Poly(methyl methacrylates) with Ruthenium Tris(bipyridine) Cores via $NiBr_2(PR_3)_2$-Catalyzed Atom Transfer Radical Polymerization (ATRP)

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ABSTRACT: Ruthenium(II) tris(bipyridine) complexes derivatized with six α-bromoester functional groups were used as multifunctional initiators for the bulk and solution (toluene) polymerizations of methyl methacrylate (MMA) and methyl acrylate (MA) using $NiBr_2(PPh_3)_2$ and $NiBr_2(PBu_3)_2$ as atom transfer radical polymerization (ATRP) catalysts. Both tertiary (**1**) and secondary (**2**) halide metalloinitiators were prepared for investigation. The resulting orange-colored polymers were characterized by gel permeation chromatography (GPC) in chloroform. The molecular weight distributions of the poly(methyl methacrylates) (PMMAs) were narrow (toluene, $M_w/M_n = 1.1-1.3$; bulk, $M_w/M_n < \sim 1.3$ at <50% conversion). The presence of $[Ru(bpy)_3]^{2+}$ in the eluting polymers was verified by in-line, diode-array UV/vis spectroscopic analysis. For polymerizations of MMA in toluene at 80 °C using the tertiary initiator and $NiBr_2(PPh_3)_2$ as the catalyst, M_n vs percent conversion and pseudo first-order kinetics plots were linear. Thus, these conditions were used to prepare a series of Ru-centered PMMA stars with molecular weights ranging from 2800 to ~350 000. The linear polymer arms were cleaved from the Ru cores using NaOMe. Polydispersities of cleaved linear PMMA arms were low (~1.10−1.24) and $M_n^{star}/M_n^{arm} \approx 6$, further confirming the efficiency of initiation and controlled nature of these reactions. As the percent toluene relative to monomer was reduced, control diminished. Likewise, all other polymerizations carried out with varied combinations of initiator (secondary or tertiary), monomer (MA or MMA), Ni catalyst (Ph or Bu), and reaction conditions (bulk vs solution) were not “living.” Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of materials revealed no evidence of chain transfer and termination processes.

Introduction

Impressive advances in atom transfer radical polymerization (ATRP) have facilitated the synthesis of a diverse array of polymers with narrow molecular weight distributions and with varied composition and architecture.[1] Polystyrenes and polyacrylates are among the most thoroughly explored systems. For example, block,[2−4] comb and graft,[5] star,[6,7] dendritic,[8,9] hyperbranched,[10] and surface-anchored[11] configurations have been constructed. Compared to most ionic polymerizations, radical polymerizations are considerably more tolerant of functionality. Several different solvents have been used in radical polymerizations,[12] and a variety of substituents have been incorporated into the resulting polymers.[13] Because certain applications require “color-free” products, investigators have described the benefits of catalysts that are transparent in the visible region[14] and have reported useful methods for catalyst removal.[15] Supported catalysts have also been explored to expedite the separation of metal catalysts from polymer products.[16] In contrast, our efforts have been devoted to the controlled introduction of inorganic chromophores into materials. Methods for preparing metal-containing polymers with well-defined binding sites are of interest for use in the design of new supported catalysts,[17] sensors,[18] and other types of responsive materials.[19]

Polymeric metal complexes of low polydispersity indices (PDIs) can be prepared using functionalized metal complexes as initiators.[20−25] Although this “core first” approach requires compatibility between the metalloreagent and the conditions for controlled polymerization and although multifunctional initiators are sometimes difficult to synthesize, higher molecular weight materials are typically accessible by this divergent route. Furthermore, the purification of polymer products is more straightforward with the “core first” strategy than for the “arm first” coupling[26] and chelation[27,28] methods. This is because, in the former case, any unreacted starting materials are monomeric and separable by evaporation or precipitation, whereas, with the latter convergent approaches, both reagents and products are polymeric. Related self-assembly strategies have been utilized in the synthesis of metal-centered dendrimers,[29] synthetic receptors,[30] molecular motors,[31] light-harvesting arrays,[32] and a wide range of other metal-containing architectures.[33]

In the design of metal-containing macromolecules there are three variable components: the metal complex, its ligand set, and the polymer. Because there are many known derivatives of α-diimine ligands, which are easily interchangeable in the inert Ru(II) coordination sphere, ruthenium tris(bipyridine) and its various heteroleptic analogues are modular templates for architectural modification and for tuning the physical properties (e.g., optical and electrochemical) of polymers.[34] Accordingly, ruthenium bipyridine (bpy) analogues with variable numbers of electrophilic halomethyl and nucleophilic hydroxymethyl substituents[35] are versatile starting points for screening a variety of different living polymerization reactions. Both halomethyl bpys and their inert Ru(II) complexes have been utilized as initiators for the generation of metal-centered polystyrenes with two, four, and six arms[20,28] using copper-catalyzed ATRP methodologies. Moreover, both labile and inert metal systems are compatible with cationic oxazoline polymerizations.[21−23]

In this study, we further explore the compatibility of metal complex reagents with living polymerization

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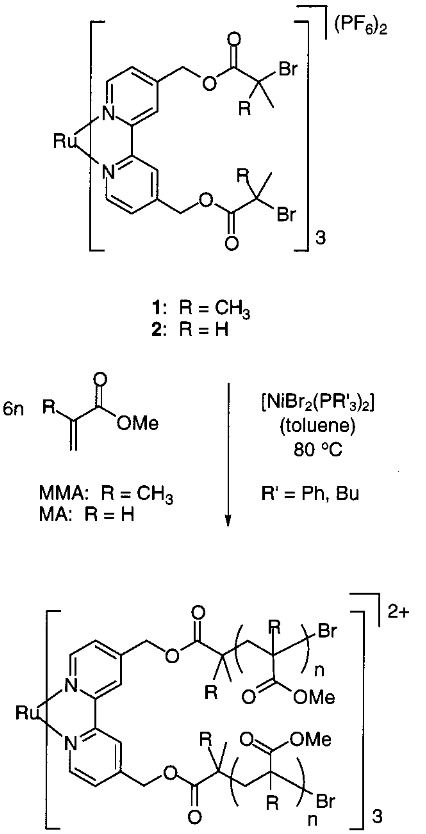

