# Reversible Catalyst Supporting via Hydrogen-Bonding-Mediated Self-Assembly for Atom Transfer Radical Polymerization of MMA

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ABSTRACT: Atom transfer radical polymerization (ATRP) is a very useful living/controlled radical polymerization process for polymer synthesis, but its products are contaminated with transition metal catalyst residue. Catalyst immobilization on solids via covalent binding has the advantages of easy catalyst separation and reuse, but it deteriorates the control of the polymerization due to the slowed radical deactivation, which causes chain termination and uncontrolled propagation. In this paper, we report a reversible catalyst supporting concept via hydrogen-bonding-mediated self-assembly. The support acts as a "catalyst sponge" releasing the catalyst as free molecules at elevated temperatures for effective catalysis but absorbing the catalyst after the polymerization for separation. The support was polystyrene gel functionalized with maleimide or thymine units, and the catalyst was tethered on a diaminopyridine unit. A triple hydrogen bond array formed between maleimide or thymine and diaminopyridine at room temperature but broke at elevated temperatures. At 60 °C, the reversibly supported catalyst efficiently polymerized MMA in a well-controlled living manner, yielding PMMA with polydispersity as low as those by unsupported catalysts. The recycled catalysts still mediated MMA polymerization with a much improved control.

## Introduction

Atom transfer radical polymerization (ATRP), a living radical polymerization based on the reversible activation/deactivation equilibrium between the active and dormant species mediated by transition metal complexes, such as CuBr/2bipyridine, is a very versatile tool for the synthesis of well-controlled polymer architectures.[1−5] It polymerizes various vinyl monomers such as styrenes, (meth)acrylates, acrylamides, vinylpyridines, and acrynitriles in a living manner.[5] It has also been used to prepare well-defined polymers with various functionalities, compositions, and architectures,[5] including liquid-crystalline polymers,[6] block,[7] star,[8] graft,[9] comb,[10] dendrimer-like,[11] and hyperbranched (co)polymers,[12] and hybrids with inorganic/organic polymers[13] as well as other complex structures.[14]

The challenge of ATRP is that its resulting polymers are contaminated with its catalyst residue, which brings the products color and toxicity. On lab scale, ATRP products are usually purified by passing a column of silica gel or alumina, reprecipitation,[15] or treatment with ion-exchanged resin.[16] However, these treatments are expensive and not applicable to large industrial scales. In addition, these methods cannot recycle and reuse the catalysts. Biphase separation from ionic liquid,[17] fluorous biphases,[18] and emulsion[19] have also been used to directly remove the catalyst residue.

Catalyst immobilization on solids is widely used in industry for efficient catalyst separation and reuse of the catalysts. This concept has also been tested by supporting the catalysts on silica gel, polystyrene beads, and Janda Jel resins for batch[20,21] and continuous ATRP.[22] Unfortunately, these solid supported catalysts generally had less control over the polymerizations, producing polymers with much higher molecular weights than theoretical ones and broader molecular weight distributions[20] due to the heterogeneous nature. Homogeneous supported catalysts were later developed and found to have better control over the polymerization.[23] Recently, an immobilized/soluble hybrid catalyst system[24] composed of an immobilized catalyst and a small amount of a soluble catalyst was found to have a good control over the polymerization and low residual level of transition metal complex in the polymer products.

Kinetic study indicates that the immobilization of catalysts on a solid substantially reduces the radical deactivation rate,[24] resulting in radical terminations and uncontrolled chain growth. More important, the catalyst immobilization sacrifices the versatility of ATRP in syntheses of polymer architectures. For example, supported catalysts may not be useful in the synthesis of hyperbranched polymers or other complex structures since the supported (even the soluble polymer-supported) catalysts cannot reach inside the structure to catalyze the polymerization (Scheme 1a).

Thus, catalysts in a free small molecule state are preferable for ATRP. Accordingly, an ideal catalyst immobilization should be reversible (Scheme 1b); that is, the ATRP catalyst is in a free small molecule form during the polymerization to effectively catalyze the polymerization but returns the support after the polymerization for catalyst separation and recovery.[25] Here, we reported a "catalyst sponge" system using this concept, in which the catalyst/ligand complex was supported on a polymer gel support via hydrogen-bonding-mediated self-assembly (Scheme 2). At room temperature, the catalyst self-assembled on the support via hydrogen bonding, while at an elevated polymerization temperature, the hydrogen bonding broke and the catalyst disassociated from the support as free small molecules for effective catalysis. Compared with covalently solid-immobilized catalysts, this reversibly supported catalyst had much improved control over the

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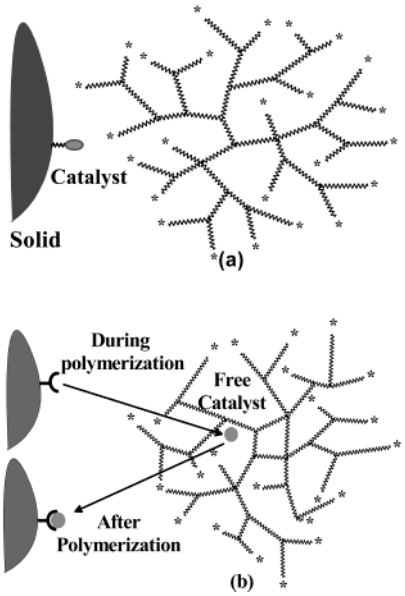
**Scheme 1. Illustrations of (a) a Covalently Solid-Supported Catalyst and (b) a Reversibly Supported Catalyst in the Synthesis of Polymer Architectures**




polymerization, producing polymers with very low polydispersity. In this paper, we report the detailed study of this system, especially the factors affecting the control of the polymerizations.

