

TiCp₂Cl-Catalyzed Living Radical Polymerization of Styrene Initiated by Oxirane Radical Ring Opening

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Over the past decade, intense research in the field of living radical polymerization (LRP) has shown that molecular weight (M_n) and polydispersity (M_w/M_n) can be controlled by the reversible termination of the growing chains using persistent radical or degenerative transfer (DT) agents.^{1,2} Mechanistically, LRP occurs by either atom transfer (ATRP), dissociation–combination (DC), or degenerative transfer (DT).^{2,3} Metal-catalyzed LRP is accomplished in ATRP by *late* (Cu, Ni, Fe, Ru)^{2,4,5} transition metal complexes in conjunction with ligands, additives, and activated halides or thermal initiators.⁶ The metal-catalyzed DC mechanism is represented by Co⁷ and Te,⁸ while Mo⁹ mediates both DC and ATRP. The restricted choice of thermal or activated halide initiators may limit chain end functionality and the substrates for grafting LRP. Availability of new functional chain ends via a wider initiator selection and of new catalysts for simultaneous one-pot living polymerizations of dissimilar monomers is highly desirable for the synthesis of complex monodisperse polymeric architectures.

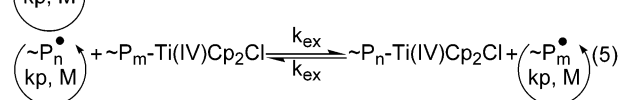
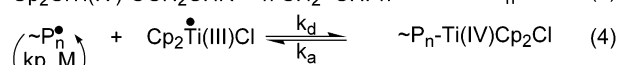
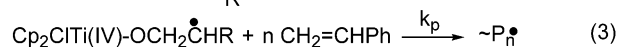
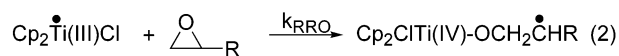
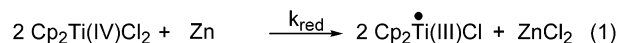
Recently, apart from the well-known applications of Ti and Zr early transition metallocenes in coordination polymerization¹⁰ and organometallic reactions,¹¹ there is increased interest in their *radical* organic chemistry.¹² A soluble paramagnetic Ti(III) complex, TiCp₂Cl,^{13,14} is inexpensively synthesized *in situ* by the reduction of TiCp₂Cl₂ with Zn.¹⁵ The lime-green (TiCp₂Cl)₂ chloride-bridged dimer¹⁶ is indefinitely stable in the absence of O₂ but readily dissociated by polar solvents to catalyze a variety of radical reactions,^{13,17} including epoxide *radical* ring opening (RRO).^{18,19} The epoxide-derived radicals add to double bonds (e.g., epoxylefin cyclization^{20,21} or addition to acrylates).²² Without substrates for addition, the radical is trapped by a second TiCp₂Cl equivalent.²³ Addition of the epoxide radical to a double bond resembles initiation of radical polymerizations. However, these reactions proceeded only with monoadduct formation.¹⁸

We believe that the epoxide RRO could be used as a very useful initiating methodology for radical polymerization. Moreover, paramagnetic Ti(III) complexes, acting as persistent radicals, may reversibly terminate the growing chains, thereby mediating LRP via the DC mechanism.

The proposed polymerization mechanism is illustrated in Scheme 1. The Zn reduction of TiCp₂Cl₂ in dioxane occurs readily at room temperature in less than 10 min, and following the injection of initiator and monomer, the reactions proceed homogeneously. In the absence of radical initiators, TiCp₂Cl alone acts as a radical polymerization inhibitor. Conversely, a Ti polymerization in progress is effectively stopped by the addition of conventional radical inhibitors (chloranil). In the presence of epoxides, 1 equiv of TiCp₂Cl ring-opens the epoxide, which adds to styrene, thereby initiating the polymerization.

We have investigated several mono- and multifunctional epoxides (Chart S1, Supporting Information). Their initiator efficiency (IE) represents the combined yield of RRO and addition to monomer

Scheme 1



and ranged from 0.2 to 0.7 (Table S1, Figure S1, Supporting Information). Depending on the epoxide substitution pattern, RRO occurs as a balance between generation of the more stable/substituted radical and minimization of steric interaction with the incoming Ti catalyst.¹⁹ Thus, by contrast with conventional thermal or alkyl halide initiators, epoxides uniquely generate a pair of reactive primary and secondary constitutionally isomeric C-centered radicals derived from the regioselectivity of RRO (e.g., epoxides based on the glycidyl [$\text{CH}_2\text{—O—CH}$] $\text{—CH}_2\text{—O}$) motif). Consequently, IE represents the average of these two initiators. These radicals may also be involved in side reactions such as coupling or deoxygenation²³ (e.g., styrene oxide) which lower IE. Larger values of IE were observed with monosubstituted, oxygen-rich diepoxides which may favorably chelate Ti (e.g., 1,4-butanediol diglycidyl ether, BDGE). Thus, the dependence of IE on epoxide structure and the relative ranking of epoxides is complex and is a subject of current investigation.