Figure 1. Nickel-catalyzed atom transfer radical polymerization of MMA and MA using Ru(II) metalloinitiators **1** and **2**.

methodologies and expand the scope of materials into which luminescent Ru tris(bpy) chromophores may be selectively incorporated. Specifically, hexafunctional α-bromoester derivatized Ru(II) complexes were utilized as initiators for the ATRP of acrylate monomers, methyl methacrylate (MMA), and methyl acrylate (MA) (Figure 1). These materials could serve as precursors to block copolymer analogues of interest for photonic applications, or, if appropriately derivatized for cross-linking, be useful for luminescent tracing of the fate of adhesives in biomedical contexts. Reactions were run in bulk monomer and in toluene solution. Among the ATRP catalysts that were screened, the commercially available $[NiBr_2(PR_3)_2]$ complexes (R = Ph, Bu), introduced by Sawamoto and co-workers[3,36] and later used extensively by Jérôme et al.,[2,9,37,38] showed the greatest promise. Thus, for this catalyst system, the effects of monomer concentration and catalyst loading on molecular weight control were investigated. Kinetics experiments were also performed to determine optimal reaction conditions and the extent to which polymerizations were controlled. In contrast to Ru-centered polystyrenes, wherein chains are attached to a Ru complex via stable carbon−carbon bonds,[20] in Ru-centered poly(methyl methacrylates) (PMMAs), arms are attached to the metal complex via cleavable ester linkages. Thus, scission reactions were conducted with Ru(II)-centered PMMA stars of different molecular weights in order to characterize the linear arms independently from the metal complex core.[7]

Experimental Section

Materials. $[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$ (**3**), $[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)_2$ ($(bpy(CH_2Cl)_2$ = 4,4′-bis(chloromethyl)-2,2′-bipyridine), and $[Ru\{bpy(C_{13}H_{27})_2\}_3](PF_6)_2$ ($bpy(C_{13}H_{27})_2$ = 4,4′-bis(tridecyl)-2,2′-bipyridine) were prepared as previously described.[20,35] THF (Mallinckrodt) and toluene (Mallinckrodt) were dried and purified by passage through alumina columns.[39] Triethylamine (Acros, 98.5%), 2-bromopropionyl bromide (Aldrich, 97%), 2-bromoisobutyryl bromide (Aldrich, 98%), anhydrous MeOH (Mallinckrodt), heptane (Aldrich, 99%) and $[NiBr_2(PPh_3)_2]$ (Strem, 99%) were used as received. MMA (Alfa AESAR, 99%) was dried over CaH_2 and distilled prior to use. MA was washed with a 10% (w/w) aqueous solution of NaOH (3×), dried over $MgSO_4$, and then distilled from CaH_2 prior to use.

Instrumentation. ^1H NMR (300 MHz) spectra were recorded on a General Electric QE 300 spectrometer in the indicated solvents. UV/vis spectra were obtained in $CHCl_3$ using a Hewlett-Packard 8452A diode-array spectrophotometer. IR spectra were obtained as Nujol mulls on a Perkin-Elmer 1600 Series FTIR spectrophotometer. Molecular weights were determined by GPC ($CHCl_3$, 25 °C, 1.0 mL/min) using multi-angle laser light scattering (MALLS) ($\lambda = 633$ nm, 25 °C), refractive index ($\lambda = 633$ nm, 40 °C), and diode-array UV/vis detection. Polymer Labs 5 μm mixed-C columns along with Wyatt Technology Corp. (Optilab DSP interferometric refractometer, Dawn DSP laser photometer) and Hewlett-Packard instrumentation (Series 1100 HPLC) and software (ASTRA) were used in the GPC analysis. Incremental refractive index (dn/dc) measurements were carried out on a series of Ru−PMMA star polymers and PMMA standards by GPC using a single-injection method that assumed 100% mass recovery from the columns. The values obtained were within experimental error of those previously reported; therefore, unless indicated otherwise, the literature dn/dc value for PMMA (0.059 mL/g of $CHCl_3$ solution) was used in the calculation of MALLS molecular weights.[40] PMMA samples were also analyzed by GPC vs linear PMMA standards. Molecular weights of PMA samples were determined by GPC by comparison with linear polystyrene standards.

Thermal measurements were performed using a TA Instruments DSC 2920 modulated DSC and a TA Instruments TGA 2020 thermogravimetric analyzer. DSC analyses were performed in modulated mode under a N_2 atmosphere (amplitude = 1 °C; period = 60 s; heating rate = 5 °C/min; range = −10 to +160 °C, cycled twice; and a final ramp from −10 to +210 °C). Reported values of thermal events are from the second heating cycle and the reversing heat flow curve (T_g = the midpoint of the change in heat capacity). Thermogravimetric analyses were carried out over a temperature range from 60 to 900 °C at a heating rate of 10 °C/min.