## Experimental Section

**Chemicals.** Methyl methacrylate (MMA) (99%, Aldrich) was distilled under vacuum and stored in a freezer. Toluene was also distilled. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%), maleimide (99%), CuBr (98%), divinylbezene (tech., 80%), chloroform (99.8%, A.C.S), *p*-(chloromethyl)styrene (90%), thymine-1-acetic acid (98%), potassium carbonate (99+%, A.C.S), *N*,*N*-dimethylformamide (DMF, 99.8%), dichloromethane (98%, A.C.S), triethylamine ($Et_3N$, 99.5%), acryloyl chloride (96%), *N*,*N*,*N*′,*N*′-tetraethyldiethylenetriamine (TEDETA, 90%), ethyl acetate (99.5+%, A.C.S), methyl α-bromophenylacetate (MBP, 97%), and tetrahydrofuran (THF, 99+%) were all from Aldrich and used without further purification. 2,6-Diaminopyridine (98% from Aldrich) was recrystallized from hot chloroform. 2,6-Bis(acrylamido)pyridine was synthesized by the method described by Yano et al.[26]

Preparation of TEDETA-Functionalized Diaminopyridine (DAP-2TEDETA) (Scheme 3). TEDETA (1.17 g, 5.44 mmol) was added to a solution of 2,6-bis(acrylamino)pyridine (0.590 g, 2.72 mmol) in methanol (10 mL). The reaction mixture was then stirred at room temperature for 48 h. The solvent was removed by rotary evaporation, producing a yellowish oil. The final product was purified by silica column chromatography (1:1 ethyl acetate/hexane) and dried in a vacuum.

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ in ppm: 9.88 (s, 2H, N*H*), 7.86−7.84 (d, 2H, =C*H*), 7.71−7.67 (t, 1H, =C*H*), 2.91−2.51 (m, 40H, C(O)C$H_2$, NC$H_2$), 1.05 (t, 24H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ in ppm: 171.12 (O=*C*), 149.94 (=*C*H), 140.16 (=*C*H), 109.13 (=*C*H), 52.40 (N*C*H$_2$), 50.83 (N*C*H$_2$), 47.37 (N*C*H$_2$), 35.06 (*C*H$_2$C(O)), 11.57 (*C*H$_3$).

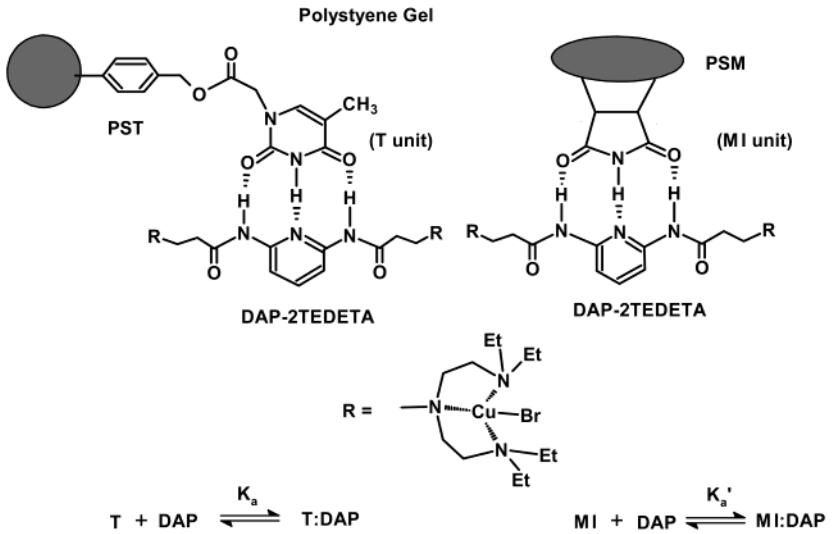
Preparation of Poly(styrene-*co*-maleimide) Gel (PSM) (Scheme 4). AIBN (0.114 g, 0.696 mmol) was added to a solution of styrene (3.41 g, 32.8 mmol), divinylbezene (0.285 g, 2.19 mmol), and maleimide (2.00 g, 20.6 mmol) in toluene (15.0 mL). After degassing for 5 min with nitrogen, the reaction mixture was heated at 60 °C for 8 h. The produced polymer gel was precipitated in methanol, dried, and ground into powder and then extracted with chloroform for 8 h. The final product was dried at room temperature and then in a vacuum. The product was white powder (4.73 g) with 75% yield. Elemental analysis: C, 71.49; H, 6.13; N, 5.87, indicating 40.7% maleimide contained.

