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Radically-initiated group transfer polymerization of methacrylates by titanium amino-phenolate complexes

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ABSTRACT: Radical initiation of methyl methacrylate polymerizations mediated by titanium amino-phenolate complexes gave exceptional control without the need for any co-catalyst or activator. The polymerization proceeds not by a classical controlled radical or coordination insertion mechanism but *via* a unique bimetallic group transfer process. Detailed experimental and computational studies support a polymerization mechanism with a titanium(IV)-enolate complex and a second titanium(III) complex that delivers an activated monomer, and provides new insight into both titanium-mediated radical reactions and polymerizations.

Titanium is a biocompatible, abundant, inexpensive metal, and thus is attractive as a catalyst in organic synthesis,¹ building from its long history in polymer chemistry, particularly in the coordination insertion polymerization of alkenes.²⁻⁹ In particular, with two well-defined and accessible oxidation states (III and IV), the use of discrete complexes of titanium in C-C bond formation *via* single electron transfer processes is increasingly popular.¹⁰⁻¹² The use of titanium complexes in controlled radical polymerization (CRP), where functional monomers are polymerized *via* a radical mechanism to predictable molecular weights and narrow dispersities (\mathcal{D}), has received little attention, especially in comparison with other first-row transition metals.¹³⁻¹⁶ While Asandei and others used titanium metallocenes (Scheme 1a)¹⁷⁻²⁶ and non-metallocenes²⁷⁻²⁹ as mediators of radical polymerisations of styrenes and (meth)acrylates,^{18,30-32} these methods had uncertain mechanisms and required expensive, pyrophoric activators (Scheme 1b). Building from our long-standing interest in sustainable, non-toxic mediators of controlled radical polymerizations,³³⁻³⁷ we sought to better design and indeed better understand these systems. We now show that a conventional azo-initiator, in the presence of novel titanium amine-phenolate complexes, can be used not to initiate a radical polymerization but rather to establish an unprecedented Ti(III)/Ti(IV) polymerization mechanism (Scheme 1c). The reaction is facile to conduct and offers

excellent control. Advantageously, a conventional azo initiator is used as activator, yielding a method which is considerably more robust than present titanium-based alternatives.

Amine-phenol ligand precursors were synthesized *via* facile Mannich-type condensation reactions in high yields (Scheme S1). Ligands were selected to explore the effect of both electronic and steric properties, and coordination geometry, on the polymerization. Complexation of the ligand precursors was straightforwardly achieved using one of two methods (Scheme S2) to yield a family of known (**1**, **7**) and novel (**2-6**) titanium(III) amino-phenolate complexes (Figure 1). Full characterization of all complexes, including several molecular structures, is detailed in the Supporting Information.

Scheme 1. Titanium-mediated methods of styrene and methyl methacrylate (MMA) polymerizations.

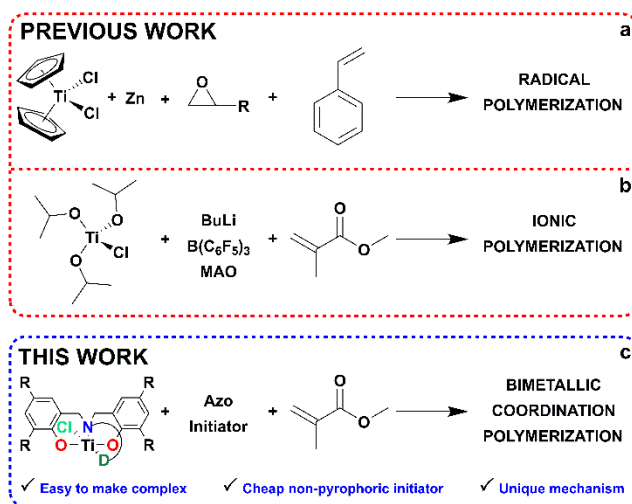
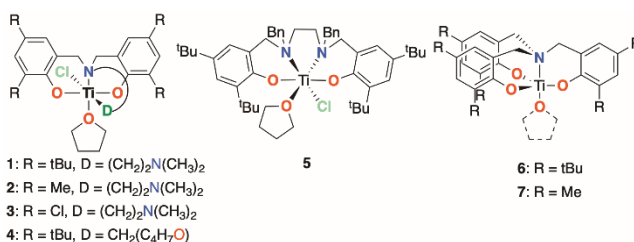


Figure 1. Titanium complexes **1-7**.