$[Ru\{bpy(CH_2OCOCBr(CH_3)_2)\}_3](PF_6)_2$ 1. A suspension of $[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$, **3**, (0.250 g, 0.240 mmol) and triethylamine (0.670 mL, 4.80 mmol) in THF (10 mL) was cooled to 0 °C, followed by dropwise addition of 2-bromisobutyryl bromide (0.450 mL, 3.60 mmol). The resulting mixture was warmed to room temperature overnight (12 h) and, subsequently, filtered through a pad of Celite. The Celite was flushed with methylene chloride (5−10 mL) until the washes were colorless, and the combined organic fractions were shaken with a 1% (w/w) aqueous solution of $NaHCO_3$ (3 × 30 mL) and with water (30 mL). The organic layer was dried over Na_2SO_4, and solvent was removed in vacuo. The crude material was dissolved in CH_2Cl_2 (5 mL) and was added dropwise to Et_2O (75 mL) with stirring. The solid that precipitated was collected by vacuum filtration, was washed on the filter paper with a large volume of ether, and was dried in vacuo to give an orange-colored powder: 0.306 g (82%). ^1H NMR (300 MHz, CD_3CN): δ 8.43 (s, 6H, H-3, H-3′), 7.69 (d, $J = 5.8$ Hz, 6H, H-6, H-6′), 7.41 (d, $J = 5.8$ Hz, 6H, H-5, H-5′), 5.39 (s, 12H, CH_2), 2.02 (s, CH_3). UV/vis ($CHCl_3$): λ_{max} (ϵ) = 461 nm (16 607 M^{-1} cm^{-1}). IR: ν = 1740 cm^{-1} (C=O). Anal. Calcd for $C_{60}H_{66}N_6O_{12}Br_6RuP_2F_{12}$: C, 37.27; H, 3.44; N, 4.35. Found: C, 37.52; H, 3.78; N, 4.25.

$[Ru\{bpy(CH_2OCOCHBrCH_3)_2\}_3](PF_6)_2$, 2. The secondary initiator **2** was prepared from $[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$, **3**, (0.100 mg, 0.096 mmol) and purified as described above for **1** with the following exceptions. Pyridine (0.150 mL, 1.92 mmol) was substituted for triethylamine, and 2-bromopropionyl bromide (0.150 mL, 1.44 mmol) was used in place of 2-bromisobutyryl bromide, to produce **2** as an orange-colored powder: 0.130 g (73%). ^{1}H NMR (300 MHz, CD_3CN): δ 8.45 (s, 6H, H-3, H-3′), 7.69 (d, $J = 5.0$ Hz, 6H, H-6, H-6′), 7.40 (d, $J = 5.0$ Hz, 6H, H-5, H-5′), 5.40 (m, 12H, CH_2), 4.65 (q, $J = 6.9$ Hz, 6H, CH), 1.83 (d, $J = 6.9$ Hz, 18H, CH_3). UV/vis (CH_3CN): λ_{max} (ϵ) = 465 nm (16 398 M^{-1} cm^{-1}). IR: ν = 1746 cm^{-1} (C=O). Anal. Calcd for $C_{54}H_{54}N_6O_{12}Br_6P_2F_{12}Ru$: C, 35.06; H, 2.94; N, 4.54. Found: C, 35.21; H, 3.24; N, 4.99.

Representative Polymerization Procedure for M_n vs Percent Conversion Studies. Bulk and solution polymerizations were performed as described by Jérôme et al.[37] A representative procedure is as follows: A Schlenk flask was charged with $[NiBr_2(PPh_3)_2]$ (0.246 g, 0.331 mmol), **1** (0.106 g, 0.055 mmol), and MMA (8.63 g, 86.0 mmol) under a N_2 atmosphere. Solution reactions were performed in an analogous manner but with toluene (50% v/v with monomer) also present. The system was subjected to three consecutive freeze/evacuation/thaw cycles, sealed under N_2, and immersed in an oil bath set at 80 °C. At regular intervals up to the point at which the reactions became highly viscous (~70% conversion), aliquots (~0.5 mL) were removed and transferred to tared vials. The reaction was quenched immediately by submerging the vials in cold water. Percent conversions were determined by gravimetric analysis. The molecular weights were measured for $[Ru(bpyPMMA_2)_3]^{2+}$ and $[Ru(bpyPMA_2)_3]^{2+}$ samples without further purification.

Representative Preparative Scale Polymerization Reaction. A dry Schlenk flask was charged with Ru initiator, **1** (0.120 g, 6.21×10^{-2} mmol), $NiBr_2(PPh_3)_2$ (0.277 g, 0.373 mmol), toluene (9.01 g), and monomer (MMA, 10.10 g, 93.4 mmol). The resulting reaction mixture was subjected to three freeze−pump−thaw cycles, sealed under N_2 and heated at 80 °C in an oil bath. The reaction was stirred for 7 h, quenched by immersion of the vessel in cold water, then an aliquot (2.2 mL) was removed and transferred to a tared 5 mL round-bottomed flask for percent conversion determination by gravimetric analysis. Toluene and unreacted monomer were removed from both the aliquot and the remainder of the reaction mixture by rotary evaporation without heating, and the samples were further dried in vacuo prior to purification. The crude polymer residue was purified by precipitation (2×) from THF/heptane (for MW < 100 000; > 100 000 precipitate from THF/MeOH). The orange-colored polymer was collected by filtration, washed with additional heptane and dried in vacuo: 0.310 g (79%) at 68% monomer conversion. UV/vis ($CHCl_3$): λ_{max} (ϵ): 465 nm (19 275 M^{-1} cm^{-1}). MALLS M_w: 129 300 (PDI = 1.11). Standards M_w: 125 100 (PDI = 1.22).

Representative Procedure for the Cleavage of PMMA Arms from Ruthenium Star Polymers. A mixture of $[Ru(bpyPMMA_2)_3]^{2+}$ (M = 129 300, 25 mg) and $NaOCH_3$ (0.125 g) in $CHCl_3$ (1 mL) and CH_3OH (1 mL) was heated at ~120 °C in a sealed tube for 2 d. The resulting suspension was cooled to room temperature, and the supernatant was decanted and concentrated in vacuo. The resulting residue was partitioned between toluene (10 mL) and water (10 mL). The organic layer was separated, dried over sodium sulfate, and filtered. Solvent was removed in vacuo to give the cleaved polymer, which was analyzed by GPC: 14.5 mg (58%). MALLS M_w = 31 800 (PDI = 1.18); Standards M_w = 26 700 (PDI = 1.21).