Preparation of PS Gel Modified with Thymine (PST) (Scheme 5). AIBN (0.100 g, 0.608 mmol) was added to a solution of styrene (5.50 g, 52.8 mmol), *p*-(chloromethyl)styrene (4.00 g, 26.2 mmol), and divinylbezene (0.500 g, 3.84 mmol) in toluene (20.0 mL). The solution was heated at 78 °C for 12 h. The produced polymer gel was then extracted with chloroform for 5 h. The final product was dried at room temperature and then in a vacuum, which yielded a white powder (5.73 g, 60% conversion).

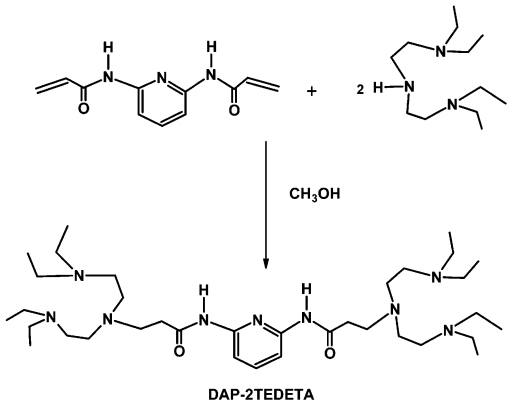
The PS gel (5 g, 0.0131 mol equiv of Cl), thymine-1-acetic acid (2.41 g, 0.0131 mol), and potassium carbonate (1.81 g, 0.0131 mol) were added in 80 mL of DMF and reacted at 65 °C for 48 h under nitrogen. The resulting suspension was filtrated and washed with distilled water and acetone, yielding a white solid powder (5.35 g). Elemental analysis: Cl, 2.14; C, 78.7; H, 7.26; N, 2.93, indicating 19.2% thymine contained.

**General Polymerization Procedures.** MMA and toluene were degassed separately for 5 min just before use. The catalyst (CuBr, 0.0270 g, 0.188 mmol) and polymer gel (0.900 g) were charged in a predried Pyrex tube. The tube was sealed tightly with a rubber septum and then degassed by applying vacuum and back-filling nitrogen (10 cycles). The monomer (MMA, 1.89 g, 0.0188 mol), ligand (DAP-2TEDETA, 0.0640 g, 0.0941 mmol), and toluene (6.0 mL) were added via nitrogen-

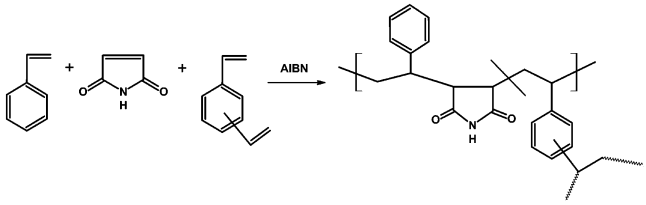
**Scheme 2. Tetraethyldiethylenetriamine (TEDETA)−CuBr Reversibly Supported onto Polystyrene Gel via a Triple Hydrogen Bond Array of the Thymine−Diaminipyridine or Maleimide−Diaminopyridine**



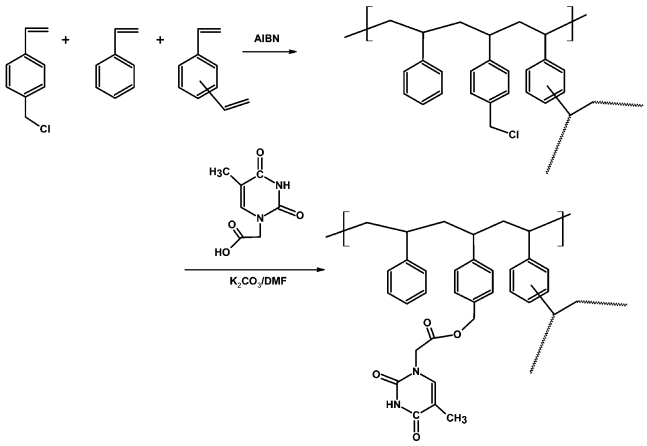
**Scheme 3. Attaching the TEDETA Ligands onto a Diaminopyridine Unit**




**Scheme 4. Synthesis of Poly(styrene-*co*-maleimide) Gel (PSM)**




**Scheme 5. Synthesis of Poly(styrene-*graft*-thymine) Gel (PST)**




purged syringes with stirring. The mixture was degassed with nitrogen for 2 min. Finally, the initiator (MBP, 30.0 $\mu$L, 0.191 mmol) was added to the mixture with stirring. The tube was then immersed in an oil bath that was preset at the specific reaction temperature. At different timed intervals, samples (about 0.050 mL solution/catalyst mixture) were withdrawn from the tube with degassed syringes, diluted with $CDCl_3$, and stored in the freezer. The conversion was determined by the intensity ratio of $OCH_3$ signals of PMMA (3.60 ppm) and monomer (3.75 ppm) in the NMR spectrum of the solution. This solution (50.0 $\mu$L) diluted with THF was injected to gel permeation chromatography (GPC) to measure the molecular weight and polydispersity of the polymer. After the polymerization was complete, the tube was removed from the oil bath. The reaction mixture was stirred at room temperature and then centrifuged. The upper layer solution was taken out by a degassed syringe and dried at room temperature for further analysis.

