

Atom Transfer Radical Polymerization with Ti(III) Halides and Alkoxides

Yuri A. Kabachii, Sergei Y. Kochev, Lyudmila M. Bronstein¹(✉), Inna B. Blagodatskikh, Peter M. Valetsky

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow 117813, Russia

E-mail: kabachi@ineos.ac.ru

¹Present address: Indiana University, Chemistry Department, Bloomington, IN 47405

E-mail: lybrunst@indiana.edu

Received: 2 January 2003 / Accepted: 28 March 2003

Summary

Ti(III) compounds (halides and *n*-butoxide) along with several mono-, bi-, and tridentate ligands have been studied for the first time in the atom transfer radical polymerization (ATRP) of styrene. The important advantage of titanium compounds is the white color of the Ti(IV) ions (Ti in the highest and air stable oxidation state) which ensures the absence of coloring in the final polymer. The better control over polymerization was realized when conditions increasing the reactivity of the intermediate Ti(IV) species and decreasing their steady state concentration were maintained. This occurred when chlorides were replaced with bromides (which decreased the bond strength), and when ligands with low donor ability were employed. Using a sulfide complex of Ti(III) chloride and 1,2-bis(hexylthio)ethane allowed styrene polymerization with kinetic and molecular weight characteristics inherent to ATRP.

Introduction

As well recognized nowadays, atom transfer radical polymerization (ATRP) catalyzed with transition metals is a robust and promising method for controlled polymerization of acrylic and styrene monomers [1]. For synthesis of well-defined polymers with different polymer architectures based on these monomers, various complexes of metals such as Cu [2-5], Fe [6-9], Ni [10-14], Ru [15, 16], Rh [17], and Mo [18] have been used. Yet, the increasing number of metals tried in ATRP reflects an effort to solve one of the main problems of these catalysts: the coloring of the polymers by the intense color of the above metal ions in their highest (and air stable) oxidation state. This requires subsequent purification of polymers to remove the catalysts, which makes any process more complicated [19]. For homogeneous catalysis, this problem can be efficiently solved in two ways. The first approach is to strongly increase the catalytic activity of the metal complex allowing facilitation of the activation-deactivation of polymer chains: this, in turn, will allow using less catalyst. Another avenue is using a metal that is not colored in its highest oxidation state so its removal is of no concern. Among transition metals this phenomenon is rare, although existent. The Ti(III) salts are intensely colored, while the Ti(IV) ion (which is a product of fast oxidation of Ti(III) under air) gives white salts and complexes [20]. For the first time,

the present paper reports the results on using Ti(III) compounds in ATRP. As catalytic systems, we studied Ti(III) *n*-butoxide, chloride, and bromide in the form of their complexes with amine- and sulfur-containing ligands.

Experimental Section

Materials

THF (Aldrich, 99%) was stored over KOH and then distilled. Benzene(99%) and toluene (99.5%) from Aldrich were distilled. Styrene (99%, Aldrich) was distilled over CaH₂ *in vacuo*. 1-Phenylethylbromide (PEBr, 97%), 2,2'-bipyridyl (BiPy, 99%), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 99%), 1,8-bis(dimethylamino)naphthalene (PSP), aluminum powder (200 mesh, 99%), thionyl chloride (99%), 1-phenylethanol (98%), titanium (III) chloride (TiCl₃, 99.999%), titanium (IV) bromide (TiBr₄, 98%), pyridine (99%) and anisole (99.7%) were obtained from Aldrich and used without any purification. 1-Phenylethyl chloride (PECl, b.p. 68 °C/8 Torr[21], 97%, GC) was prepared by reaction of 1-phenylethanol with thionyl chloride. Titanium (III) bromide (TiBr₃) was prepared according to ref. [22] by reduction of TiBr₄ with 1/3 equivalent of aluminum powder in a sealed tube at 300 °C. Aluminum bromide along with traces of TiBr₄ were removed by sublimation. Titanium(III) *n*-butoxide (TBO) [23], 1,2-bis(hexylthio)ethane (HTE) [24], and bis(2-dimethylaminoethyl) sulfide (DMAES) [25] were prepared according literature procedures.