Results and Discussion

Synthesis of Metalloinitiators. To investigate the compatibility of ruthenium reagents with the conditions necessary for the ATRP of acrylates, appropriate metalloinitiators were synthesized. Generally, ATRP is most controlled when initiation is fast relative to propagation, which is typically the case when the initiating and propagating radicals are appropriately related in reactivity.[41] Consequently, the tertiary halide initiator, $[Ru\{bpy(CH_2OCOCBr(CH_3)_2)_2\}_3](PF_6)_2$, **1**, should be a good choice for MMA polymerizations, whereas the secondary halide initiator, $[Ru\{bpy(CH_2OCOCHBrCH_3)_2\}_3](PF_6)_2$, **2**, was generated for the polymerization of MA. The hexafunctional initiators **1** and **2** were prepared by esterification of $[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$, **3**, using excess 2-bromoisobutyryl bromide and 2-bromopropionyl bromide, respectively, in the presence of triethylamine (Figure 2). In the latter case, yields of **2** increased when pyridine, a weaker base, was used in place of triethylamine (73% vs 43% yield, respectively). This observation suggested that partial deprotonation of the relatively acidic α-proton of the 2-bromopropionyl groups in **2** may lead to the formation of side products and, thus, depressed yields. Complexes were obtained as analytically pure, orange-colored powders after standard isolation protocols and purification by precipitation from CH_2Cl_2/Et_2O. In addition to initiators **1** and **2**, a hexachloro initiator, $[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)_2$, was prepared from complex **3** using a previously reported procedure.[35]

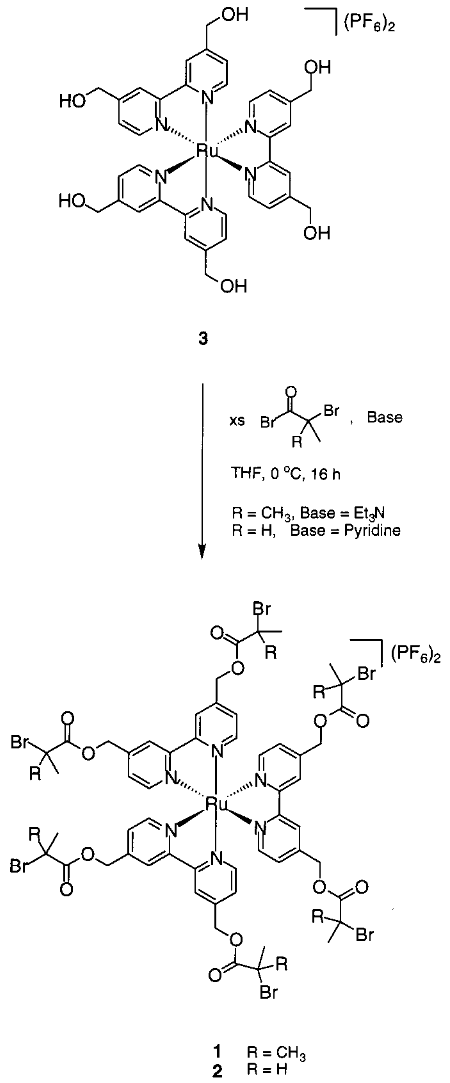

Figure 2. Synthesis of the α-bromoester functionalized ruthenium tris(bipyridine) metalloinitiators **1** and **2**.

Preliminary Catalyst Screening. The compatibility of the Ru(II) metalloinitiators **1** and **2** with several ATRP catalysts was explored. Because the field of ATRP is rapidly evolving, and new catalysts continue to be reported, there are multiple options for catalysis in the ATRP of acrylates. For example, transition metal complexes of various bipyridine,[42] chelating amine,[43] and imine systems,[44] as well as a multitude of phosphine[45] ligands have produced polymers with low PDIs. Although general guidelines are beginning to be outlined for certain catalyst systems, reaction optimization is, nonetheless, required for each monomer, catalyst, and initiator combination.

Haddleton's copper diimine catalyst system[44] was initially investigated in polymerizations of MMA and MA using the secondary hexafunctional initiator, **2**, copper(I) bromide, and *n*-octyl-2-pyridyl methanimine in toluene for 10 h at 80 °C. However, polymerizations of MA resulted in only trace amounts of polymer ($<10\%$ conversion) with narrow molecular weight distributions (e.g., $M_n = 175\,300$; PDI = 1.15). Viscous solutions were produced when using the same catalyst system in the polymerization of MMA, but GPC analysis of the resulting polymers revealed broad molecular weight distributions (e.g., $M_n = 48\,640$, PDI = 1.61). These poor results led to the exploration of other Cu catalyst systems. Because bipyridyl PMMA macroligands, bpyPMMA and $bpyPMMA_2$, have been generated with control by CuBr/HMTETA-catalyzed ATRP of MMA in anisole,[46] these conditions were also tested for the Ru(II) initiator **1**. Yet in this case, polymerizations failed to exhibit first-order kinetics and gave polymers with high PDIs.

In ensuing studies, reactions were screened using $NiBr_2(PPh_3)_2$. A $NiBr_2(PBu_3)_2$ catalyst was also of particular interest because of its potentially greater thermal stability and solubility in the monomer.[36] Both Ni catalysts presumably operate by halide abstraction from initiators or halide-capped propagating chains to generate reactive species, with concomitant one-electron oxidation of Ni(II) to Ni(III). The use of these catalysts in the preparation of metal-centered PMMA star polymers is outlined in subsequent sections.