**Catalyst Reuse.** After the polymer solution was removed, the residual solid was washed three times with 5.0 mL each of degassed toluene under nitrogen. Finally, the degassed solvent, monomer, and initiator with the amounts same as those in the first run of polymerization were added. The tube was then immersed in an oil bath with stirring. The same procedure as that of the first run was repeated.

**Characterization.** $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded in $CDCl_3$ (99.8%, 0.030% v/v TMS) on a Bruker Avance DRX-400 NMR. Molecular weights and polydispersity of PMMA were measured using a Waters SEC equipped with a Waters 2414 refractive index detector and 300 mm solvent-saving GPC columns ($5 \times 10^2-2 \times 10^4$, $5 \times 10^2-3 \times 10^4$, $5 \times 10^3-6 \times 10^5$) using THF as the solvent at 30 °C at a flow rate of 0.30 mL/min with polystyrene as standards.

The Cu concentrations in the polymer products were measured by ICP-MS at the Department of Geology at the University of Wyoming or elemental analysis by Guelph Laboratories Ltd., Canada. The polymer solution was dried at room temperature and under vacuum. The polymer powder (50.0 mg) was dissolved in nitric acid (A.C.S, EM) with heating, and the solution was diluted to 25.0 mL for ICP-MS analysis.

## Results and Discussion

The hydrogen bond is an ideal chemical bonding for reversible immobilization. It forms at low temperature but breaks at elevated temperature. Single hydrogen bonding is too weak to be used. The DAD:ADA (D = donor, A = acceptor) type triple hydrogen bonding array between maleimide (MI) or thymine (T) and diaminopyridine (DAP) was used (Scheme 2). The catalyst was attached on a diaminopyridine unit via the functionalization of the tetraethyldiethylenetriamine (TEDETA) ligand (Scheme 3). The polystyrene gel was functionalized either with maleimide (PSM) by copolymerization (Scheme 4) or with thymine (PST) by postreactions (Scheme 5).

MMA was polymerized with methyl α-bromophenylacetate (MBP) as initiator mediated by CuBr/TEDETA reversibly supported on the polystyrene gel (PSM or PST) in toluene at elevated temperatures. The gel particles became green upon the addition of the initiator MBP.

**PSM/DAP-2TEDETA System. PSM Support Effects.** At room temperature, the DAP unit forms hydrogen bonding with the maleimide (MI) unit to anchor the catalyst on the PSM support (Scheme 2) and establishes an equilibrium. The catalyst concentration in the solution is thus related to the hydrogen bonding strength ($K_a$) and the MI concentration on the support, as shown in eq 1.

$$[\mathrm{CuBr}] = 2[\mathrm{DAP}] = 2\frac{[\mathrm{DAP{:}MI}]}{K_a[\mathrm{MI}]} \qquad (1)$$

where $K_a$ is the equilibrium constant of the hydrogen bonding, [DAP] is the DAP-2TEDETA concentration, and [MI] is the maleimide concentration.

Accordingly, the presence of extra MI will decrease the catalyst residue in the final product. The effects of the MI/DAP ratio on the polymerization and the residual catalyst concentration in the resulting polymer were first investigated. MMA was polymerized at 60 °C in the presence of different amounts of PSM support with MI/DAP ratios at 14, 22, and 40. All the polymerizations were in first order with respect to the monomer concentration at the early stage of the polymerization. An increase in MI/DAP ratio only slightly slowed the polymerization rate (Figure 1), suggesting that the catalyst indeed disassociated from the support for catalysis at this temperature.

Figure 2 shows the resulting PMMA molecular weight and polydispersity as a function of MMA conversion prepared at different MI/DAP ratios. The PMMA mo-

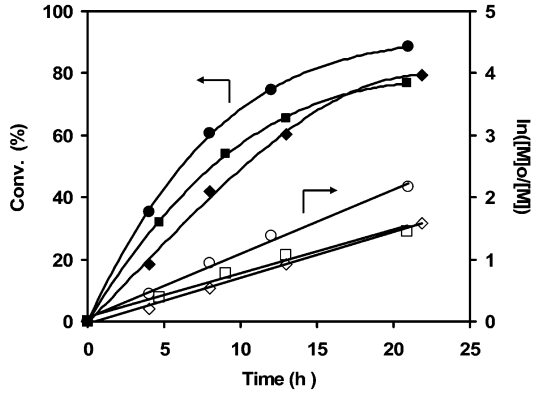



**Figure 1.** MMA polymerization in toluene at different PSM/DAP ratios. [MMA] = 2.34 mol/L; [CuBr] = 0.0234 mol/L; [MBP] = 0.0234 mol/L; DAP-2TEDETA/CuBr = 1/2; 60 °C. MI/DAP (molar) = 40 (♦, ◊), 22 (■, □), and 14 (●, ○).