Polymerization

All operations were carried out in argon atmosphere. In a typical experiment, a three-neck glass double-jacketed reactor connected to thermostat and containing a rubber septum, gas inlet and outlet, and a Teflon stir bar was flushed with Ar and charged with titanium (III) compound (50.3 mg TiCl₃ or 93.8 mg TiBr₃ or 76.7 mg TBO; 3.26×10^{-4} mol), degassed anisole (3.80 mL; 3.50×10^{-2} mol) and a ligand (for DMAES, 0.063 mL; 3.26×10^{-4} mol). After that the mixture was stirred at room temperature overnight. Next day degassed styrene (3.80 mL; 3.26×10^{-2} mol) and initiator (0.044 mL PECl or 0.045 mL PEBr; 3.26×10^{-4} mol) were added to the reaction mixture using previously purged syringes and the reactor was heated up to 110 °C. At timed intervals, approximately 0.1 mL samples were withdrawn from the reactor using a degassed syringe, weighed, mixed with 3.60 mL of THF and 0.185 mL of toluene (internal standard) and used for GC analysis. The solutions were filtered over alumina to remove Ti complexes before GPC analysis. For styrene polymerization using TiCl₃/DMAES and PECl as initiator, conversion was 47% ($M_n = 5160$, $M_w/M_n = 1.24$) in a 5.9 hour reaction.

Characterization

Monomer content and conversion were determined with gas chromatography (GC) using Chrom-5 equipped with 2 m length columns filled with 3% SP-2100 on

Chromaton N-Super of 0.16-1.2 mm. Toluene was used as internal standard. Analysis conditions: injector temperature 240 °C; detector temperature 250 °C; column temperature 100 °C, isothermal.

Molecular weights and molecular weight distributions were measured by GPC using Waters chromatograph consisting of pump M600, UV-VIS M484 detector at $\lambda = 260$ nm, equipped with two Ultrastaygel Linear columns with the linear calibration range from 100 to 3×10^6 D and mean bead size of 7 μ . THF was used as the eluent at 30 °C with the flow rate of 1 mL/min. Calibration was carried out using polystyrene standards. "Maxima" software was applied for data processing.

Results and discussion

For complexes of Ti(III) halides with amines, esters, and sulfides, the characteristic coordination numbers are 5 and 6 depending on the ligand type. As shown for trimethylamine [26], dioxane [27], and dimethylsulfide [22], the coordination number is 5, while the coordination number is 6 for pyridine [26] and 2,2'-bipyridyl [28]. With 1,2-ethylenediamine, Ti(III) halide is able to form a polynuclear complex [29]. For Ti(IV) complexes, typical coordination numbers are 6 and 8, yet the latter is characteristic of the majority of the ligands [20]. As a rule, a particular feature of all the titanium compounds is their very poor solubility in common solvents.

In this work, Ti(III) complexes were prepared *in situ* under 12 h stirring at room temperature. Homogeneous solutions of Ti(III) chloride and bromide (solutions were dark-violet and dark-brown, respectively) were obtained only for ligand containing n-hexyl group (bidentate HTE). Such ligands as monodentate Py, bidentate BiPy, and tridentate PMDETA and DMAES gave only partially soluble complexes. TBO itself or in the presence of the above ligands practically did not dissolve in anisole, but dissolved vigorously during reaction when halide was added.

As shown in Figure 1, the kinetic curves of polymerization initiated with PECl or PEBr and catalyzed with complexes of T(III) halides with PMDETA or TBO without a ligand are not linear, as is characteristic of ATRP [2]. These curves consist of two parts. In the first hour, polymerization occurs with a higher rate than after 1 h. The intensely colored solutions lose much of their color in the first hour. This color change is evidence of the transition of the majority of Ti(III) ions (strongly colored) to colorless Ti(IV) ions. As the reaction progressed, the color did not change anymore, and the reaction rate decreased. Dependences of the molecular weights on styrene conversion for these complexes (Fig. 2) differ from the calculated one. This and the broad molecular weight distribution (polydispersity, $M_w/M_n=1.9-2.3$) were the result of detectable irreversible termination caused by poor control over polymerization especially in an initial unsteady period. The worst control was observed using TBO without and with a ligand (BiPy). Replacement of initiator PECl with PEBr in the polymerization catalyzed with Ti(III) chloride (i.e. partial replacement of chlorine for bromine) improves the control over the polymerization. Even better results (molecular weights are closer to expected ones) were obtained when Ti(III) bromide is used along with PEBr.

