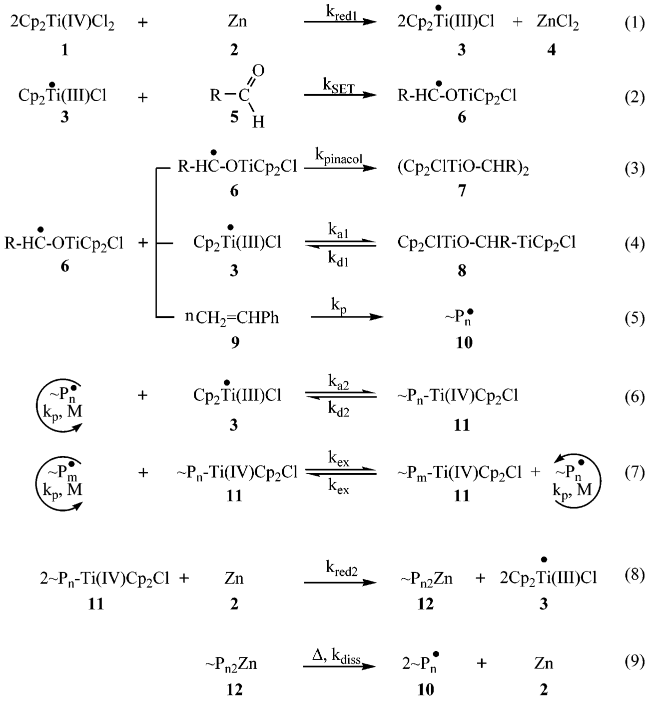
Techniques. ^{1}H NMR (500 MHz) spectra were recorded on a Bruker DRX-500 at 24 °C in $CDCl_3$ (Aldrich; 1% v/v tetramethylsilane (TMS) as internal standard). FTIR spectra (KBr) were recorded FT-IR using a Nicolet Magna-IR 560. GPC analyses were performed at 34 °C on a Waters 150-C Plus gel permeation 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 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.

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 10 min and was accompanied by the characteristic lime-green color of $Cp_2Ti(III)Cl$. The tube was then cooled to −78 °C in an acetone/dry ice bath. Styrene (1 mL, 8.7 mmol) and benzaldehyde (8.9 μL, 0.087 mmol) were injected through the sidearm, and the mixture was redegassed by several freeze−pump−thaw cycles and was heated at 90 °C in an oil bath. Samples were taken under Ar using an airtight syringe and were used for conversion and M_n determination by NMR and respectively by GPC.

Results and Discussion

The proposed polymerization mechanism is outlined in Scheme 1. Zn reduction of $Cp_2Ti(IV)Cl_2$ to $Cp_2Ti(III)Cl$ 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 excess aldehyde (e.g. benzaldehyde, BA) into a green Cp_2TiCl solution leads to the fast appearance of the yellow-orange color of the Ti(IV) alkoxide ($Cp_2TiClOR$), indicating the occurrence of carbonyl reduction (eq 2). Similarly to epoxides,[32] aldehydes may also be activated toward reduction by $ZnCl_2$. In the absence of a substrate for addition, and without excess Cp_2TiCl over aldehyde, conventional pinacol coupling occurs (eq 3).[21] However, excess Cp_2TiCl may reversibly trap the aldehyde-derived radical and suppress the pinacol coupling via the persistent radical effect[2] (eq 4). In the presence of an unsaturated substrate, the nucleophilic α-titanoxyketyl radical adds to the double bond, thus initiating the polymerization (eq 5) which is mediated in a living fashion by the reversible end-capping of the propagating radical with a second equivalent of Cp_2TiCl.[23] The reversible homolysis of the C−Ti bond occurs via a combination of the DC and DT mechanisms (eqs 6 and 7). The possible involvement of Zn in the catalysis of the reversible termination is outlined (vide infra) in eqs 8 and 9.[23g] The structures of the aldehydes investigated are presented in Chart 1 and include substituted aromatic, conjugated, α,*β*-unsaturated, and linear aliphatic substrates.