Polymerization of Acrylates with Ruthenium Initiators. Polymerizations of MMA were first carried out using $NiBr_2(PPh_3)_2$. As mentioned above, the use of this catalyst is especially convenient because it is stable and commercially available. Thus, solution polymerizations were performed using catalyst, MMA, and hexafunctional initiator **1** in toluene at 80 °C. A 1:1 toluene:monomer ratio was employed with typical loadings of 250:1:1 (monomer:catalyst:initiator site). Reactions were monitored over time to determine whether the number-average molecular weight was a linear function of percent conversion and whether the polymerizations exhibited first-order kinetics with respect to monomer over the course of the reaction—both features characteristic of a controlled or "living" process.

Indeed, solution polymerizations in 1:1 (v/v) toluene/monomer mixtures exhibited number-average molecular weights that paralleled calculated values (Figure 3). First-order kinetics plots were linear (Figure 4), suggesting that polymerizations were controlled. Moreover, molecular weight distributions were narrow, which was also indicative of a "living" system. UV/vis analysis and arm scission reactions (vide infra) were also consistent with the production of Ru–PMMA star polymers. Preparative scale reactions were carried out in a similar manner to generate $[Ru(bpyPMMA_2)_3]^{2+}$ samples with weight-average molecular weights ranging from 2800 (PDI = 1.22) to ~318 500 (PDI = 1.29). Higher molecular weight materials could be obtained; however, broader molecular weight distributions were observed, presumably due to star–star coupling at high conversion.

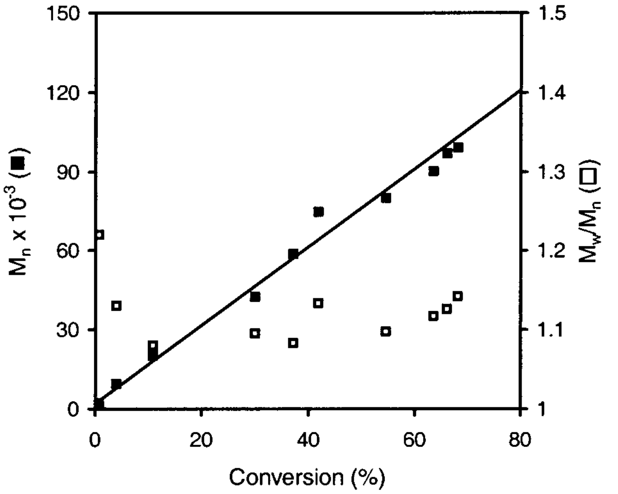

Figure 3. Number-average molecular weight vs percent conversion plot for the polymerization of MMA with the tertiary Ru(II) metalloinitiator **1** using the $NiBr_2(PPh_3)_2$ catalyst in toluene solution at 80 °C (— = M_n calcd).

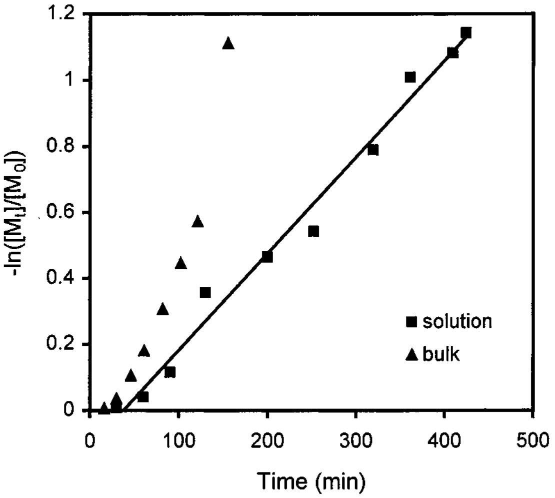

Figure 4. Kinetics plots for the bulk and toluene solution polymerizations of MMA at 80 °C using the $NiBr_2(PPh_3)_2$ catalyst.

As the concentration of MMA with respect to toluene was increased, kinetics plots became somewhat curved. The induction period observed for each system is most likely a result of the establishment of equilibrium in the initial stages of the reaction.[47] Bulk MMA polymerizations did not exhibit first-order kinetics plots (Figure 4) but did result in reasonably linear M_n vs percent conversion plots. However, the molecular weights deviated from those expected based on the monomer to initiator loading (see Supporting Information). Molecular weight distributions were typically narrow for low percent conversions and broadened with the emergence of a high molecular weight shoulder in GPC traces obtained at higher percent conversions (PDI $<$ 1.2 for $<$40% conversion; PDI $>$ 1.4 for $>$40% conversion). Even for reactions run in toluene, there was evidence of a slight sloping on the high molecular weight side of the eluting polymer peak. Because similar observations were made in the GPC traces of samples obtained at early time points in kinetics studies, a small degree of disproportionation or radical coupling of initiators (or of short oligomers formed soon after initiation) is likely occurring. This early nonstationary phase, which corresponds to persistent radical buildup, is quite characteristic of ATRP processes.[48] The fact that no sloping was observed in GPC traces of PMMA arms obtained after cleaving the arms from their corresponding Ru core lends further support for this hypothesis. Moreover, the GPC traces of polymers produced using a related difunctional Ru(II) α-bromoester initiator did not possess a shoulder, suggesting that this side reaction may be diminished when carrying out polymerizations with complexes that possess fewer initiating sites.

An additional small, Ru-free low molecular weight fraction is also sometimes evident in GPC traces of the polymers (see, e.g., Figure 9, vide infra). Although one might suspect that redox-lability of $[Ru(bpy)_3]^{2+}$ and growth of polymer from the resulting free ligand initiators could account for this side product, $Ru(bpy)_3$ complexes are inert and are not expected to be oxidized or reduced by Ni species present in the reaction mixture during polymerization, as confirmed by cyclic voltammetry. Moreover, in independent studies, polymerizations were very poorly controlled when metal-free ligand initiators were coupled with Ni catalysts. The fact that similar metal-free polymer fractions were noted in certain control reactions run with MMA, $NiBr_2(PR_3)_2$ catalysts, and a soluble Ru analogue, $[Ru\{bpy(C_{13}H_{27})_2\}_3](PF_6)_2$, that lacks initiator sites suggests instead that a minor polymerization pathway could be operative—one that is independent of bromoester initiator functionalities attached to bipyridine ligands or complexes.