All complexes were screened for their efficacy as mediators in the polymerization of styrene and MMA, with titanium(III) amino-bis(phenolate) (ABP) complexes **1-4** the top performers for rapid, controlled polymerization of MMA under the reaction conditions outlined in Scheme 2. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70), which was used as polymerization initiator, is very similar to the ubiquitous AIBN, but permits lower reaction temperatures as the half-life time (at 80 °C) of V-70 is 1.9 mins compared to 73 mins for AIBN. Polymerizations were fast, achieving high conversions with good control over the molecular weight of the polymer (Table S1 and Figure S1). For example, complex **1** reached 88% conversion within 1 hour, with $M_{n,th} = 8800$, $M_n = 37800$ and $\bar{D} = 1.13$. This initially seems to be

a well-controlled radical polymerization. However, it was surprising to observe that the tacticity of the resultant poly(methyl methacrylate) (PMMA) was significantly dependent on the titanium(III) complex used (Table 1). In a typical free-radical polymerization the mm:rm:rr ratio (a measure of the isotactic:heterotactic:syndiotactic character of a polymer) is ca. 3:33:64. PMMA synthesized using both chloro-substituted **3** and methyl-substituted **2** possesses a slight isotactic bias compared to a free-radical polymerization. The bulky *t*-butyl-substituted **1** displayed an even more pronounced isotactic bias. In a typical metal-mediated controlled radical polymerization, one would expect the tacticity of the resultant polymer to be very similar to that of a free-radical polymerization, since monomer addition to a radical chain end occurs away from the metal center and thus is not influenced by the ligand framework. The fact that such a noticeable isotactic bias is present when complexes **1-4** are used as mediators suggested that the initial presumptions about the mechanistic pathway may be wrong, even though a standard radical polymerization protocol had been employed.

Scheme 2. Representative MMA polymerization.

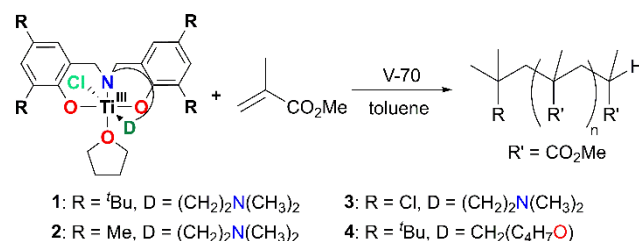


Table 1. Polymerization screening of MMA with complexes **1-4**.

Polym. No.	Complex	PMMA Tacticity
		mm:rm:rr
1^a	-	3:33:64
2^b	1	15:47:38
3^b	2	6:39:55
4^a	3	6:39:55
5^a	4	18:48:34

Conditions: [MMA]:[Ti(III)]:[V-70] = 100:1.0:1.0, MMA:toluene = 1:1 (v/v), 80 °C. ^a1 hour. ^b2.5 hours.

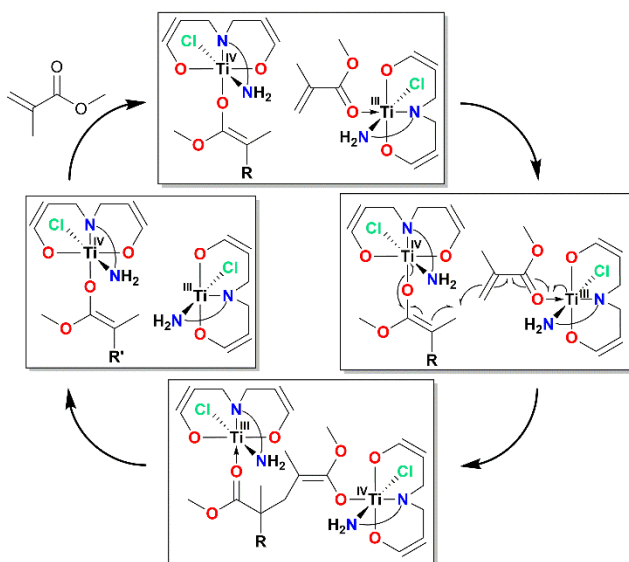
A non-radical pathway was further supported through the addition of a radical scavenger such as dihydroanthracene (DHA, Table S2). In a free-radical MMA polymerization the addition of dihydroanthracene results in a lower monomer conversion, as radical chain ends irreversibly terminate by reacting with the scavenger. However, the use of DHA in a polymerization mediated by **1** showed negligible change in monomer conversion, which suggests that there are no radical chain ends for the scavenger to react with.

A variety of possible mechanisms were explored to better understand how the complexes control the polymerization of MMA. A combination of experimental and computational techniques were used. DFT studies using a simplified amino-phenolate ligand framework (see Supporting Information) strongly suggest that the polymerization mechanism is not ionic, with a ΔG in excess of +31 kcal/mol to form the ion pair. A typical coordination-insertion polymerization, where the monomer coordinates to the titanium *via* the alkene bond, was also found to be unlikely, due to the large steric bulk of the ligand framework preventing the monomer from being sufficiently close to the metal center for coordination to occur in this way.