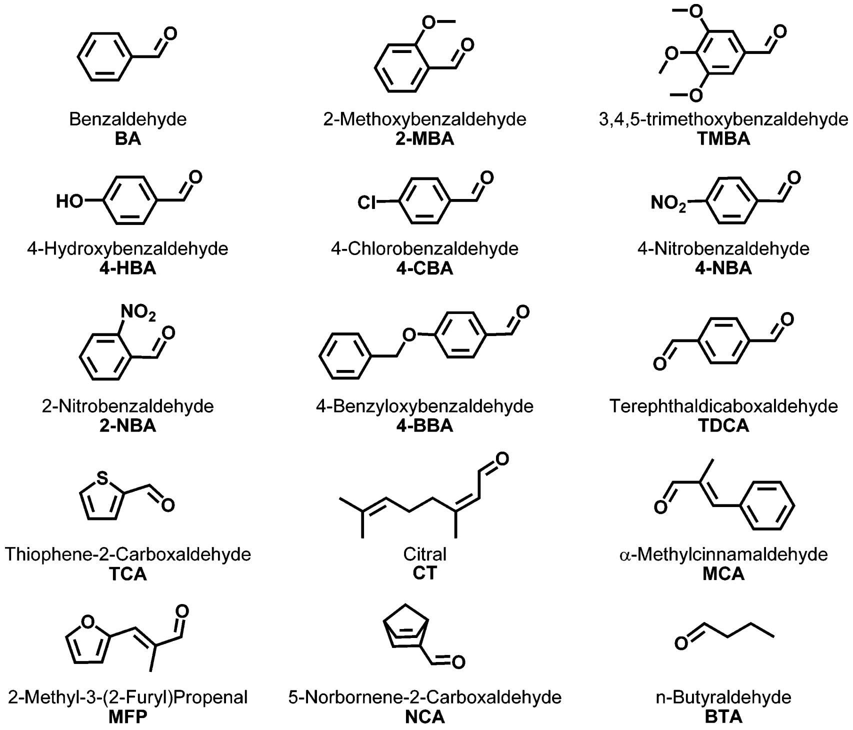
Scheme 1. Mechanism of the Cp_2TiCl-Catalyzed LRP of Styrene Initiated from Aldehydes



The NMR spectrum of a PSt sample initiated from 3,4,5-trimethoxybenzaldehyde (TMBA) is shown in Figure 1. This aldehyde was selected since it provides NMR signals which do not overlap with polystyrene resonances. The presence of the TMBA fragment on the PSt chain end is supported by the strong methoxy resonances ($(CH_3O)_3Ph-$, $\delta = 3.4-3.8$ ppm). Their integration vs the main chain affords a reasonable correlation of the molecular weight obtained by NMR and GPC ($M_n^{NMR} = 3890$ g/mol, $M_n^{GPC} = 3660$ g/mol). As expected, the distinctive ∼C*H*O aldehyde peak ($\delta = 9.87$ ppm) is absent. Benzyl alcohol ($(CH_3O)_3Ph-CH(OH)\sim$) resonances can also be observed at $\delta = 4.2-4.4$ ppm. However, during workup, some of the benzyloxy Ti derivative eliminates $Cp_2TiClOH$.[33] The dehydration is driven by the formation of an unsaturation conjugated with the initiator phenyl ring ($(CH_3O)_3Ph-CH{=}CH-CHPh\sim$) and is partially visible at $\delta = 5.8-6.2$ ppm. FTIR investigations (Figure S1 in Supporting Information) are consistent with the NMR results and support the aldehyde initiation as well. Thus, the characteristic carbonyl signal at 1682 cm^{-1} is absent from the TMBA-initiated PSt, indicating complete aldehyde consumption, while typical aryl alkyl ether resonances at 1258−1235 and 1131−1024 cm^{-1} (asymmetrical and symmetrical C−O−C stretching)[34] as well as a broad OH peak (3600−3300 cm^{-1}) confirm the presence of the initiator fragment on the chain end.