In bulk polymerizations, the emergence of a high molecular weight shoulder and higher PDIs is likely a result of star−star coupling at the end of the reaction once most monomer is consumed. For reactions of styrene with Ru initiators, radical coupling late in the polymerization was diminished with lower catalyst loadings.[20] However, this was not the case for bulk MMA polymerizations using the aforementioned Ni catalyst. Polymerizations employing less than 1 equiv of catalyst per bromide initiating site were not controlled. Non-first-order kinetics was observed, and there was no consistency in the relationship between the experimental M_n vs percent conversion plots and those predicted theoretically, based on monomer to initiator stoichiometry.

To determine if catalyst solubility and thermal stability were issues in bulk polymerizations using the ruthenium metalloinitiators, and for comparison with results obtained for $NiBr_2(PPh_3)_2$, reactions were also carried out using $NiBr_2(PBu_3)_2$. Again, the butyl groups in this catalyst were expected to afford the Ni catalyst greater stability at elevated temperatures. In summary, MMA polymerizations using $NiBr_2(PBu_3)_2$ resulted in linear M_n vs percent conversion plots that were slightly higher than theoretically predicted, indicative of inefficient initiation. In kinetics plots, there was an induction period of ~15 min, after which the rate of reaction was first-order with respect to monomer up to ~40% conversion. After this point, the kinetics plot gradually curved upward, indicating that the rate of polymerization increased as monomer was consumed. Increasing the catalyst loading by 100% increased this curvature, while having no effect on the M_n vs percent conversion plot. In both cases, PDIs were significantly higher than for reactions using $NiBr_2(PPh_3)_2$ (1.6−1.8 vs 1.1−1.2), and reaction rates were slower. Increasing monomer loading (1000:1:1 MMA:initiator site:catalyst) had no effect on the nonliving character of this reaction. Molecular weight distributions remained quite broad, and the kinetics was not first-order. Surprisingly, no polymer formed for reactions run in the presence of $NiBr_2(PBu_3)_2$ in toluene with either the Ru reagent **1** or ethyl 2-bromopropionate as the initiator.

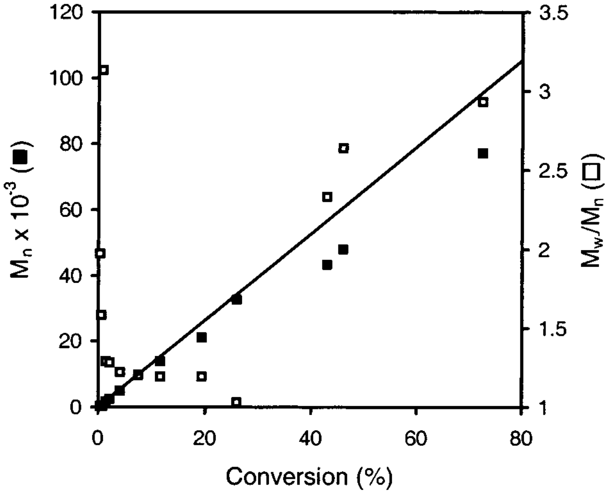

Figure 5. Number-average molecular weight vs percent conversion plot for the polymerization of MA with the secondary Ru(II) metalloinitiator, **2** using the $NiBr_2(PPh_3)_2$ catalyst in toluene solution at 80 °C (— = M_n calcd).

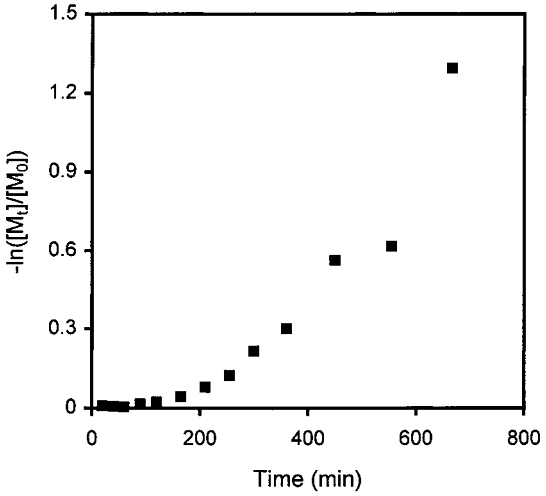

Figure 6. Kinetics plot for the polymerization of MA with the secondary Ru(II) metalloinitiator **2** using the $NiBr_2(PPh_3)_2$ catalyst in toluene solution at 80 °C.

Polymerizations with methyl acrylate (MA) were also carried out in bulk and in solution (toluene) using the secondary halide initiator, **2**. Reactions in bulk MA exhibited non-first-order kinetics with respect to monomer but displayed M_n vs percent conversion plots that were nearly linear for loadings of 250:1:1 (MA:$NiBr_2(PPh_3)_2$:initiator site) (Figures 5 and 6). Molecular weight distributions were moderate at low conversion (<40%; 1.2−1.5) and increased markedly as monomer was consumed (>40% conversion; 2.3−3.0). In toluene, the aforementioned reaction system produced no polymer after nearly 30 h. However, when using $NiBr_2(PBu_3)_2$, although kinetics were non-first-order, M_n vs percent conversion plots were reasonably linear with results corresponding quite well to those predicted theoretically. Lower PDIs were observed for polymers prepared with the butyl Ni catalyst (1.2−1.4 for <80% conversion; 1.6−1.8 for >80%) as compared with those

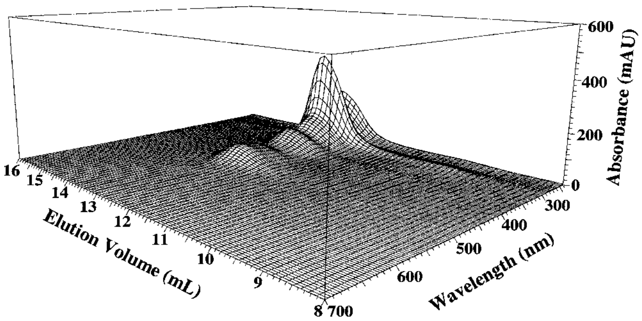

Figure 7. 3D correlation of the GPC elution volume and in-line diode array UV/vis spectra for a Ru tris(bipyridine)-centered six armed PMMA star.

generated using the phenyl catalyst under the same reaction conditions.

