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3-Aminopropyl Silica Supported Living Radical Polymerization of Methyl Methacrylate: Dichlorotris(triphenylphosphine)ruthenium(II) Mediated Atom Transfer Polymerization

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ABSTRACT: 3-Aminopropyl-functionalized silica support (APSS) has been used as a solid support for the heterogeneous atom transfer polymerization of methyl methacrylate (MMA), to poly(methyl methacrylate) (PMMA), mediated by adsorbed $RuCl_2(PPh_3)_3$ as catalyst. This system displays characteristics of a living radical polymerization as indicated by (i) an increase in the number-average molecular weight (M_n) with conversion, (ii) relatively low polydispersity indexes (PDI), and (iii) linear first-order rate plots. When PMMA of $M_n = 20\,000$ g mol^{-1} was targeted, the reaction reached 91% conversion after 4 h with a measured $M_n = 21\,500$ g mol^{-1} and PDI = 1.49. It was found that polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ in the presence of APSS does not require the addition of an aluminum alkoxide (e.g., Al(O*i*Pr)$_3$) as an activating reagent. The rate of reaction is higher than for similar homogeneous reactions; however, the polydispersity indexes are also higher. The ruthenium content of polymers thus produced is typically approximately 0.1% w/w, corresponding to about 90% of the metal remaining adsorbed onto the surface of the support. This is thus an effective method of minimizing the metal content of the final polymer without postreaction purification. It is also shown that the supported catalyst can be reused for subsequent polymerization reactions. The polymers produced via this heterogeneous process can be subsequently used as macroinitiators to synthesize block copolymers and hence contain active halogen end groups.

Introduction

The synthesis of methacrylate polymers using living radical polymerization techniques has been the focus of much attention in the literature of recent years.[1] The advantages of using a radical/radical-like based process, as compared to an anionic process, is that reaction is tolerant to many impurities and protic species present in the medium (e.g., from solvents, monomers, impurities, etc.).

Transition metal mediated living radical polymerization, or atom transfer polymerization, has developed as probably the most efficacious technique for the controlled polymerization of acrylic monomers under free-radical-like conditions. Atom transfer polymerization has been developed by Matyjaszewski[2−4] and Sawamoto,[5−8] utilizing Cu(I)X/bipyridines (X = Cl, Br) and $RuCl_2(PPh_3)_3$, respectively. This approach to polymerization is derived from the Kharash reaction which is used widely in organic synthesis for intramolecular cyclizations.[9] A number of different systems using transition metal complexes to polymerize styrenes, methacrylates, and acrylates have been reported including $[Ni(PPh_3)_3X_2]$,[10] $[Ni(o,o'(CH_2NMe_2)_2C_6H_3)Br]$,[11] $[Pd(OAc)_2(PPh_3)_4]$,[12] $[Rh(PPh_3)_3Cl]$,[13] and $FeCl_3/PPh_3$.[14] In our laboratories we have been developing catalysts based on Cu(I)X and *N*-alkyl-2-pyridylmethanimine Schiff base ligands.[15−19] The attraction of these catalysts is that the Schiff base ligands are relatively simple to synthesize and allow scope to vary the catalyst properties (e.g., redox potential, solubility) by changing the appropriate substituent groups in the ligand. As a result, polymers of specific architectures and functionalities can be produced in undemanding conditions. Reactions may be carried out at relatively high temperatures (60−130 °C) in a range of solvents. High-purity solvents are not required, precluding the need for distillation steps, and indeed the presence of conventional stabilizers and acids (present from monomer manufacturing processes) can accelerate reaction rates.[17,19]

Perhaps the main disadvantage of all these systems is the high concentrations of *catalyst* required in the polymerizations for acceptable overall rates of reaction. Typical [monomer]:[catalyst] ratios are 100:1 with stoichiometric amounts of initiator and catalyst for polymers with $M_n = 10\,000$ g mol^{-1}. These high concentrations of catalyst cause the reaction solutions to be highly colored and increase the cost of the process. A potential solution to this problem is the use of supported catalysts. The advantage of using solid supported catalysts is that they are easily removed from the final product, even if present in high concentrations, and have the potential to be recycled (which reduces the net cost). The use of inorganic supports, e.g. silica, has found widespread use in the polymerization of olefins.[20] The extension of this approach to the use of functionalized inert poly(styrene) as supports for vanadium ethylene polymerization catalysts has also been recently described.[21] Previously we have published the effective polymerization of MMA mediated by supported Cu(I)Br complexes (using supported Schiff base ligands), prepared from both primary 3-aminopropyl-functionalized silica support and cross-linked poly(styrene) resins, via an atom transfer polymerization process.[22]