From the kinetic and computational data, we propose that the polymerization mechanism is bimetallic, and involves both a titanium(IV) and titanium(III) species (Scheme 3). This mechanism has previously been termed group transfer polymerization (GTP), and primarily uses organosilicon mediators.^{38,39} To the best of our knowledge, this mechanism has not previously been observed with titanium. We propose that during the initiation phase of the polymerization, a titanium(IV) enolate species is formed, most likely after a few radical monomer additions and this would explain the imperfect PMMA dispersity. DFT studies (Scheme S3) show that this enolate is considerably more energetically favorable than other titanium(IV) species that could feasibly form, such as Ti-R₀ (R₀ = primary radical of V-70) and Ti-MMA_n-R₀ (with a Ti-C bond) adducts. This suggests that the proposed mechanism is energetically preferred to an organometallic-mediated radical polymerization (OMRP) mechanism, which would require the formation of a stable but homolytically-reversible Ti-C bond. The computational data suggests that this bond strength is insufficient for OMRP.

The polymerization proceeds *via* a reaction between this Ti(IV)-enolate species and a Ti(III)-MMA adduct, with the MMA coordinating *via* the carbonyl. Once in close proximity, the polymer chain and the monomer unit undergo a one-electron Michael-type addition, with the Ti(IV) metal center becoming Ti(III) and *vice versa*. The carbonyl bound to the new Ti(III) metal center then dissociates, allowing the subsequent coordination of a new monomer unit, and completion of the catalytic cycle.

Scheme 3. Proposed bimetallic group transfer polymerization mechanism.

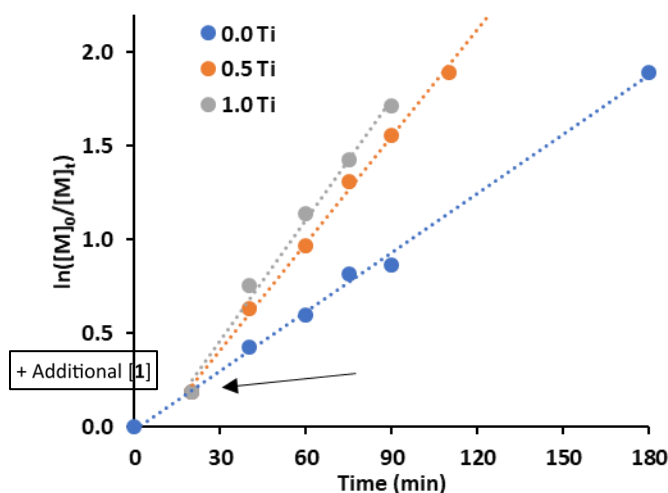


Experimental data also supports a bimetallic GTP mechanism. With the proposed mechanism, one would expect that varying the coordinating nature of the polymerization solvent would have a significant effect on the conversion (Table S3 and Figure S2). With toluene, a non-coordinating solvent, polymerizations were fast and reached high conversions. This rate decreased when using the more-coordinating solvent 1,4-dioxane and decreased further using THF. This is most clearly evidenced with complex **1**, with conversion decreasing from 93% (entry S6) to 12% (entry S12) upon the use of a more-coordinating solvent. This suggests that a vacant coordination site is required on the metal for productive polymerization.

Comparing the kinetics between free-radical and **1**-mediated MMA polymerization further supports this theory (Figure S3). One would expect a controlled radical polymerization to be slower than the free-radical equivalent. However, using **1** as mediator resulted in a faster polymerization than without, which suggests that the mediator both controls and catalyzes the polymerization.

Furthermore, in a typical free radical polymerization one would expect the polymerization rate to increase with increased initiator concentration (as shown in Figure S3). However, the opposite trend is observed when mediated by **1**, with the polymerization rate decreasing as the concentration of the initiator was increased (Figure S4). Molecular weights decreased with increased initiator concentration, which is as expected. These results strongly support the proposed bimetallic mechanism. Increasing the initiator concentration increases the concentration of Ti(IV)-enolate, from which the chains grow. Therefore, the concentration of Ti(IV)-enolate dictates the molecular weight. However, increasing Ti(IV) concentration results in a decreased Ti(III) concentration. As both are required in the bimetallic mechanism, the slow polymerization rate with high V-70 concentration can be attributed to the low Ti(III) concentration.

Figure 2. Addition of extra **1** during MMA polymerization.



Conditions: [MMA]:[**1**]:[V-70] = 100:1.00:2.00, MMA:toluene = 1:1 (v/v), 80 °C, 20 min. Subsequently, add x eqv. **1** and continue heating.