In summary, whereas $NiBr_2(PPh_3)_2$ was the preferred catalyst for MMA polymerizations, for MA, $NiBr_2(PBu_3)_2$ afforded faster rates and produced polymers with greater molecular weight control in both bulk monomer and in solution. These striking differences in reactivity and catalyst selection underscore the continuing need to screen a variety of conditions for reaction optimization, if ATRP is to be used as a practical method for preparing well-defined polymeric materials.

As an aside to studies mentioned thus far, "benzylic" halide metalloinititiators were also of interest for use in acrylate polymerizations. Along these lines, to produce Ru-centered poly(acrylic acids), it is necessary to prepare Ru-centered poly(acrylates) and to hydrolyze the pendant ester groups to acids. The aforementioned initiators, **1** and **2**, are not suitable for this purpose because polymer arms are attached to the Ru center via cleavable ester linkages that would likewise be severed during hydrolysis. Thus, acrylate polymerizations were attempted using $[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)_2$. With this initiator, bulk polymerizations of MMA exhibited a ~50 min induction period and non-first-order kinetics. Although the PDIs of the resulting PMMA samples were low, M_n vs percent conversion plots were not linear. Previously, it has been noted that chlorides are poor initiators for MMA.[48] Moreover, results with $[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)_2$ correlate with those previously reported by Sawamoto et al. using nonmetallic chloride initiators with the same family of $NiBr_2(PR_3)_2$ ATRP catalysts.[49]

Metal Content of Polymers. The presence of ruthenium in the polymeric samples was verified by GPC using in-line UV/vis, diode-array detection. A representative three-dimensional chromatograph of a $[Ru(bpyPMMA_2)_3]^{2+}$ sample is shown in Figure 7. Specifically, metal-to-ligand charge transfer (MLCT) bands were observed in eluant peaks at 465 nm—a signature of the $[Ru(bpy)_3]^{2+}$ core of the polymers. For a series of $[Ru(bpyPMMA_2)_3]^{2+}$ samples prepared under controlled conditions (i.e., $NiBr_2(PPh_3)_2$ catalyst in toluene), molar extinction coefficients (ϵ) were measured by UV/vis analysis using number-average GPC molecular weights to calculate polymer concentrations (Table 1). The ϵ values obtained in this manner were typically comparable to that of metalloinitiator **1** ($\lambda_{max} = 465$ nm, $\epsilon = 16\,607$ M^{-1} cm^{-1}), as anticipated for the targeted molecular structure bearing a single Ru ion at the center. However, the fact that these values are somewhat higher than the corresponding initiator and increase as the reaction progresses is consistent with aforementioned radical coupling reactions that occur to a minor extent at the start and end of the polymerizations. Both processes are expected to terminate active sites and to lead to Ru/polymer ratios that are slightly higher than anticipated.

Table 1. Molecular Weight and UV/Vis Data for a Series of Ru-Centered PMMA Star Polymers

M_n(MALLS) × 10^{-3}	M_w(MALLS)[a] × 10^{-3}	PDI	M_n(lin)[b] × 10^{-3}	M_w(lin)[b] × 10^{-3}	PDI	ϵ(465 nm)[c] (M^{-1} cm^{-1})
11.8	12.3	1.04	9.4	10.7	1.12	17 200
54.0	57.7	1.07	42.4	46.9	1.10	18 800
74.7	81.8	1.09	64.8	74.7	1.15	19 300
114.1	123.6	1.08	90.6	102.4	1.13	20 100
116.9	129.3	1.11	102.5	125.1	1.22	19 300

[a] Molecular weight determined by GPC in $CHCl_3$ at 25 °C using MALLS/RI detection. [b] Molecular weight determined by GPC in $CHCl_3$ at 25 °C using linear (lin) PMMA standards. [c] Molar extinction coefficient of the metal-to-ligand charge-transfer band determined using M_n(lin) to calculate sample concentration.

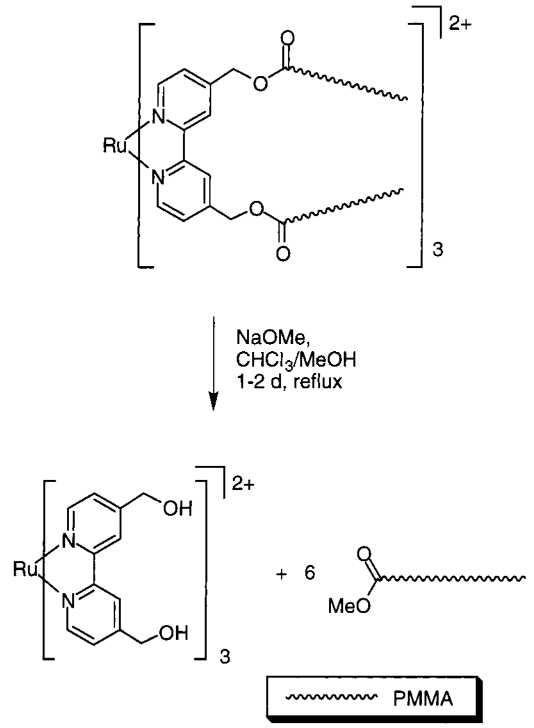

Figure 8. Schematic representation of the sodium methoxide catalyzed cleavage of PMMA linear arms from a $[Ru(bpyPMMA_2)_3]^{2+}$ star-shaped polymer.