In this work we have used 3-aminopropyl-functionalized silica support as a solid support (APSS) for $RuCl_2$-

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Table 1. Mole Ratios of Reactants Used in Polymerization Reactions[a]

expt	MMA	In[b]	Ru[c]	Si−NH$_2$[d]
1	100	0.5	1	4
2	100	1	1	4
3	100	2	1	4
4	100	2	1[e]	4[e]
5	100	1	1	2
6	100	0.338[f]	1	2
7	63[g]	0.338[f]	1	2
8	100	1	1	2[h]
9	100	1	0.5	2
10	100	1	0.5	silica[i]
11	100	1	0.5	alumina[j]
12	100	1	1	8
13	100	1	2	8

[a] All reactions 25 vol % monomer in toluene at 90 °C. [b] Ethyl 2-bromoisobutyrate. [c] $RuCl_2(PPh_3)_3$. [d] $[NH_2]$ on 3-aminipropyl-functionalized silica support (APSS). [e] Reused the catalyst from experiment 3. [f] MMA macroinitiator, as per experiment 5, conversion = 41%, $M_n = 9470$, and PDI = 1.26 after precipitation into petroleum spirit. [g] Benzyl methacrylate (BzMA). [h] 4 equiv of $Al(O\mathit{i}Pr)_3$. [i] Standard silica gel. [j] Basic aluminum oxide.

Table 2. Results from Polymerization Reactions

expt	time/min	conv/%	$k_p^{app}/10^{-4}$ s^{-1} [a]	M_n^{theo} [b]	M_n[c]	PDI[c]
1	240	91.1	1.76	18 400	21 500	1.49
2	240	96.2	2.35	9 820	10 800	1.57
3	180	90.9	2.25	4 740	6 780	1.56
4	240	88.5	1.44	4 620	6 770	1.73
5	180	85.2	2.16	8 720	11 350	1.39
6	200	73.0		30 800	25 100	1.42
7	200	91.6		39 300	27 000	1.35
8	180	64.6	0.762	6 660	6 220	1.39
9	180	77.7	1.44	7 970	10 500	1.55
10	240	42.2	0.226	4 420	7 850	1.67
11	240	39.5	0.226	4 150	7 240	1.57
12	120	88.5	2.88	9 050	11 300	2.22
13	180	94.2	2.80	9 620	11 900	1.54

[a] Apparent first-order rate coefficient determined from the slope of the line of best fit, $\ln [M]_0/[M] = k_p[Pol^*]t = k^{app}t$, where k_p is the propagation rate coefficient and $[Pol^*]$ is the concentration of growing polymer chains. [b] Theoretical M_n = conv/100 × [M]/[In] × $MW_M + MW_{In}$. [c] Determined using SEC against poly(MMA) standards.

$(PPh_3)_3$ to mediate the polymerization of MMA. To investigate this system, several of the reaction parameters were varied, as well as, demonstrating reinitiation, to produce block copolymers, and reuse of the catalyst in subsequent reactions. The reactions were performed with 25 vol % MMA in toluene solution with ethyl 2-bromoisobutyrate as the initiator.

After this paper was submitted, Matyjaszewski and co-workers published work on the immobilization of copper catalysts for effective atom transfer radical polymerisation.[23]

Experimental Section

General Information. Methyl methacrylate (MMA) (Aldrich, 99%) was purified by passing through a column of activated basic alumina so as to remove the inhibitor. Toluene (Fisons, 99.8%), dichlorotris(triphenylphosphine)ruthenium(II) ($RuCl_2(PPh_3)_3$) (Johnson Matthey, 98%), ethyl 2-bromoisobutyrate (Aldrich, 98%), 3-aminopropyl-functionalized silica gel (Aldrich, ~9% functionalized, ~1.05 mmol of NH_2 g^{-1}), and diethyl ether (BDH, 98%) were used as received. MMA and toluene were deoxygenated by purging with nitrogen for 1 h prior to use.

Polymerization Procedure. A typical polymerization procedure is as follows (experiment 2): 0.45 g of $RuCl_2(PPh_3)_3$ (4.69×10^{-4} mol) and 1.80 g of 3-aminopropyl-functionalized silica (1.89×10^{-3} mol of NH_2) were added to a Schlenk tube and subjected to three vacuum/nitrogen cycles. To this mixture was added 5 mL of deoxygenated MMA (4.67×10^{-2} mol) and 15 mL of deoxygenated toluene. Complexation of the catalyst to the support is considered to be instantaneous. The mixture was subsequently heated to 90 °C with magnetic stirring. Polymerization was initiated by the addition of ethyl 2-bromoisobutyrate, 0.069 mL (4.69×10^{-4} mol); periodically 1−2 mL samples were removed for conversion and molecular weight analysis. Table 1 shows the exact experimental conditions for each experiment.