The effect of temperature and of the aldehyde/Cp_2TiCl_2, Cp_2TiCl_2/Zn, and St/aldehyde ratios was subsequently investigated using benzaldehyde (BA) as a model initiator and is outlined in Tables 1 and 2 and in Figures 2−7. The effect of the aldehyde/Cp_2TiCl_2 ratio is presented in Figure 2 and Table 1, experiments 1−4. According to the proposed mechanism (vide supra), one Cp_2TiCl equivalent is required for the carbonyl reduction, while a second Cp_2TiCl equivalent mediates the reversible termination of the growing chains. Indeed, while using

Chart 1. Structures of the Aldehyde Initiators



a slight excess of Zn over Cp$_2$TiCl$_2$ (Ti/Zn = 1/2), even a BA/Cp$_2$TiCl$_2$ = 1/1 ratio already provides a linear dependence of molecular weight on conversion. However, the initiator efficiency (IE) is very low (IE = 0.08), and the molecular weight distribution is broad. Increasing the amount of catalyst from BA/Cp$_2$TiCl$_2$ = 1/2 to BA/Cp$_2$TiCl$_2$ = 1/3 and 1/4 allows for a continuous increase in the initiator efficiency (IE ~ 0.7) and a satisfactory decrease of polydispersity (M_w/M_n ~ 1.15), while linear kinetics are observed in all cases. The decrease in M_w/M_n is the result of the increase in the rate of initiation, while the increase in IE follows the suppression of pinacol coupling with increasing the persistent radical concentration.[2] This is also

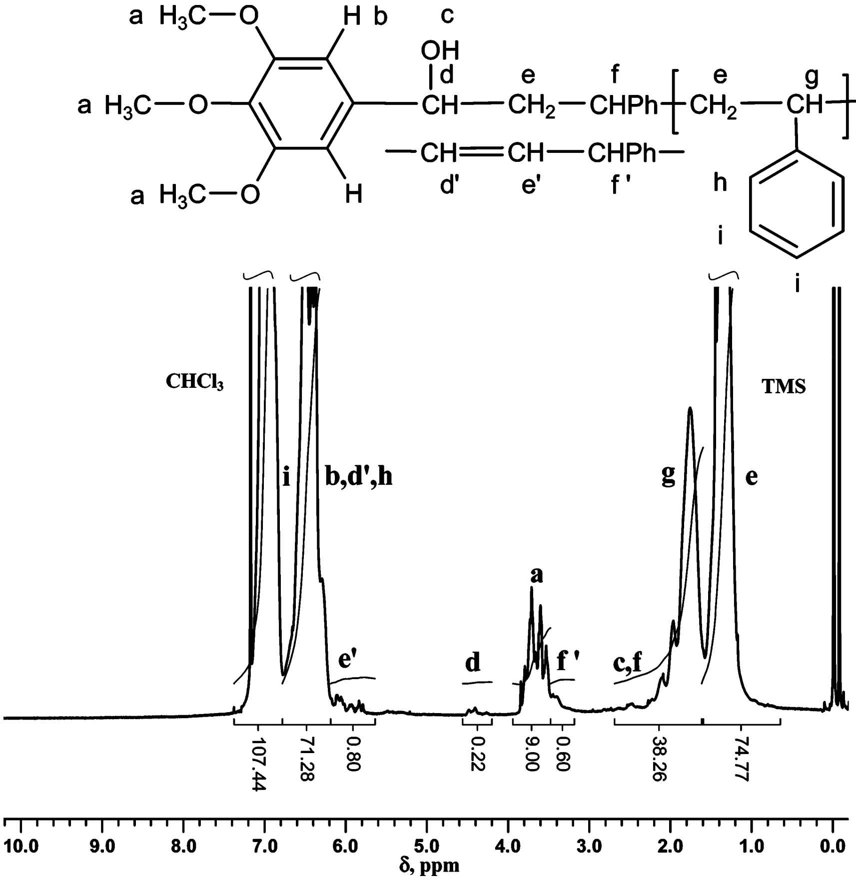


Figure 1. 500 MHz ^{1}H NMR spectrum of polystyrene initiated from 3,4,5-trimethoxybenzaldehyde.