This evolution of molecular weights is probably caused by the decrease of the strength of the metal-halide bond in the forming Ti(IV) halides and the corresponding increased reactivity when chlorine is replaced with bromine. This facilitates the

reaction controlling the increase of molecular weight, i.e. halogen transfer from Ti(IV) by radicals of the propagating chains.

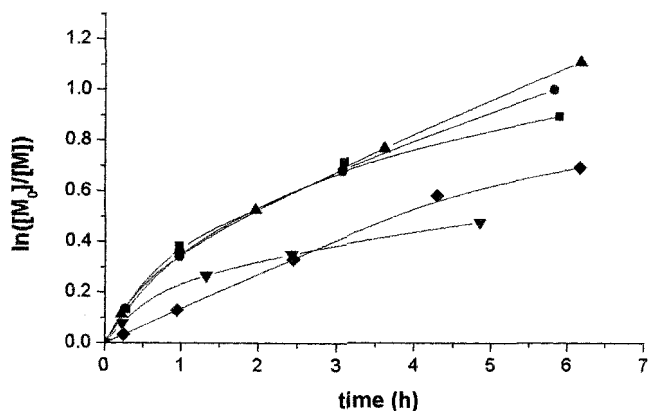


Figure 1. Kinetic plots of the styrene ATRP using PMDETA complex of (i) TiCl_3 and PECl (●), (ii) TiCl_3 and PEBr (■), (iii) TiBr_3 and PEBr (▲), and (iv) $\text{TiBr}_3/\text{TiBr}_4$ and PEBr (◆). $\text{Ti}(\text{OBu})_3$ and PEBr were used without a ligand (▼). Other conditions were: 110°C ; anisole solution; $[\text{Styrene}]_0 = 4.4 \text{ M}$; $[\text{Ti}]_0 = [\text{PECl}]_0 = [\text{PEBr}]_0 = [\text{PMDETA}]_0 = 0.044 \text{ M}$.

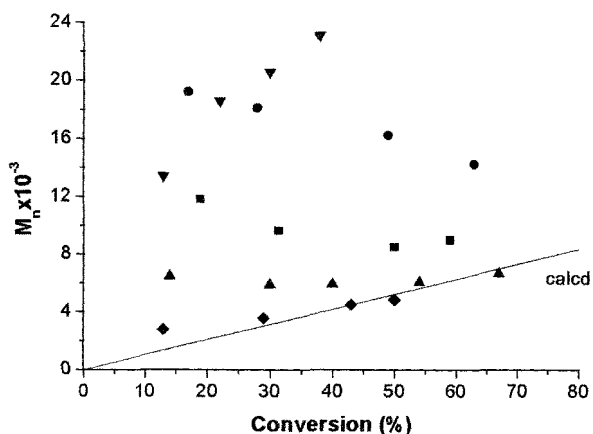


Figure 2. Dependence of molecular weights (M_n) on styrene conversion using PMDETA complex of (i) TiCl_3 and PECl (●), (ii) TiCl_3 and PEBr (■), (iii) TiBr_3 and PEBr (▲), and (iv) $\text{TiBr}_3/\text{TiBr}_4$ and PEBr (◆). $\text{Ti}(\text{OBu})_3$ and PEBr were used without a ligand (▼). See Fig. 1 for conditions. The straight line corresponds to a calculated dependence.

We believe that presence of two well-defined parts on the kinetic curves is determined by evolution (for the first hour) of styrene ATRP to steady state which is characterized with high concentration of Ti(IV) halides and low concentration of T(III) halides.