Catalyst Reuse. After the polymerization reaction the solution was left to stand, without stirring, so as to allow the support to settle. The resulting clear polymer solution was removed via cannula and the solid support washed twice with 20 mL of degassed toluene and then dried in vacuo. To the dry solid support was added MMA, toluene, and initiator (no additional $RuCl_2(PPh_3)_3$ or APSS), and the mixture was heated to 90 °C.

Reinitiation. To demonstrate reinitiation, the A block was isolated by first decanting the reaction solution (after allowing the catalyst to settle) and dilution with dichloromethane prior to precipitation into cold petroleum spirit; residual solvent was removed in vacuo at ambient temperature ($M_n = 9190$, PDI = 1.24). The purified polymer (1.45 g) was then used as a macroinitiator, in place of ethyl 2-bromoisobutyrate, to polymerize both MMA and benzyl methacrylate (BzMA) under identical polymerization conditions.

Residual Ruthenium Analysis. The residual ruthenium was determined using a Leeman Labs inductively coupled plasma atomic emission spectrophotometer calibrated with Leeman Labs ICP standards. Samples were prepared by digesting approximately 6 mg of polymer in 2.5 mL of concentrated H_2SO_4/1 mL of concentrated HNO_3 (Fischer, Primar Grade) and then diluting the solutions up to 50.0 mL with deionized water.

Polymer Analysis. Polymer conversions were determined by gravimetry, initially evaporating the majority of the volatiles in a fume cupboard at ambient temperature and then taking to constant weight in a vacuum oven at 70 °C. Molecular weight distributions were measured using size exclusion chromatography (SEC), on a system equipped with a guard column, two 30 cm mixed D columns (Polymer Laboratories), and a differential refractive index detector, using tetrahydrofuran at 1 mL min^{-1} as eluent. The SEC was calibrated with 12 poly(MMA) standards in the range 6.85×10^5 to 200 g mol^{-1}.

Results and Discussion

Methyl methacrylate (MMA) was polymerized with ethyl 2-bromoisobutyrate as initiator and mediated by $RuCl_2(PPh_3)_3$ in conjunction with 3-aminopropyl-functionalized silica support (APSS) in toluene at 90 °C (experiment 1). The concentration of NH_2 groups, from the APSS, was chosen to be 4 times the $RuCl_2(PPh_3)_3$ concentration. The exact nature of the interaction between the support and the catalyst has not been investigated, but it is envisaged that the amino group on the support acts as a N-donor ligand displacing a phosphine ligand. Experimental conditions are given in Table 1 and results in Table 2. Reaction 1 yielded PMMA in 91% conversion after 4 h with a number-average molecular weight (M_n) of 21 500 g mol^{-1} and a polydispersity index (PDI) of 1.49. Figure 1 shows the linear increase of M_n with conversion, as would be expected for a living polymerization system. At low conversion the M_n is significantly higher than the theoretical value; however, beyond 50% conversion M_n does increase linearly with conversion (although remaining at slightly higher than the theoretical value). The PDI decreases from 1.9 to 1.49 as the reaction proceeds. The PDI of the final product is higher than a

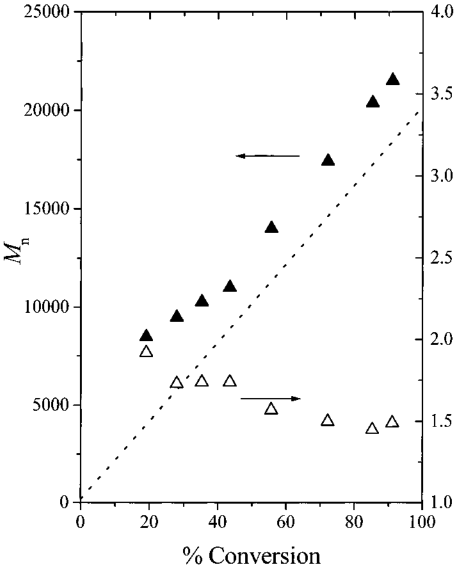

Figure 1. Dependence of M_n and PDI on conversion for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiment 1). [MMA]:[EBrIB]:[$RuCl_2(PPh_3)_3$]:[Si−NH_2] = [100]:[0.5]:[1]:[4], 25 vol % in toluene at 90 °C. Dotted line is the theoretical M_n.

comparable homogeneous reaction, with the same initiator and Al(O*i*Pr)$_3$, as cocatalyst (PDI = 1.3);[6] however, it is significantly lower than that obtained for conventional free-radical polymerization and suggests that the reaction is proceeding in a *living fashion* by reversible activation of C−Br ω-terminii of the growing polymer chains, as in conventional atom transfer polymerization (i.e., in the absence of an inorganic support).