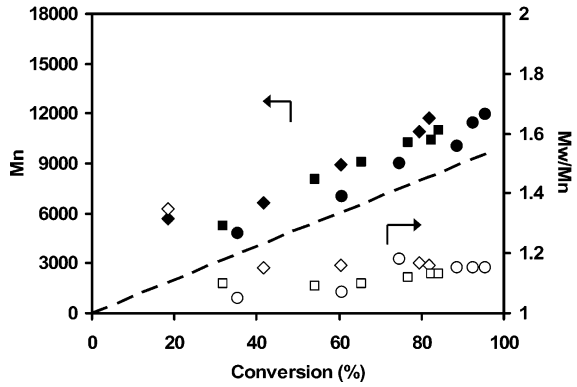



**Figure 2.** Dependence of PMMA molecular weights and polydispersity on conversion in the polymerizations of MMA in toluene at different PSM/DAP ratios. See Figure 1 for experimental conditions. MI/DAP (molar) = 40 (♦, ◊), 22 (■, □), and 14 (●, ○); theoretical $M_n$ (- - -).

lecular weight linearly increased with conversion in all the three experiments. The polydispersity of PMMA was in the range 1.1−1.2, indicating that the control of the polymerization by the reversibly supported catalyst was much improved compared with that by covalently supported catalysts,[20] but comparable to that of unsupported systems.[1] The PMMA molecular weights were higher than theoretical values, especially those prepared with MI/DAP = 40. This may be caused by the fact that the initiator was added at room temperature, at which the catalyst assembled on the solid support. The generated radicals thus could not be deactivated fast enough, causing radical termination. We found that if the polymerization solution was heated at 60 °C first and then the initiator was added, the initiator efficiency could be improved.

The color of the resultant polymer became lighter with the increase of MI/DAP ratio. At MI/DAP = 14, the resulting polymer was slightly greenish, while PMMA prepared at MI/DAP = 40 did not have any color at all, and the copper concentration was 4.0 wt % of the originally used catalyst, which indicates that 96.0% of the catalyst self-assembled to the support at room temperature for separation. These results also suggest that it is necessary to use large extra MI units to remove the catalyst from the polymer to an acceptable level. This is because of the weak hydrogen bond and the steric effect. The DAD:ADA type triple hydrogen bond array is weak due to its repulsion effect of the acceptors (O and N atoms).[27] Meanwhile, the PSM gel support was

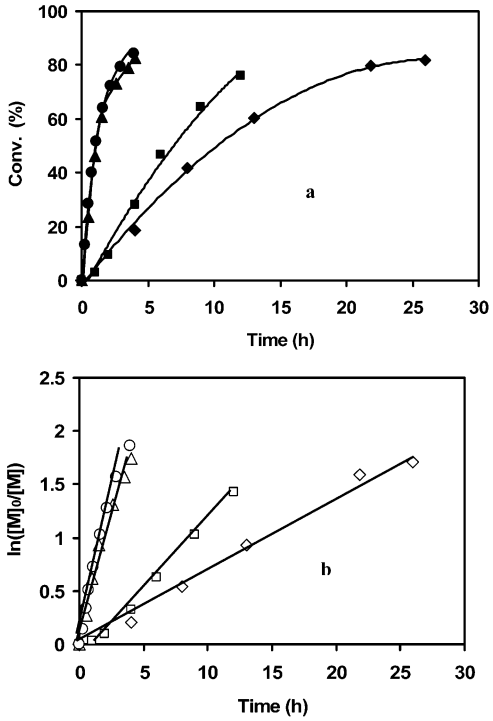



**Figure 3.** MMA polymerization in the presence or absence of the PSM gel support in toluene at different temperatures. [MMA] = 2.34 mol/L; [CuBr] = 0.0234 mol/L; [MBP] = 0.0234 mol/L; DAP-2TEDETA/CuBr = 1/2; with support at MI/DAP (molar) = 40; 60 °C (♦, ◊), 90 °C (▲, △); without support 60 °C (■, □), 90 °C (●, ○).

made by the copolymerization of styrene and maleimide cross-linked by divinylbenzene. A portion of maleimide units was trapped in closed domains and thus not available to form hydrogen bonding with DAP. In addition, the two bulky catalyst groups on the DAP moiety may also impede its hydrogen bond formation.

**Temperature Effects.** Hydrogen bonding is temperature dependent. MMA polymerizations at different temperatures catalyzed by the reversibly supported catalyst were thus investigated and compared with those without the PSM support. Both polymerizations catalyzed by the supported and unsupported catalysts at 90 °C were much faster than those at 60 °C (Figure 3). At 90 °C, there was very little difference in the polymerization rate between the polymerizations with and without the PSM support, which suggests that all the catalyst disassociated from the PSM support for catalysis at this temperature. At 60 °C, the polymerization catalyzed by the supported catalyst was slower than that without the PSM support, which indicates that a fraction of the catalysts did not disassociate from PSM support to catalyze the polymerization. This comparison also confirms that the catalyst indeed can disassociate from the support from the support for catalysis and higher temperatures facilitate this disassociation.