This, in turn, is a result of a significantly lower reactivity of Ti(IV) halides compared to Ti(III) halides. This conclusion is confirmed by using equimolar mixture of Ti(III) and Ti(IV) bromides (Fig. 1) instead of Ti(III) bromide alone which resulted in disappearance of the first region on the kinetic curve. The polymerization rate became close to the rate of the second region, while the dependence of molecular weight on conversion (Fig. 2) became close to calculated one. The molecular weight distribution (MWD) also became narrower, although still broad (polydispersity $[M_w/M_n]$ was about 1.7). This result also shows that steady concentration of Ti(IV) species is not less than 50% of all the metal. On the other hand, judging by the color of the reaction solution during polymerization (solution is nearly colorless) this value is probably even higher than that. In addition, this experiment shows that styrene polymerization is a result of ATRP, but not carbocationic polymerization. [30] If the latter mechanism would be true, addition of Ti(IV) bromide, which is a stronger Lewis acid than Ti(III) one, would increase (but not decrease) the polymerization rate. Low Ti(III) concentration results in a low initiation rate and as a consequence a low polymerization (catalytic reaction) rate in general (apparent rate constant in the latter case was $3.4 \cdot 10^{-5} \text{ s}^{-1}$).

According to ref. [31], standard oxidation potentials for Ti(III) and Cu(I) are -0.04 V and $+0.153 \text{ V}$, respectively. Essentially low potential of Ti(III) means that in the same conditions (solvents and ligands), it can undergo more easily oxidation to Ti(IV) with halide transfer and have a higher reactivity in initiation than Cu(I). Respectively, ability to reduction and reactivity of Ti(IV) in reversible chain termination with halide transfer can be lower than for Cu(II). This can be expected if to consider that the transition state both of oxidation and reduction with halogen transfer is the same. Taking into account that for efficient catalysis and control over polymerization, both parts of the metal oxidative-reductive transformations are equally important, we tried to influence these properties varying donor-acceptor properties of the organic ligand as mentioned in ref. [32]. The logic of this effort is supported by the improvement of the control over polymerization when a ligand with lower basicity (PMDETA with Ti(III) halides) is used instead of higher basic ligand (*n*-butoxide anion in TBO). To vary the donor-acceptor properties, we used Py, BiPy, and two sulfur-containing ligands: HTE and DMAES which presumably might better stabilize metal in low oxidation state than in high oxidation state due to a weaker donor effect or an effect of the back donation. This might equalize the reactivity of Ti(III)/Ti(IV) pair. Here, as initiators PECl was used for Ti(III) chloride, and PEBr was used for Ti(III) bromide. Results of these experiments are shown in Figures 3 and 4.

The best results were obtained when Ti(III) chloride was used with HTE along with PSP (15 mol. % from HTE amount). In this case, polymerization occurred faster (apparent rate constant was about $7.8 \cdot 10^{-5} \text{ s}^{-1}$), as a controlled process (according to kinetics characteristic of ATRP) and led to polymer with a comparatively low polydispersity (about 1.26). It should be noted that primary dark-brown color of Ti(III) ion was preserved during all polymerization time which is an evidence of considerable concentration of Ti(III) ions in a steady state. When final polymer solution was exposed to air, the color disappeared showing oxidation of Ti(III) to Ti(IV). PSP was used to absorb HCl (forming probably due to partial hydrolysis of the catalyst with trace water). Without this additive, molecular weights of polymers were much lower than calculated ones. This was likely caused by formation of additional PECl when HCl was coupled with styrene by Markovnikoff rule. When polymerization was carried out with Ti(III) bromide in the presence of HTE and PSP,

a dark-brown precipitate of Ti(III) bromide complexes deposited on the reactor walls which diminished styrene conversion to only 16% in 5 h. A similar situation was observed when Ti(III) was used with one equivalent of BiPy. Probably, this is determined by the lower stability of a bromide complex [22] with weak donor ligands at elevated temperatures due to stronger electron-donor properties of bromide ion compared to chloride ion.