Scission of Polymer Arms from Ru Cores. To ascertain the uniformity of the arms of Ru PMMA star polymers (i.e., those in Table 1), the arms were cleaved from their corresponding ruthenium cores. Scission was effected by transesterification with NaOMe in MeOH/$CHCl_3$ at 120 °C in a sealed tube for 1–2 days (Figure 8).[7,50] Cleaved PMMA samples were analyzed by GPC with MALLS and RI detection. A summary of molecular weight data is given in Table 2, and a representative GPC overlay of the refractive index traces for a star polymer and the corresponding cleaved linear PMMA is shown in Figure 9. In short, molecular weights for the polymer arms were, in general, roughly one-sixth of the M_n of the star polymers, as was expected for six-arm architectures. Again, the occurrence of some radical coupling reactions at the start and end of the polymerizations accounts for arm/star ratios that are slightly lower than anticipated. PDIs for the polymer arms were

Table 2. Molecular Weight Data for PMMA Arms Cleaved from Ru-Centered Star Polymers[a]

M_n(calcd)(MALLS) × 10^{-3}	M_n(MALLS)[b] × 10^{-3}	PDI	arms/star	M_n(calcd)(lin) × 10^{-3}	M_n(lin)[c] × 10^{-3}	PDI	arms/star
8.9	8.1	1.08	6.6	6.9	8.0	1.13	5.2
12.3	12.5	1.15	5.9	10.7	13.6	1.17	4.7
18.9	21.1	1.03	5.4	15.0	21.3	1.10	4.3
19.3	22.9	1.09	5.1	16.9	22.9	1.24	4.4

[a] Star polymers from Table 1 (last four entries) were used in arm scission reactions. The molecular weight of the arms of the star polymer in entry one (Table 1) was too low to measure accurately using standards or MALLS/RI detection. [b] Molecular weight determined by GPC in $CHCl_3$ at 25 °C using MALLS/RI detection. [c] Molecular weight determined by GPC in $CHCl_3$ at 25 °C using linear (lin) PMMA standards.

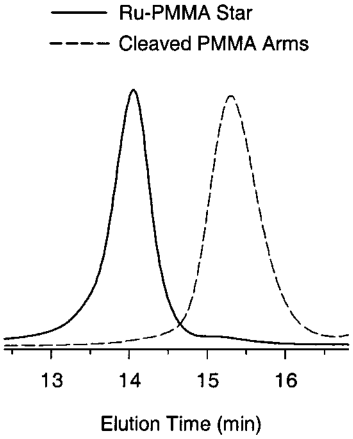

Figure 9. GPC overlay of a ruthenium-centered PMMA star (M_n = 54 000) and the linear PMMA arms (M_n = 8060) obtained after scission.

low (1.10−1.24), suggesting that the arms of the Ru−PMMA precursors were of uniform length and that initiation from **1** was efficient and fast relative to propagation. These results compare favorably with previous arm scission reactions for PMMA stars prepared from multifunctional calixarene initiators.[7] The MLCT band characteristic of the ruthenium core was also absent in the polymers, as determined by GPC analysis with in-line UV/vis detection (vide supra) and UV/vis analysis of purified polymers.

Thermal Stability of Ruthenium-Centered PMMA. DSC analysis of Ru-centered PMMAs prepared from **1** using 1 equiv of catalyst per initiating site displayed glass transitions at 126 °C, a temperature (T_g) that is comparable to values reported by Jérôme et al. for linear PMMA prepared with the same catalyst under identical conditions.[37] TGA analysis indicated a slight loss of mass (<5%) at ~230 °C. Thus, coupling and disproportionation reactions, which result in degradation at 160 and 270 °C, respectively, appear to be minor.[37,51] The onset of thermal degradation occurred at 362 °C, as expected.[37]

The DSC analysis of a Ru-centered PMA displays a T_g at 17 °C. The polymer shows a slight loss of mass (<10%) at ~230 °C, with the onset of further thermal degradation occurring at ~340 °C.

Conclusions

Using the commercially available catalyst $NiBr_2(PPh_3)_2$, the synthesis of ruthenium-centered, six arm star-shaped poly(methyl methacrylates), $[Ru(bpyPMMA_2)_3]^{2+}$, with molecular weights ranging from M_w = ~3000−350 000 (PDIs < 1.3) has been achieved. Results from kinetics experiments and arm scission reactions likewise indicate that solution polymerizations are controlled. In this manner, chromophores may be selectively introduced into well-defined PMMA architectures, and this further demonstrates that metal complexes serve as useful, functional templates for polymer synthesis. The effects of side reactions on molecular weight control are often amplified for multifunctional initiators. The fact that such reactions are minimal with hexafunctional initiator **1** and preliminary results obtained with a difunctional Ru complex suggest that the synthetic approach reported herein should readily extend to analogous $[Ru(bpy)_3]^{2+}$ reagents with one to five initiating sites to generate other linear and star-shaped polymer architectures. For methyl acrylate, Ru-containing polymers with relatively narrow molecular distributions were obtained. Although molecular weight increases in a linear fashion with percent monomer conversion for $[Ru(bpyPMA_2)_3]^{2+}$ preparations, kinetics plots for both solution and bulk reactions are not consistent with "living" polymerizations. The controlled Ni-catalyzed ATRP metalloinitiator methodology may be applied to different metal complexes and monomers. Combination with different approaches to polymeric metal complexes and other controlled polymerization methodologies promises to yield even more elaborate block copolymer targets.

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Supporting Information Available: Figures showing the ^1H NMR spectrum of metalloinitiator **2** in CD_3CN and a number-average molecular weight vs percent monomer conversion plot with polydispersities indicated for the bulk polymerization of MMA catalyzed by $NiBr_2(PPh_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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