The molecular weights of PMMA increased linearly as the MMA conversion increased, and the polydispersity was low (Figure 4). The molecular weights of PMMA prepared in the presence of the PSM support only very slightly deviated more from the theoretical values than those prepared in the absence of the PSM support, but the polydispersities of PMMA were almost the same. The polydispersity of PMMA produced by the polymerization with the support at 90 °C increased at high

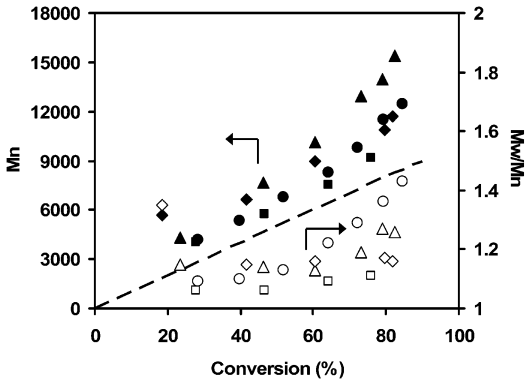



**Figure 4.** Dependence of PMMA molecular weights and polydispersity on conversion in the MMA polymerizations in the presence or absence of the PSM gel at different temperatures. See Figure 3 for experimental conditions. With support at 60 °C (♦, ◊), 90 °C (▲, △); without support 60 °C (■, □), 90 °C (●, ○); theoretical $M_n$ (- - -).

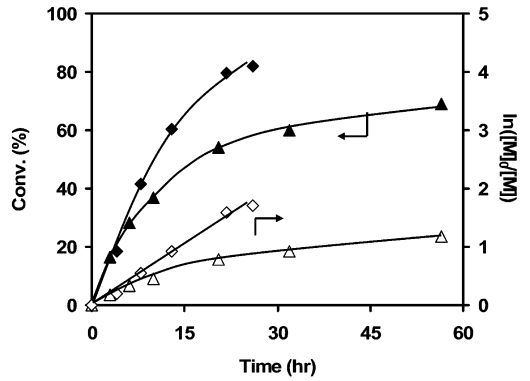



**Figure 5.** MMA polymerization in different solvents with the reversibly supported catalyst on PSM gel. [MMA] = 2.34 mol/L; [CuBr] = 0.0234 mol/L; [MBP] = 0.0234 mol/L; DAP-2TEDETA/CuBr = 1/2; 60 °C; MI/DAP (molar) = 40; toluene (♦, ◊); anisole (▲, △).

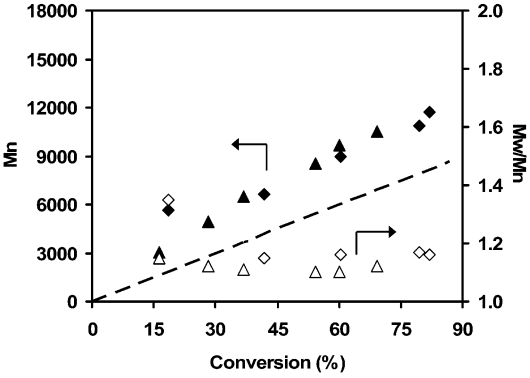



**Figure 6.** PMMA molecular weights and molecular weight distributions as a function of conversion in the polymerization in different solvents catalyzed by the reversibly supported catalyst on PSM gel. See Figure 5 for experimental conditions. Toluene (♦, ◊) and anisole (▲, △); theoretical $M_n$ (- - -).

conversion, but those prepared by the polymerization without the PSM support followed the same trend. These results suggest that the PSM support had little effect on the control of the polymerization due to the reversible nature.

**Solvent Effects.** A hydrogen bond becomes weaker in polar solvents.[28] The polymerization in a low polar solvent anisole was thus compared with that in toluene (Figures 5 and 6). The polymerization rates were the same in toluene and anisole at the early stage of the

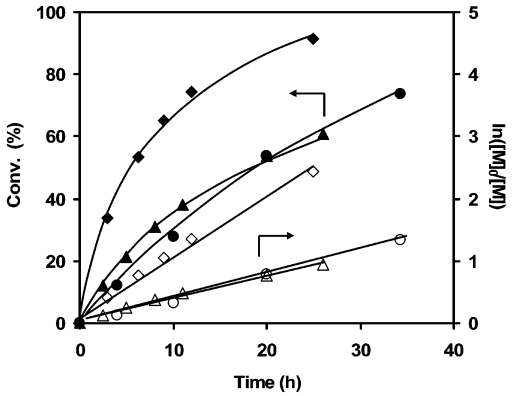



**Figure 7.** Polymerization of MMA in toluene at different T/DAP ratios with catalysts reversibly supported on PST gel. [MMA] = 2.34 mol/L; [CuBr] = 0.0234 mol/L; [MBP] = 0.0234 mol/L; DAP-2TEDETA/CuBr = 1/2; 60 °C. T/DAP ratio (molar) = 3 (♦, ◊), 6 (▲, △), and 10 (●, ○).