Table 1. Cp_2TiCl-Catalyzed Styrene Polymerizations Initiated from Benzaldehyde

expt	[St]/[BA]/[Ti]/[Zn]	temp (°C)	M_n (g/mol)[a]	M_w/M_n[a]	k_p^{app} (h^{-1})	IE
1	100/1/1/2	90	68357	1.72	0.079	0.08
2	100/1/2/4	90	14662	1.35	0.238	0.36
3	100/1/3/6	90	7400	1.19	0.358	0.70
4	100/1/4/8	90	7180	1.11	0.223	0.73
5	100/1/3/1.5	90	9692	1.34	0.139	0.54
6	100/1/3/9	90	6266	1.17	0.392	0.88
7	50/1/3/6	90	3632	1.14	0.394	0.72
8	200/1/3/6	90	15890	1.31	0.241	0.66
9	400/1/3/6	90	38420	1.33	0.206	0.54
10	100/1/3/6	70	7079	1.13	0.094	0.74
11	100/1/3/6	110	10304	1.27	0.987	0.51
12	100/1/3/6	130	11 166	1.32	1.313	0.47

[a] At 50% conversion.

Table 2. Cp_2TiCl-Catalyzed Polymerization of Styrene Initiated from Aldehydes[a]

no.	aldehydes	M_n (g/mol)[b]	M_w/M_n[b]	k_p^{app} (h^{-1})	IE
1	NCA	9366	1.17	0.198	0.56
2	BTA	5891	1.25	0.241	0.88
3	CT	5592	1.16	0.326	0.90
4	MCA	6465	1.13	0.334	0.91
5	MFP	5313	1.35	0.299	0.95
6	4-HBA	7740	1.38	0.091	
7	4-NBA	15049	1.43	0.223	
8	2-NBA	7455	1.44	0.174	
9	TDCA	6135	1.16	0.379	0.85
10	TCA	7025	1.10	0.191	0.75
11	4-CBA	5725	1.12	0.423	0.88
12	4-BBA	5475	1.22	0.365	0.95
13	2-MBA	5122	1.13	0.443	0.98
14	TMBA	5158	1.16	0.444	0.98
15	BA	7180	1.11	0.223	0.73

[a] [Sty]/[Ald]/[Ti]/[Zn] = 100/1/4/8, $T = 90$ °C. [b] At 50% conversion.

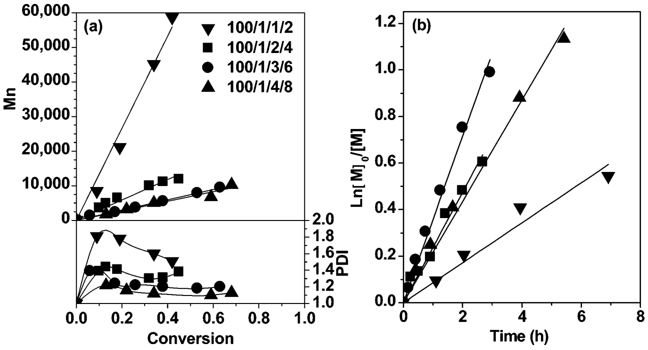


Figure 2. Effect of the BA/TiCp$_2$Cl ratio in the Cp_2TiCl-catalyzed styrene polymerization initiated from BA: (a) dependence of M_n and M_w/M_n on conversion; (b) first-order kinetics. [St]/[BA]/[Cp_2TiCl_2]/[Zn] = 100/1/1/2 (▼), 100/1/2/4 (■), 100/1/3/6 (●), and 100/1/4/8 (▲); $T = 90$ °C.

consistent with the beneficial effect of the slight excess of Cp_2TiCl over the initiator, which we have observed for epoxides.[23] However, while a large excess of Cp_2TiCl may also lead to epoxide deoxygenation[35] and lower IE, this reaction is not possible for aldehydes, and thus initiator efficiency increases with Cp_2TiCl concentration.