The reaction mixture remained a deep red/brown color throughout the polymerization, typical for this type of reaction. Once agitation was ceased, the supported catalyst settled to the bottom of the flask, leaving a lightly orange-colored solution which can be easily separated from the catalyst by filtration, decanting, etc.

All of the reactions reported here were performed without an aluminum cocatalyst such as methylaluminum bis(2,6-di-*tert*-butylphenoxide)[5] or aluminum triisopropoxide (Al(O*i*Pr)$_3$)[6] which Sawamoto reports is necessary to effect polymerization. Presumably, in the present system, the 3-aminopropyl-functionalized silica support plays a comparable role to the aluminum compound.

Effect of Initiator Concentration. The effect of the initiator concentration was assessed by targeting three final molecular weights: 5000, 10 000, and 20 000, experiments 3, 2, and 1, respectively. Figure 2 shows a comparison of the theoretical and measured M_n for these three experiments The theoretical M_n is proportional to conversion, in the case of a living polymerization, and hence this the figure shows evolution of molecular weight with conversion. In each case the molecular weight increases relatively linearly with conversion. Initially, the M_n's are higher than predicted; however, as conversion proceeds, the values approach the theoretical line. The final point in each experiment is close to the theoretical value (Table 2), which suggests a high initiator efficiency.

The first-order rate plots for these experiments (Figure 3) are linear, which suggests a constant concentration of active species throughout the reaction. There is no sign of an induction period, which is often present due to the presence of residual oxygen or the time taken to form the active catalytic species. Surprisingly, experiments 1 and 2 have almost the same rate of polymerization even though the initiator concentration differs by a factor of 2 (Figure 2), while experiment 3 has a slower rate; however, not half the rate as might be predicted. Thus, the atom transfer reaction in the presence of APSS *does not* follow a simple first-order dependence in initiator as in homogeneous atom transfer polymerization.

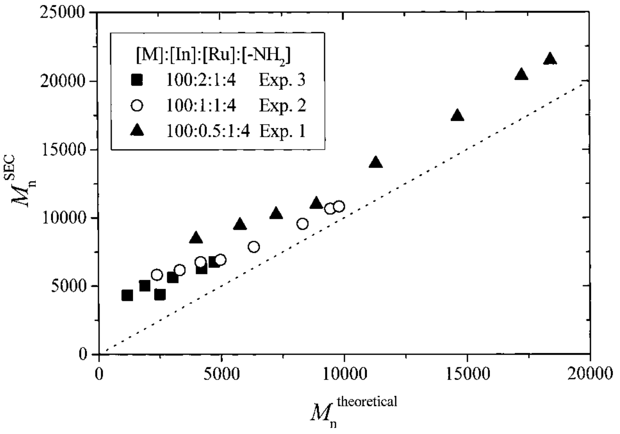

Figure 2. Effect of the initiator concentration on the evolution of M_n with conversion. Comparison of measured M_n (SEC) with the theoretical M_n (proportional to conversion) for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiments 1−3). Lines are the theoretical M_n in all cases.

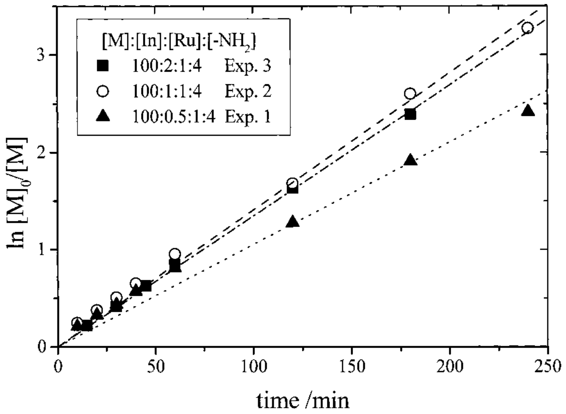

Figure 3. Effect of the initiator concentration on the first-order rate for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiments 1−3). Lines are best fits from linear regression analysis.