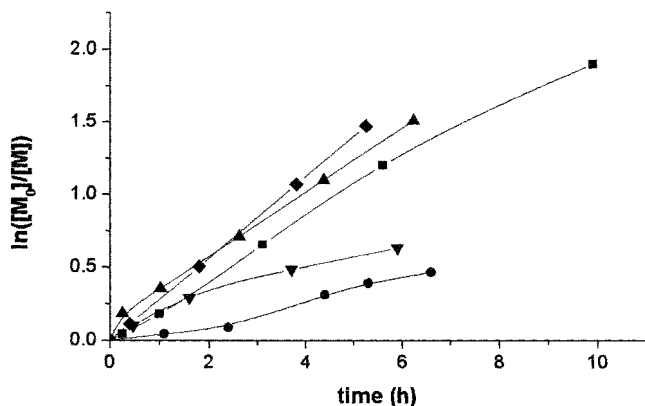


Figure 3. Kinetic plots of the styrene ATRP using BiPy complex of (i) TiBr_3 (●) and complexes of TiCl_3 with (ii) BiPy (■), (iii) three equivalents of Py (▲), (iv) HTE + PSP (◆), and (v) DMAES (▼). See Fig. 1 for conditions.

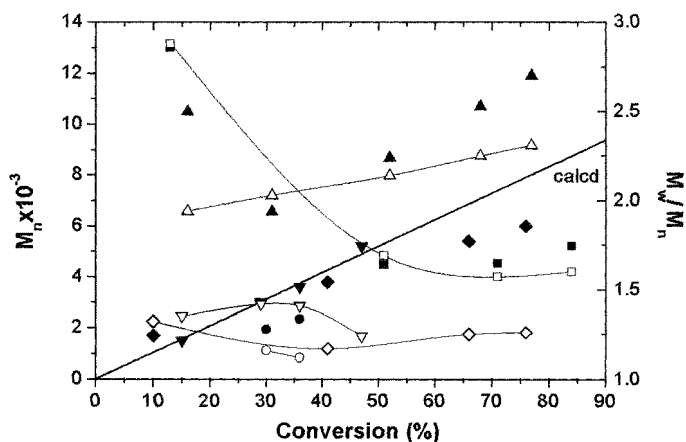


Figure 4. Dependence of molecular weights (M_n) and polydispersities M_w/M_n on styrene conversion using BiPy complex of (i) TiBr_3 (●) and complexes of TiCl_3 with (ii) BiPy (■), (iii) three equivalents of Py (▲), (iv) THE + PSP (◆), and (v) DMAES (▼). See Fig. 1 for conditions. A straight line corresponds to a calculated dependence. Non-filled symbols indicate polydispersity (M_w/M_n).

Polymerization using Ti(III) chloride in combination with weak donor amine ligands (one equivalent of BiPy or three equivalents of Py) occurred faster than with PMDETA. For Py, two-part character of the kinetic curve is weakly presented, while for BiPy, no two parts are observed. Nevertheless, judging by MWD, these systems do not provide control over polymerization. Deviation of molecular weights from calculated ones toward smaller values for BiPy and HTE should be related to partial hydrolysis of titanium chloride.

Polymerization catalyzed with the complex of Ti(III) chloride with DMAES had kinetic parameters (rate, change of color and presence of two parts on the kinetic curve) similar to its non-sulfur-containing analog: PMDETA. Probably replacement of one nitrogen atom with a sulfur atom did not much influence the donor-acceptor properties of the ligand. On the other hand, DMAES use led to a good match of molecular weights to calculated ones and narrower MWD. Probably, it improved the Ti(IV) electronic state and did not change the electronic state of Ti(III) so a steady concentration of the Ti(III) species and correspondingly the polymerization rate were low.

Conclusions

Our study of styrene ATRP with the Ti(III) compounds as catalysts revealed the possibility of using this system when certain ligand environment of the metal is formed. These factors, which increased activity of Ti(IV) halides in reduction with halogen transfer, promoted better control over polymerization. These factors are (i) decrease of the bond strength when chlorides are replaced with bromides or (ii) use of ligands with low donor ability. However, in both cases the problems with complex stability are crucial. Sulfide complex of Ti(III) chloride and HTE is sufficiently stable with low metal basicity (probably, due to effect of back donation) which provided styrene polymerization with kinetic and molecular weight characteristics inherent to ATRP. Hydrolytic instability of Ti(III) halides required using water-free media and small amounts of substances absorbing hydrogen halide. Exposure of final product to air allowed transformation of Ti(III) ions to Ti(IV) ones and colorless polymer solution.