To demonstrate the Ti-catalyzed initiation step, we synthesized a low M_n polystyrene using 2,3-epoxypropyl-*p*-methoxyphenyl ether as initiator. A very good correlation between M_n values determined by GPC and by NMR (Figure S2, Supporting Information; $M_{n,\text{NMR}} = 2730$, $M_{n,\text{GPC}} = 2807$, PDI = 1.11) was observed. In addition, ¹³C NMR confirmed the presence of atactic polystyrene,²⁴ as expected for a radical polymerization.²⁵ Multifunctional epoxides were employed in the synthesis of star polymers. The presence of the initiator was again supported by NMR and IR (Figure S3, Supporting Information).

Examples of the styrene polymerization initiated from BDGE are presented in Figure 1. A linear dependence of M_n on conversion and a continuous decrease of M_w/M_n to values of about 1.1 are observed in conjunction with monomodal and symmetric GPC traces and no loss of chain ends in the corresponding linear kinetics (Figure S4, Supporting Information). Moreover, reinitiation experiments from both mono- and diepoxides (Figure S5, Supporting Information) demonstrated that the polymerization continued from the active chain end. These are typical features of living polymerizations.²⁶ Furthermore, substituted styrenes (4-Cl, 4-ⁱBu, 4-OMe)

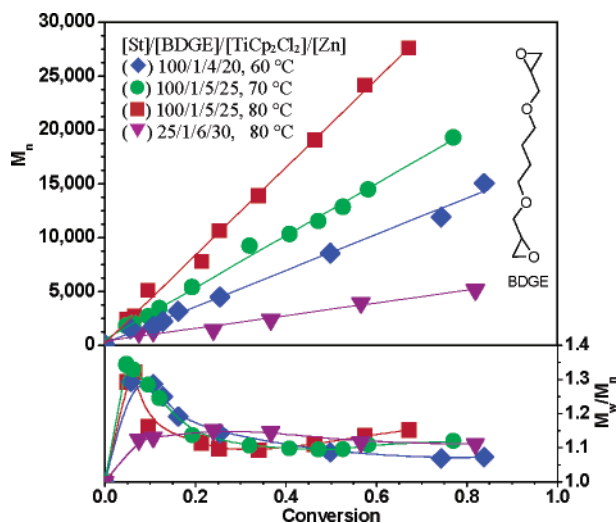


Figure 1. Dependence of M_n and M_w/M_n on conversion in the TiCp_2Cl -catalyzed LRP of styrene initiated by the RRO of BDGE.

were also polymerized and copolymerized (Figures S6 and S7, Supporting Information).

While detailed mechanistic investigations are in progress, we believe that the living radical character is most likely afforded by a combination of the DC and DT mechanisms and not an atom transfer²⁷ process. DC and DT occur via the Zn-assisted²⁸ reversible formation of thermally labile C–Ti bonds between the propagating chain end and a second TiCp_2Cl equivalent. This is consistent with the fact that a 2:1 ratio or slight excess of Ti vs epoxide group is sufficient to control the polymerization and with the relatively low C–Ti bond dissociation energy (BDE) in Ti derivatives reminiscent of the dormant polystyrene chain end ($\text{Cp}_2\text{ClTi}-\text{CH}_2\text{Ph}$, BDE = 30 kcal/mol).²⁹ As such, the polymerization can be carried out at temperatures where thermal initiation of styrene is negligible.³ Thus, while at 130 °C the polymerization is less controlled, decreasing the temperature from 110 to 40 °C leads to continuous improvements in M_w/M_n , linear dependence of M_n on conversion, and higher initiator efficiencies (Table S1). An optimum is observed between 60 and 90 °C.

In summary, we have demonstrated for the first time that the Ti-catalyzed radical ring opening of oxiranes can be successfully used in the initiation of a radical polymerization and, moreover, that the polymerization is mediated by Ti in a living fashion. Thus, we have further expanded the synthetic usefulness of both epoxides and early transition metal complexes as novel classes of initiators and catalysts, respectively, for living radical polymerizations. The advantages of this methodology are based on the multitude and structural diversity of available epoxides which provide convenient access to a variety of other functional chain ends for the synthesis of complex polymer architectures via transformations of the epoxide-generated alcohol group. In addition, this homogeneous catalyst, formed in situ from readily available, inexpensive starting materials, does not require extra ligands, additives, and activators. Furthermore, the epoxide-derived Ti alkoxides act as initiators for ring opening and other polymerizations,³⁰ thus providing an unprecedented, convenient avenue toward intricate block, graft, or star structures via one-pot simultaneous living polymerizations of different classes of monomers by different polymerizations mechanisms. Further fine-tuning of this concept through a judicious

selection of the steric and electronic nature of the Ti complexes and the use of other initiating systems and monomers is currently under investigation.

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Supporting Information Available: Experimental procedures, epoxide structures, characterization table, kinetic and M_n plots, GPC traces, and NMR and IR characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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