Reuse of the Catalyst. The $RuCl_2(PPh_3)_3$/3-aminopropyl silica support isolated from experiment 3 was reused in a subsequent polymerization so as to demonstrate that it is still active after a polymerization reaction, experiment 4. Following polymerization, experiment 3, the reaction solution was left to stand so as to allow the $RuCl_2(PPh_3)_3$/3-aminopropyl silica support to settle to the bottom of the Schlenk tube. The clear/transparent polymer solution was removed via cannula and the residual solid washed twice with 20 mL of degassed toluene prior to being dried in vacuo. Reuse of the catalyst was achieved by the addition of MMA, toluene, and initiator (no additional $RuCl_2(PPh_3)_3$ or APSS) to the washed supported catalyst. The first-order rate plots are shown in Figure 4. It is clear that the catalyst is still active when reused. The activity is lower in the second polymerization with the rate of reaction decreasing by approximately 25% compared to

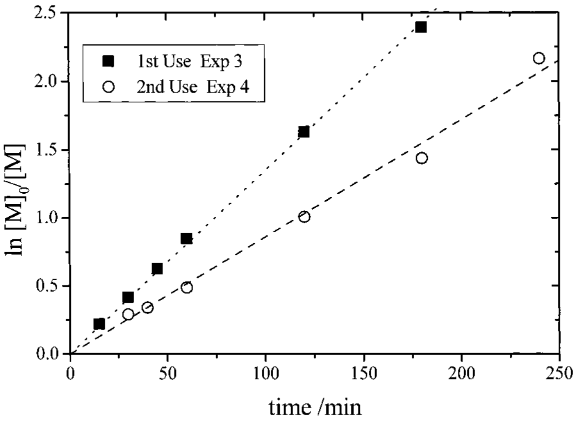

Figure 4. Reuse of the catalyst. First-order rate plots for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiments 3 and 4). Lines are best fits from linear regression analysis.

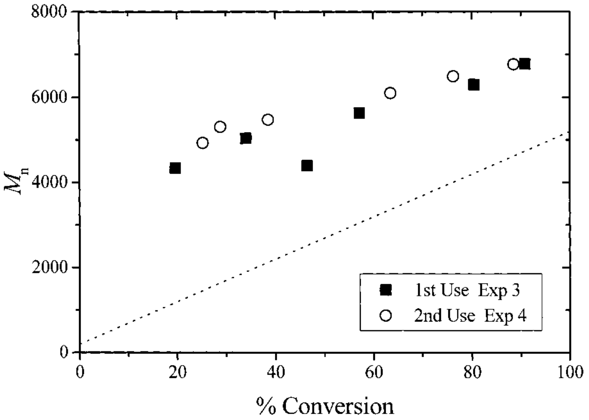

Figure 5. Reuse of the catalyst. Dependence of M_n with conversion for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiments 3 and 4). Dotted line is the theoretical M_n.

the first polymerization. The reduction in catalytic activity may be due to several reasons: (i) some loss of the supported catalyst when removing the polymer solution and during subsequent washings, (ii) oxidation and thus deactivation of the Ru(II) to Ru(III) during the first polymerization reaction, an inherent reaction during atom transfer polymerization, and (iii) degradation of the catalyst due to unidentified side reactions. The M_n vs conversion behavior is very similar for both reactions (Figure 5), and the polydispersity index of the polymer made with reused catalyst is higher than in the initial reaction (1.71 vs 1.56).

Reinitiation To Make Block Copolymers. To confirm that the polymers made with the silica support contain active ω-halogen end groups, reinitiation experiments with polymers from supported atom transfer polymerization were used as macroinitiators to polymerize both MMA and benzyl methacrylate (BzMA). The first block MMA was synthesized under the same conditions as experiment 5, but the reaction was stopped after 41% conversion and isolated by precipitation into petroleum spirit. The polymer was subsequently used in as a macroinitiator in a second silica supported reaction. Figure 6 shows the molecular weight distribution of the starting MMA macroinitiator, as detected by DRI (first block), and the subsequent regrowth with more MMA (experiment 6) and block copolymer with BzMA (experiment 7). The M_n increased from 9190 to 25 100 and 27 000 for MMA and BzMA, respectively. The final polydispersity indexes were 1.42 and 1.35, respectively. From Figure 6 it is clear that the second growth polymers only have a very small low molecular weight tail which indicates that the majority of chains from the first block undergo reinitiation. Thus, it is possible to synthesize block copolymers by supported polymerization using $RuCl_2(PPh_3)_3$ in the presence of APSS.