The effect of the Ti/Zn ratio is presented in Figure 3 and Table 1, experiments 3, 5, and 6, using a BA/Cp_2TiCl = 1/3 ratio. A stoichiometric Cp_2TiCl_2/Zn = 3/1.5 ratio already provides a linear dependence of M_n on conversion, but the IE is only 0.5 and the polydispersity is ~1.4. However, upon increasing the amount of Zn to Cp_2TiCl_2/Zn = 3/6 and 3/9, the IE increases to 0.7−0.8 while the polydispersity decreases to below 1.2. While these trends reflect the heterogeneous nature of the metal, they also indicate that Zn is a vital ingredient for the realization of low polydispersity and polymerization livingness. We thus speculate that Zn is involved in the catalysis of the reversible termination step.[23g,36] This could most likely be achieved (Scheme 1, eqs 8 and 9) by Zn transmetalation of the Ti end-capped dormant chains (~P_n−Cp_2TiCl) to regenerate $Cp_2Ti(III)Cl$ and form a transient dibenzyl-like organozinc species, ~$P_{n2}Zn$. Subsequent homolysis of ~$P_{n2}Zn$ regenerates Zn(0) and liberates the propagating radical which adds more monomer units until it is trapped again by $Cp_2Ti(III)Cl$. Therefore, both Cp_2TiCl and Zn are involved in the reversible termination catalytic cycle. The effect of the styrene/aldehyde ratio is presented in Figure 4 and Table 1, experiments 3 and 7−9. A linear dependence of M_n on conversion and a reasonable scaling of M_n with DP_{th} = [St]/[BA] is observed over a wide range of ratios, from St/BA = 50 to St/BA = 400. Lower polydispersity and higher IE values ($M_w/M_n \sim 1.2$, IE ~ 0.7) are obtained at lower St/BA ratios while larger St/BA ratios are accompanied by slightly higher polydispersity (M_w/M_n = 1.3−1.4) and slightly lower initiator efficiencies (IE = 0.5−0.6).

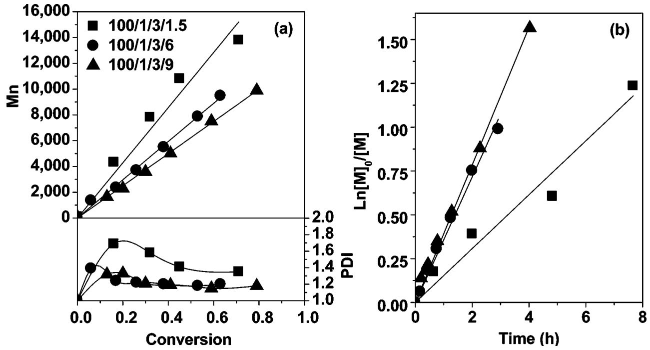


Figure 3. Effect of the Cp_2TiCl_2/Zn ratio in the Cp_2TiCl-catalyzed styrene polymerization initiated from BA: (a) dependence of M_n and M_w/M_n on conversion; (b) first-order kinetics. [St]/[BA]/[Cp_2TiCl_2]/[Zn] = 100/1/3/1.5 (■), 100/1/3/6 (●), and 100/1/3/9 (▲); $T = 90$ °C.

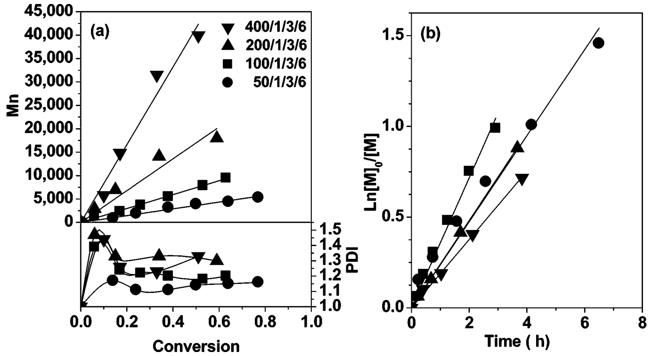


Figure 4. Effect of St/BA ratio in the Cp_2TiCl-catalyzed styrene polymerization initiated from BA: (a) dependence of M_n and M_w/M_n on conversion; (b) first-order kinetics. [St]/[BA]/[Cp_2TiCl_2]/[Zn] = 50/1/3/6 (●), 100/1/3/6 (■), 200/1/3/6 (▲), and 400/1/3/6 (▼); $T = 90$ °C.