Acknowledgements. Authors sincerely acknowledge financial support of this work provided by DuPont.

References

1. Patten TE, Matyjaszewski K (1999) *Acc Chem Res* 32:895
2. Matyjaszewski K, Patten TE, Xia J (1997) *J Amer Chem Soc* 119:674
3. Matyjaszewski K, Wang J-L, Grimaud T, Shipp DA (1998) *Macromolecules* 31:1527
4. Ohno K, Goto A, Fukuda T, Xia J, Matyjaszewski K (1998) *Macromolecules* 31:2699
5. Pascual S, Coutin B, Tardi M, Polton A, Vairon J-P (1999) *Macromolecules* 32:1432
6. Kotani Y, Kamigaito M, Sawamoto M (1999) *Macromolecules* 32:6877
7. Matyjaszewski K, Wei M, Xia J, McDermott NE (1997) *Macromolecules* 30:8161
8. Lourie J, Grubbs RH (2000) *Chem Commun* 1479
9. Teodorescu M, Gaynor SG, Matyjaszewski K (2000) *Macromolecules* 33:2335
10. Uegaki H, Kamigaito M, Sawamoto M (1999) *J Polym Sci Polym Chem* 37:3003

11. Granel C, Dubois P, Jerome R, Teyssie P (1996) *Macromolecules* 29:8576
12. Uegaki H, Kotani Y, Kamigaito M, Sawamoto M (197) *Macromolecules* 30:2249
13. Uegaki H, Kotani Y, Kamigaito M, Sawamoto M (1998) *Macromolecules* 31:6756
14. Johnson RM, Corbin PS, Ng C, Fraser CL (2000) *Macromolecules* 33:7404
15. Watanabe Y, Ando T, Kamigaito M, Sawamoto M (2001) *Macromolecules* 34:4370
16. Kotani Y, Kamigaito M, Sawamoto M (1998) *Macromolecules* 31:5582
17. Moineau G, Granel C, Dubois P, Jérôme R, Teyssié P (1998) *Macromolecules* 31:542
18. Le Grogneac E, Claverie J, Poli R (2001) *J Amer Chem Soc* 123:9513
19. Angot S, Ayres N, Bon SAF, Haddleton DM (2001) *Macromolecules* 34:768
20. Luchinski GP (1971) *Chemistry of Titanium*. Khimia, Moscow
21. *Methods of Organoelement Chemistry. Chlorine. Aliphatic compounds* (1973). Ed. Nesmeyanov AN, Nauka, Moscow
22. Fowles GW, Lester TE, Walton RA (1968) *J Chem Soc A* 196
23. Nesmeyanov AN, Nogina OV, Freidlina RK (1954) *Doklady AN, USSR* 95:813
24. Brookes RF, Cranham JE, Cummings WA, Greenwood D, Jackson BS, Stevenson HA (1957) *J Sci Food Agr* 8:31
25. Marxer A, Miescher K (1951) *Helv Chim Acta* 34:924
26. Fowles GW, Hoodless RA (1963) *J Chem Soc* 33
27. Clark JH, Lewis J, Machin DJ, Nyholm RS (1963) *J Chem Soc* 379
28. Fowles GW, Hoodless RA, Walton RA (1965) *J Inorg Nucl Chem* 391
29. Fowles GW, Hoodless RA, Walton RA (1965) *J Inorg Nucl Chem* 1999
30. Storey RF, Chisholm BJ (1993) *Macromolecules* 26:6727
31. Ephimov AI (1983) *Properties of Inorganic Compounds*. Khimia, Leningrad
32. Matyjaszewski K, Paik H, Zhou P, Diamanti S (2001) *Macromolecules* 34:5125