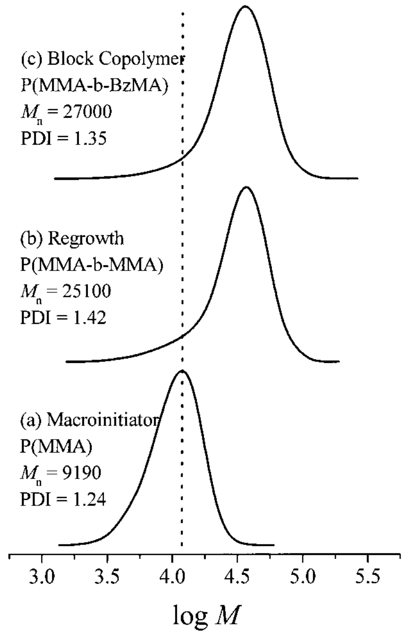

Figure 6. Molecular weight distributions of (a) initial MMA block (as per experiment 5), (b) regrowth with more MMA (experiment 6), and (c) regrowth with BzMA to make block copolymer (experiment 7). (a) The first block is made under the same conditions as experiment 5 but stopped at conversion = 41%, M_n = 9190, and PDI = 1.24 after precipitation into petroleum spirit. (b) MMA regrowth: conversion = 73%, M_n = 25 100, and PDI = 1.42 (unprecipitated). (c) BzMA block copolymer: conversion = 92%, M_n = 27 000, and PDI = 1.35 (unprecipitated).

Residual Ruthenium in Polymers. The residual ruthenium content in the polymers was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The polymers were obtained directly from the reaction solution, after allowing the APSS to settle, by evaporation of the solvent; no purification steps were performed; i.e., they were not passed over any column or precipitated. The ruthenium content in the polymers obtained from experiments 5, 6, and 13 were 0.11, 0.08, and 0.12% w/w, respectively, which is significantly less than the theoretical value of 1% w/w if all of the ruthenium remained in the polymer. Thus, the presence of the 3-aminopropyl silica support reduces the ruthenium level in the final polymers by approximately 90%.

Effect of $Al(OiPr)_3$. In the work of Sawamoto, aluminum triisopropoxide (or similar aluminum alkoxide compound) has been used in conjunction with $RuCl_2(PPh_3)_3$ to ensure polymerization.[5-8] Without the aluminum alkoxide as cocatalyst it was reported that no polymerization ensues.[5] In the present work it has been found that aluminum alkoxide is not required in order for the polymerization to proceed. To test the importance of a cocatalyst, the effect of $Al(OiPr)_3$ on the APSS supported reaction was investigated. Figures 7 and 8 show the first-order rate plots and M_n vs conversion

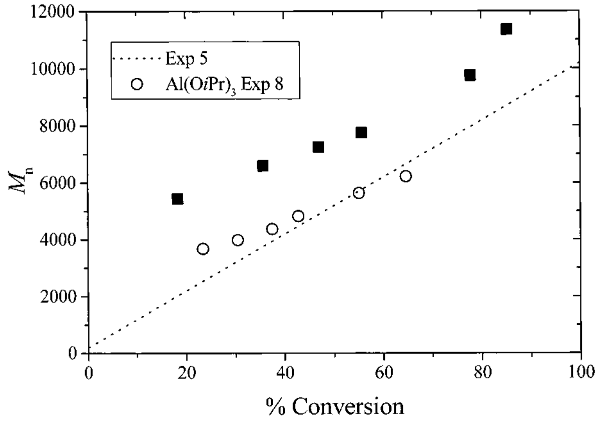

Figure 7. Effect of Al(O*i*Pr)$_3$. First-order rate plots for the polymerization of MMA mediated by RuCl$_2$(PPh$_3$)$_3$ with APSS (experiments 5 and 8). Lines are best fits from linear regression analysis.

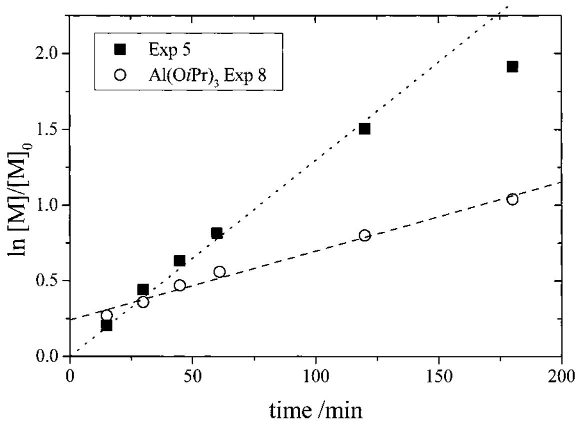

Figure 8. Effect of Al(O*i*Pr)$_3$. Dependence of M_n and PDI on conversion for the polymerization of MMA mediated by RuCl$_2$(PPh$_3$)$_3$ with APSS (experiments 5 and 8). Dotted line is the theoretical M_n.

plots, respectively, with and without added Al(O*i*Pr)$_3$ (experiments 8 and 5). Surprisingly, under these reaction conditions (in the presence of APSS), the addition of Al(O*i*Pr)$_3$ slows the rate of polymerization. However, better molecular weight control is achieved with cocatalyst with M_n vs conversion following the theoretical line more closely; the final PDI's from both reactions are similar. Since the addition of Al(O*i*Pr)$_3$ did not significantly improve the reaction, it was not used as an additive in subsequent reactions.