If the concentration of Ti(IV)-enolate controls the molecular weight and the relative concentration of Ti(IV) to Ti(III) controls the polymerization rate, it would be expected that adding additional Ti(III) complex **1** midway through the polymerization would result in a faster rate with no new chains being formed. This is clearly observed in Figure 2 (and Figure S5), where different concentrations of **1** were added after

20 minutes. The polymerization rate was faster with higher concentrations of added **1**, whilst no new chains were formed. This is further strong evidence for the proposed bimetallic polymerization mechanism.

DFT calculations were performed to understand this bimetallic mechanism in greater detail, and to determine whether the proposed mechanism is theoretically feasible. It is energetically favorable to form both the Ti(IV)-enolate (Scheme S4, $\Delta G = -34.46$ kcal/mol) and the Ti(III)-MMA adduct (Scheme S4, $\Delta G = -16.48$ kcal/mol). There is a very small energy barrier to overcome to bring the two species into close proximity, and subsequently an accessible transition state for the chain propagation step with a ΔG^\ddagger of +21.86 kcal/mol. The overall reaction has a ΔG of -5.19 kcal/mol, which is as expected for a typical polymerization.

DFT additionally supports a monometallic GTP mechanism (Scheme S5), also starting from a Ti(IV)-enolate, with the necessary vacant coordination site for monomer activation arising from dissociation of the pendant amine donor arm on the ligand framework. However, the chain propagation transition state of this pathway yields a ΔG^\ddagger of +24.61 kcal/mol, which is significantly higher than for the bimetallic pathway. This suggests that the bimetallic mechanism is preferred.

The presence of both mechanisms has been proved experimentally (Figure S6). Whilst attempts to isolate and characterize a Ti(IV)-enolate analogue of **1** were unsuccessful, it was possible to generate *in situ* a macroinitiator comprising approximately 30 monomer units. In the presence of this macroinitiator and excess monomer, but the absence of **1**, chains grew slowly. This slow polymerization illustrates the presence of the monometallic mechanism, as there is no Ti(III) present. Upon addition of **1**, the polymerization rate increased by an approximate factor of nine, demonstrating that the bimetallic pathway is significantly more favored.

Complexes **5-7** (Scheme S2) have a substantially more rigid and bulky ligand framework than complexes **1-4**, in which the flexible nitrogen donor arm is replaced by either a bulkier amine donor (**5**) or a further phenolate donor (**6** and **7**). It is expected that these complexes would be incompatible with the proposed mechanisms, since the rigid and bulky ligand framework would make the processes of formation of the Ti(IV)-enolate and dissociation of a donor arm energetically unfavorable. As a result, polymerization would proceed *via* an uncontrolled mechanism. This is consistent with the polymerization results (Table S1), where dispersities were considerably larger for complexes **5-7** than for complexes **1-4**.

We can conclude that for effective polymerization control, there are some constraints over the ligand framework. A strongly donating or overly bulky framework prohibits the proposed group transfer mechanism, with ligand flexibility promoting formation of the required Ti(IV) species. On the other hand, steric bulk on the phenolate has the positive effect of increasing isotactic bias in the resultant PMMA. This tunability allows for the precise synthesis of PMMA with control over both molecular weight and tacticity.

Complexes **1** and **2** were also used as mediators in the polymerization of other methacrylates (Table S4). Control over the polymerization of *n*-butyl methacrylate (ⁿBuMA) was highly dependent on the ligand framework of the metal. Use of **1** as mediator led to a well-controlled polymerization (Figure S7) with a narrow dispersity ($\mathcal{D} = 1.14$). However, use of **2** as mediator led to a poorly-controlled polymerization with a much broader dispersity ($\mathcal{D} = 2.12$). No polymer was produced during the attempted polymerization of *t*-butyl methacrylate (^tBuMA) using either **1** or **2**. It is believed that the need for an additional two *t*-butyl-containing molecules to interact with the metal center is too energetically unfavorable for polymerization.

In this contribution, we have demonstrated the exceptional control that titanium(III) amino-phenolate complexes have over the polymerization of MMA. Furthermore, the polymerization can be activated using a conventional azo initiator instead of typical expensive and pyrophoric alternatives. The polymerization is suggested to proceed *via* a unique group transfer mechanism, with a primary bimetallic and secondary monometallic mode of operation. The presence of both mechanistic pathways has been demonstrated experimentally and computationally.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Detailed experimental synthetic procedures, characterization data, polymerization and kinetic data, mechanistic schemes and computational data. (PDF)

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Notes

The authors declare no competing financial interests.

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