The effect of temperature is presented in Figure 5 and Table 1, experiments 3 and 10−12. A linear increase in M_n with conversion occurs at all temperatures in the 70−130 °C range. The IE decreases with increasing temperature from IE ~ 0.7 at 70−90 °C to IE ~ 0.5 at 110−130 °C. The larger polydispersity observed at 110 and 130 °C is the result of the shift the dissociation equilibrium of the C−Ti bond toward the active species.[23] The polymerization kinetics are linear in all cases, and the rate increases with temperature as expected. An optimum

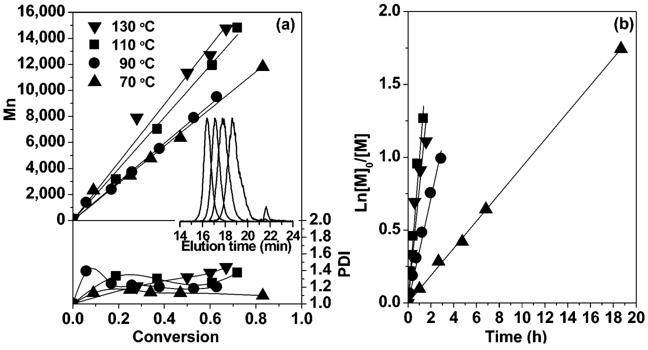


Figure 5. Effect of temperature in the Cp_2TiCl-catalyzed styrene polymerization initiated from BA. $T = 70$ (▲), 90 (●), 110 (■), and 130 °C (▼); $[St]/[BA]/[Cp_2TiCl_2]/[Zn] = 100/1/4/8$. Inset: selected GPC traces of the polymerization carried out at 70 °C.

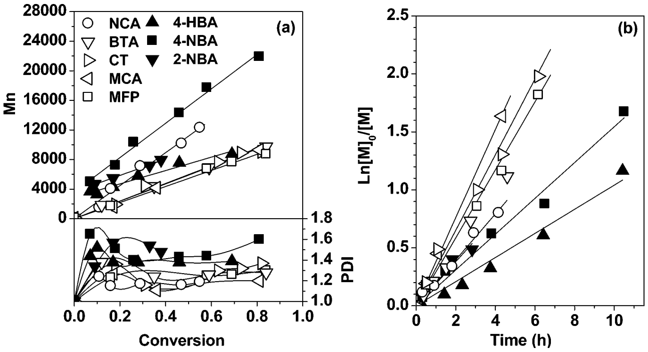


Figure 6. Cp_2TiCl-catalyzed styrene polymerizations initiated from aliphatic, α,β-conjugated, and aromatic aldehydes: (a) dependence of M_n and M_w/M_n on conversion; (b) first-order kinetic plots: NCA (○), BTA (▽), CT (right-pointing △), MCA (left-pointing △), MFP (□), 4-HBA (▲), 4-NBA (■), and 2-NBA (▼). $[St]/[Ald]/[Cp_2TiCl_2]/[Zn] = 100/1/4/8$, $T = 90$ °C.

in terms of IE and PDI is observed at 70−90 °C. An example of GPC traces of the St polymerization initiated from BA at 70 °C is also included in Figure 5 and shows that the peaks are symmetric and move continuously to higher molecular weight. The linear dependence of M_n on conversion, the linear kinetics, and the low polydispersity values in conjunction with the presence of the initiator fragment on the polymer chain end converge to support the living nature of this polymerization as well as the initiation from the aldehyde group.

The dependence of the molecular weight and polydispersity on conversion and the corresponding kinetics of the polymerizations initiated from various aliphatic, α,β-conjugated, and aromatic aldehydes are presented in Figures 6 and 7 and summarized in Table 2. The aldehydes were compared using a $[St]/[Ald]/[Cp_2TiCl_2]/[Zn] = 100/1/4/8$ ratio at 90 °C. With the exception of NCA which may undergo an intramolecular cyclization to decrease the initiator efficiency to about 0.5, all other aliphatic and α,β-conjugated aldehydes such as CT, MCA, and MFP provide a high initiator efficiency (IE ~ 0.9), a linear dependence of molecular weight on conversion, linear kinetics, and polydispersities of about 1.2−1.35 (Figure 6). In the case of substituted benzaldehyde derivatives (Table 2, experiments 6−15, Figures 6 and 7), while a linear dependence of M_n on conversion occurs again in all cases, two distinct behaviors are observed. First, a higher M_n intercept at low conversion ($M_n \sim 4000$ g/mol, Figure 6) and polydispersities of 1.4−1.6 are obtained in the polymerizations initiated from 4-HBA, 4-NBA, and 2-NBA. In these cases, reaction of Cp_2TiCl with either the $-OH$[11] or $-NO_2$[37] groups reduces the amount of available catalyst in the early stages of the polymerization, and thus not all initiating radicals are efficiently trapped by Cp_2TiCl. However, all other substituted benzaldehydes (Figure 7) provide high initiator efficiency (IE = 0.8−0.9) and afford narrow molecular weight distributions ($M_w/M_n \sim 1.2-1.35$).