Different Supports. To assess the importance of the primary amino functionality on the 3-aminopropyl-functionalized silica support, two other solid support additives were investigated: standard silica gel (experiment 10) and basic aluminum oxide (experiment 11). Both of these agents are commonly used to remove soluble catalysts from polymer solutions following homogeneous atom transfer polymerization reactions. From the first-order rate plots (Figure 9) it can be seen that the rates of polymerization in the presence of both standard silica gel and basic aluminum oxide are significantly lower than in the presence 3-aminopropyl-functionalized silica support. There was no apparent effect on the dependence of either the M_n, Figure 10, or the PDI's on conversion, Table 2 (experiments 9–11). Thus, the primary amino groups on the surface of the APSS seem to be important for the formation of the active catalyst species.

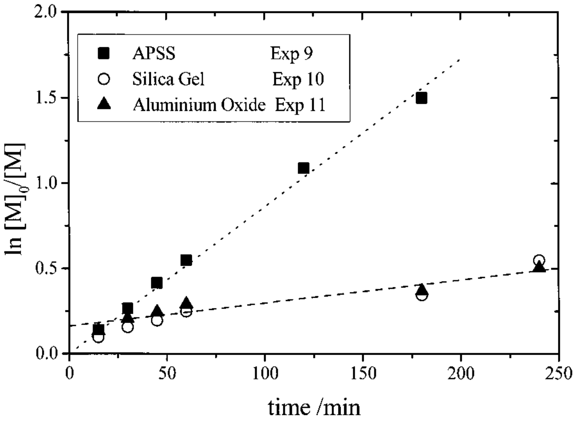

Figure 9. Effect of the type of support. First-order rate plots for the polymerization of MMA mediated by RuCl$_2$(PPh$_3$)$_3$ with various additives (experiments 9–11).

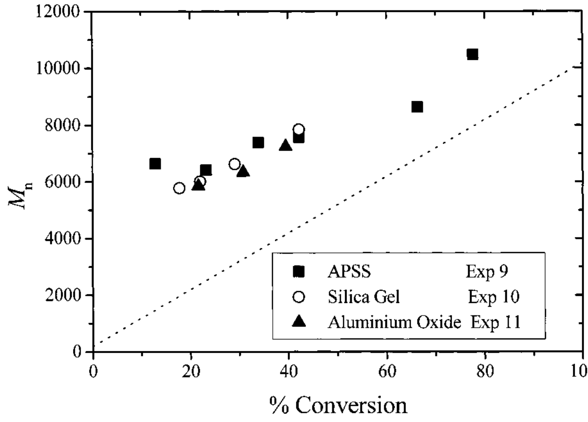

Figure 10. Effect of the type of support. Dependence of M_n and PDI on conversion for the polymerization of MMA mediated by RuCl$_2$(PPh$_3$)$_3$ (experiments 9–11). Dotted line is the theoretical M_n.

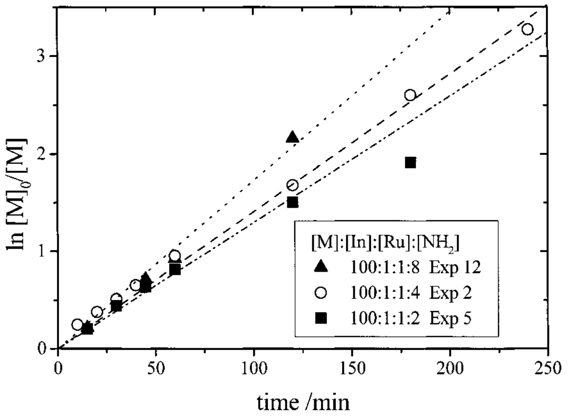

Figure 11. Effect of the concentration of APSS. First-order rate plots for the polymerization of MMA mediated by RuCl$_2$(PPh$_3$)$_3$ with APSS (experiments 12, 2, and 5). Lines are best fits from linear regression analysis.

Effect of APSS Concentration. The effect of the 3-aminopropyl-functionalized silica support concentration on the reaction (experiments 2, 5, and 12) is shown in Figures 11 and 12 and Table 2. Figure 11 shows that there is only a slight increase in the rate of polymerization as [$-$NH$_2$]/[Ru] is increased from 2 to 8. The M_n vs conversion data (Figure 12) are also quite similar. The PDI's (Table 2) show a significant dependence on the APSS concentration, reducing from 2.22 for the highest level down to 1.39 for the lowest level. Thus,