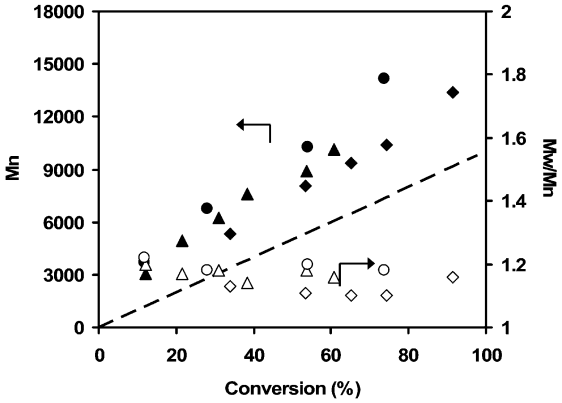



**Figure 8.** Dependence of PMMA molecular weights and polydispersity on conversion in the polymerization of MMA in toluene with the catalyst reversibly supported on PST gel. See Figure 7 for experimental conditions. T/DAP ratio (molar) = 3 (♦, ◊), 6 (▲, △), and 10 (●, ○); theoretical $M_n$ (- - -).

polymerization, which confirms that at this temperature the majority of the catalyst disassociated from the support for catalysis. As the reaction proceeded, the rate of the polymerization in anisole decreased and leveled off at ca. 60% conversion, indicating a significant of radical termination. The exact reason for this phenomenon is not known to us and is under investigation. Nevertheless, the control of the molecular weights of PMMA was good with polydispersity less than 1.2.

**Thymine/Diaminopyridine System.** A thymine−diaminopyridine hydrogen bonding array (Scheme 2) was also tested to support the catalyst on the polystyrene gel for the MMA polymerization, as shown in Figures 7 and 8. Similar to the maleimide−diaminopyridine supporting system, the supported catalyst effectively mediated the polymerization, producing polymers with polydispersity less than 1.2. In contrast to the maleimide−diaminopyridine supported system, where the MI/DAP ratio had only a very slight effect on the polymerization rate, the T/DAP ratio strongly effected the polymerization rate. The MMA polymerization at the T/DAP ratio of 3 was much faster than those at ratio of 6 and 10, while the polymerizations at T/DAP of 6 and 10 were similar. On the other hand, the residual catalyst in the resulting polymers decreased with an increase of the T/DAP ratio. The residual catalyst concentration was 0.025%, 0.020%, and 0.020% in the polymers prepared at T/DAP ratios of 3, 6, and 10,

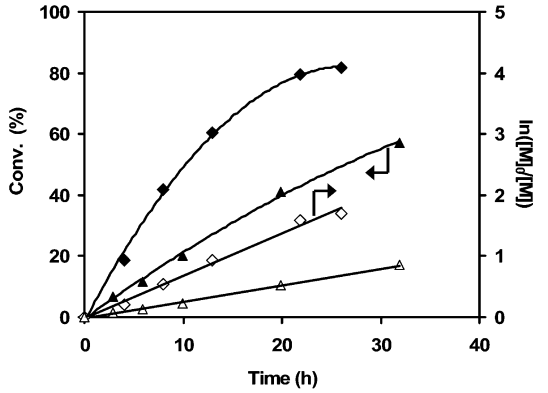



**Figure 9.** Polymerization of MMA with the fresh and recycled catalysts reversibly supported on PSM gel. [MMA] = 2.34 mol/L; [CuBr] = 0.0234 mol/L; [MBP] = 0.0234 mol/L; DAP-2TEDETA/CuBr = 1/2; MI/DAP (molar) = 40; 60 °C fresh catalyst (♦, ◇); recycled catalyst (▲, △).

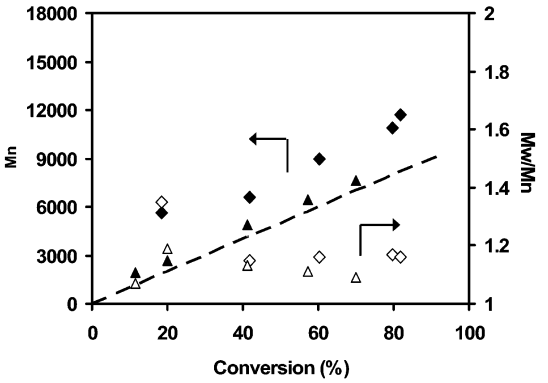



**Figure 10.** Dependence of PMMA molecular weights and polydispersity on conversion in the polymerization of MMA with the fresh and recycled catalysts reversibly supported on PSM gel. See Figure 9 for experimental conditions fresh catalyst (♦, ◇); recycled catalyst (▲, △); theoretical $M_n$ (- - -).

respectively. Therefore, similar to using PSM as support, an excess amount of PST support was required to remove the catalyst residual to a low level. This required T/DAP ratio, however, was far less than the needed MI/DAP ratio (about 40) in the maleimide−diaminopyridine system. The steric effect may account for this large difference. The PST gel support was made by the reaction of the polystyrene gel functionalized *p*-chloromethyl groups with thymine-1-acetic acid. Therefore, the thymine moieties were on the available gel surface and thus had much lower steric hindrance to form hydrogen bonding with the diaminopyridine units compared with the PSM support.