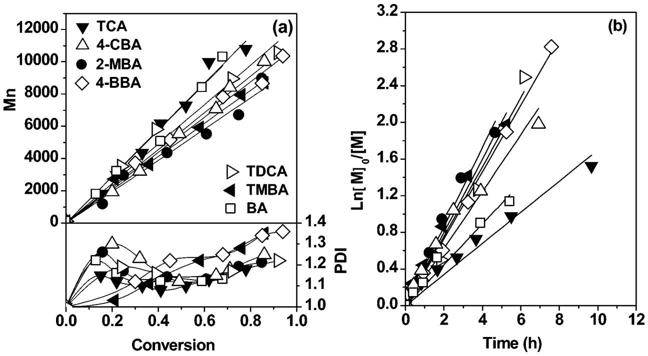


Figure 7. Cp_2TiCl-catalyzed styrene polymerizations initiated from aromatic aldehydes: (a) dependence of M_n and M_w/M_n on conversion; (b) first-order kinetic plots: TDCA (right-pointing △), TCA (▼), 4-CBA (△), 2-MBA (●), 4-BBA (◇), TMBA (left-pointing ▲), and BA (□). $[Sty]/[Ald]/[Cp_2TiCl_2]/[Zn] = 100/1/4/8$, $T = 90$ °C.

Conclusion

The Cp_2TiCl-catalyzed SET reduction of α,β-conjugated or aromatic aldehydes generates allylic or benzylic captodatively[38] stabilized α-titanoxy radicals which add readily to styrene and initiate a radical polymerization. The linear dependence of molecular weight on conversion in conjunction with the relatively narrow molecular weight distributions ($M_w/M_n \sim 1.2$) and linear kinetics support the living character of the process which is mediated by the reversible termination of the growing chains with Cp_2TiCl. The investigation of the effect of the reaction variables carried out with benzaldehyde as initiator reveals a living polymerization in all cases. However, progressively narrower molecular weight distributions ($M_w/M_n \sim 1.2$) and larger initiator efficiencies (IE = 0.7−0.9) are obtained with increasing the Cp_2TiCl_2/aldehyde, aldehyde/styrene, and Zn/Cp_2TiCl_2 ratios and with decreasing temperature. Thus, an optimum is observed for $[St]/[BA]/[Cp_2TiCl_2]/[Zn] = 100/1/4/8$ at 70−90 °C. Qualitatively, based on a combination of initiator efficiency and polydispersity of the resulting polymers, the aldehydes rank as 4-NBA ~ 2-NBA~ 4-HBA ≪ NCA < BA ~ TCA ~ MFP ~ BTA ~ TDCA < CT ~ 4-BBA ~ 4-CBA ~ MCA ≤ TMBA ~ 2-MBA. Thus, aldehydes are introduced as a new class of initiators for living radical polymerizations. Carbonyl groups are ubiquitous in organic chemistry and thus available with a wide variety of structures suitable as polymerization initiators and as sites for graft or block copolymerization. Similarly to our previously reported Cp_2TiCl/epoxide system,[23] aldehydes also provide chain ends which can be utilized in further derivatization and block copolymer synthesis. In addition, as they do not undergo deoxygenation, aldehydes allow for larger initiator efficiencies. Accordingly, the Ti alkoxide generated in situ can be exploited in the catalysis of the ring-opening polymerizations of cyclic esters. Research along these lines is in progress in our laboratory and will be reported soon.

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Supporting Information Available: FTIR spectra of TMBA, PSt, and TMBA-initiated PSt and IR discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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