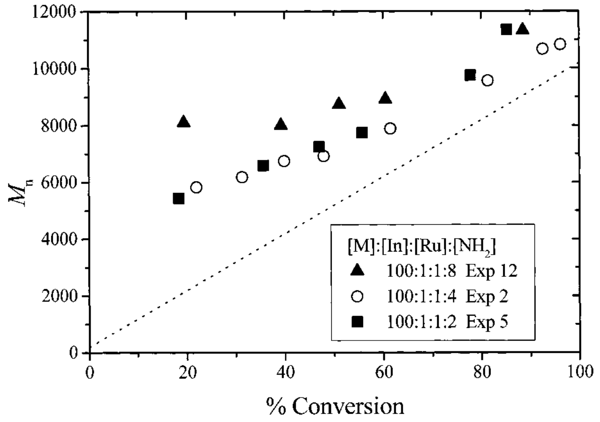

Figure 12. Effect of the concentration of APSS. Dependence of M_n and PDI on conversion for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiments 12, 2, and 5). Dotted line is the theoretical M_n.

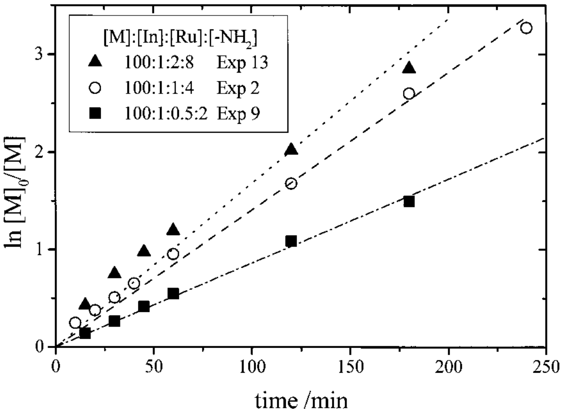

Figure 13. Effect of the $RuCl_2(PPh_3)_3$ concentration. First-order rate plots for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiments 13, 2, and 9).

the increase in rate observed is at the expense of the polydispersity index. This is as expected as an increase in rate for atom transfer polymerization always results in a higher concentration of polymer based radicals which leads to an increase in the rate of termination and a broadening of PDI.

Effect of Catalyst Concentration. The effect of catalyst concentration was assessed by varying the $RuCl_2(PPh_3)_3$ (experiments 2, 9, and 13; Figures 13 and 14). In each case $[-NH_2]/[Ru]$ was maintained at 4. The rate of reaction increases as the catalyst concentration is increased; however, the rate dependence is not first order in catalyst. The dependence of M_n on conversion similar for each reaction, with experiment 2 being slightly better than the other two.

Conclusions

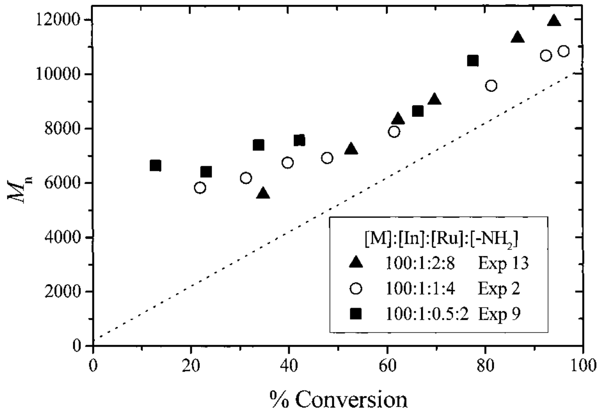

Figure 14. Effect of the $RuCl_2(PPh_3)_3$ concentration. Dependence of M_n and PDI on conversion for the polymerization of MMA mediated by $RuCl_2(PPh_3)_3$ with APSS (experiments 13, 2, and 9). Dotted line is the theoretical M_n.

This work has shown that it is possible to use 3-aminopropyl-functionalized silica support as a solid support for the atom transfer polymerization of methyl methacrylate mediated by $RuCl_2(PPh_3)_3$. It is envisaged that the amino functionality of the support act as a donor ligand to ruthenium, displacing at least one of the phosphine ligands. Although this reduces the acceptor capability of the ligand system, effective atom transfer polymerization is observed. The overall rate of polymerization is higher than observed for similar homogeneous reactions which manifests as polymer products with broader PDI's. The supported catalyst can be reused for subsequent polymerization reactions. The polymers produced from this system contain the active ω-halogen end group which can be used to reinitiate polymerization and hence allows for the synthesis block copolymers. The presence of the APSS in the reaction medium reduces the residual ruthenium content of the final polymer by approximately 90%. When using APSS, it was found that it is not necessary to use an activating agent such as $Al(O\textit{i}Pr)_3$.

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Supporting Information Available: Tables giving further polymerization conversion and molecular weight data. This material is available free of charge via the Internet at http://pubs.acs.org.

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