**Catalyst Reuse.** After the polymerization was complete, the green solid was isolated and used as the catalyst for the second polymerization run. Figures 9−12 show the MMA polymerization with the recycled PSM or PST-supported catalysts. In both systems, the recycled catalysts still mediated a first-order reaction and retained about a half of the catalyst activities of their fresh catalysts. However, the recycled catalysts had much better control over the MMA polymerization than the fresh catalysts. The initiator efficiency catalyzed by the recycled supported catalyst was increased to 0.75 from 0.52 by the fresh catalyst in PST-supported system and to 0.92 from 0.70 in PSM supported system. The polydispersities were all less than 1.2.

This reduction in the catalytic activity but improved control of the polymerization by the recycled catalyst

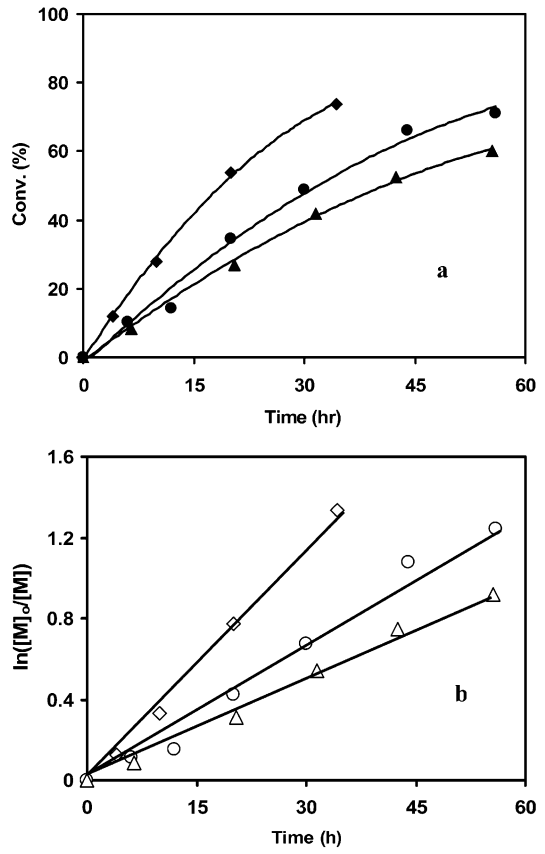



**Figure 11.** Polymerization of MMA with the fresh and recycled catalysts reversibly supported on PST gel. [MMA] = 2.34 mol/L; [CuBr] = 0.0234 mol/L; [MBP] = 0.0234 mol/L; DAP-2TEDETA/CuBr = 1/2; T/DAP (molar) = 10; 60 °C fresh catalyst (♦, ◇); recycled catalyst (▲, △); fresh catalyst with 48% $CuBr_2$ (●, ○).

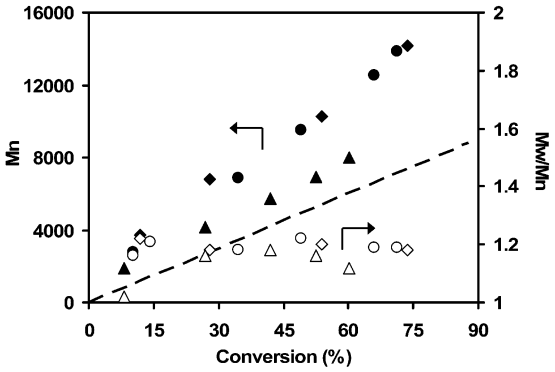



**Figure 12.** Dependence of PMMA molecular weights and polydispersity on conversion in the polymerization of MMA with the fresh and recycled catalyst reversibly supported on PST gel. See Figure 11 for experimental conditions fresh catalyst (♦, ◇); recycled catalyst (▲, △); fresh catalyst with 48% $CuBr_2$ (●, ○). Theoretical $M_n$ (- - -).

was also found in the covalently supported ATRP systems, such as the silica gel supported catalysts.[29] Since only less than 2% catalyst was lost during the catalyst recovery, this reduction of the catalytic activity was not caused by the loss of the catalyst but caused by the presence of the Cu(II) produced in the first run of the polymerization. Because in the first run of the polymerization, the initiator efficiency was less than 100%, indicative of that some radicals were terminated and an excess of Cu(II) was produced due to the persistent radical effect.[5] The Cu(II) species reduced the

radical concentration according to the dynamic equilibrium of ATRP process[5] and thus decreased the rate of the polymerization. We have confirmed that in the presence of the similar amount of $CuBr_2$ the polymerization rate was reduced to a similar level to that catalyzed by the recycled catalyst (Figure 11). Therefore, the presence of Cu(II) in the recycled catalyst reduced the catalyst activity but improved the control of the polymerization.

The resultant polymer catalyzed by recycled catalyst had no color and had even lower concentration of the residual copper. The copper concentration was less than 0.01 wt %.

## Conclusion

This work has demonstrated that the reversibly supported catalyst via hydrogen-bonding-mediated self-assembly could associated on the support for separation and recycling by forming hydrogen bonding while dissociated from the support as free molecules at reaction temperatures for effective catalysis. The catalyst mediated the ATRP of MMA as effective as the unsupported catalyst and had an excellent control over the polymerization similar to free catalysts, producing very low polydispersed polymers. The optimization of the hydrogen bonds for catalyst supporting and its application in polymer synthesis are still underway.

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