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An Immobilized/Soluble Hybrid Catalyst System for Atom Transfer Radical Polymerization

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ABSTRACT: A new two-component catalyst system consisting of an immobilized catalyst and a soluble catalyst in ppm quantities was applied to atom transfer radical polymerization (ATRP). A high conversion of monomer (>90%) was achieved with a predetermined molecular weight and narrow molecular weight distribution ($M_w/M_n = 1.1-1.3$) in the ATRP of methyl methacrylate and methyl acrylate. The immobilized catalyst was removed by a filtration or sedimentation procedure. The casting of the reaction solution afforded clear and colorless polymer films. It was confirmed by the inductively coupled plasma (ICP) analysis that the residual amount of Cu in the resulting polymer was as low as 20 ppm.

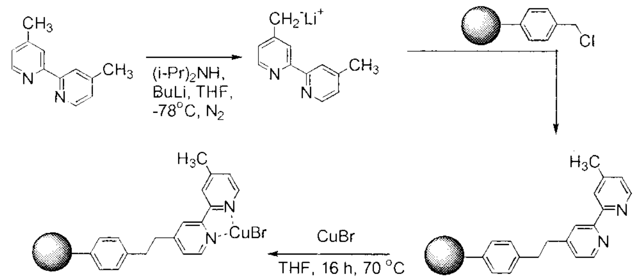
Atom transfer radical polymerization (ATRP)[1,2] is one of the most promising methods in the field of controlled/"living" radical polymerizations[3,4] which can be applied to a wide variety of monomers and provide well-defined polymers.[5,6] However, one of the limitations of ATRP is the presence of a transition metal catalyst, which should be removed after the polymerization.

A possible solution is to immobilize the catalytic species on a solid support. Several examples of immobilized ATRP catalysts have been presented in the literature. ATRP catalysts immobilized on silica,[7−11] cross-linked polystyrene beads,[7,8] or attached to polymer chains[12] provide an efficient way of separating and recycling the catalyst. However, these techniques offer limited control over the polymerization of vinyl monomers, originating from the heterogeneous nature of the process. Insufficient deactivation rates[8] of the growing radical, which result from the slow diffusion of the polymer chains to the immobilized deactivator complexes, lead to a much higher molecular weight and broader molecular weight distribution than in homogeneous systems.

To overcome this diffusion limitation, a small amount of soluble catalyst was used along with an immobilized catalyst in a "hybrid" catalyst system. A small amount of the low molecular weight catalyst exists in the solution phase to accelerate the deactivation process of the growing radical and reduce the diffusion barrier.

Copper complexes in conjunction with tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was chosen as the soluble catalyst in the hybrid system due to its high deactivation rate constant and preference to remain in the Cu^{II} state. In the deactivation kinetic studies using the 1-phenylethyl radical, $CuBr_2/Me_6TREN$ showed that the deactivation rate constant $k_d = 1.4 \times 10^7$ L mol^{-1} s^{-1}, which was only slightly lower than that of $CuBr_2$/4,4′-di(5-nonyl)-2,2′-bipyridine ($CuBr_2$/dNbpy, $k_d = 2.5 \times 10^7$ L mol^{-1} s^{-1}) and higher than that of $CuBr_2$/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine ($CuBr_2$/PMDETA, $k_d = 6.1 \times 10^6$ L mol^{-1} s^{-1} at 75 °C in acetonitrile).[13] $Cu^{I/II}/Me_6TREN$ catalyst is a stronger reducing agent than $Cu^{I/II}$/2,2′-bipyridine (bpy). The ratio of the corresponding equilibrium constants ($K_{Me_6TREN}/K_{bpy} = [Cu^{II}_{Me_6TREN}][Cu^{I}_{bpy}]/[Cu^{I}_{Me_6TREN}][Cu^{II}_{bpy}]$) was estimated to be $10^{4\pm1}$ by UV−visible analysis in methanol[14] and by cyclic voltametry[15] in acetonitrile at 25 °C. This indicates that dynamic halogen exchange reaction between $CuBr_2$/bpy and CuBr/Me_6TREN occurs to predominantly yield CuBr/bpy and $CuBr_2/Me_6TREN$.

Scheme 1



The synthetic approach to prepare the immobilized catalyst (CuBr/PS-bpy) is shown in Scheme 1. The 4,4′-dimethyl-2,2′-bipyridine ligand was covalently immobilized on a Merrifield resin containing benzyl chloride functional groups in an effort to minimize the leaching of the catalyst. The Merrifield resin was composed of a lightly cross-linked polystyrene (5 mol % divinylbenzene) with an average particle size of 8 μm. The metallation of the ligand with CuBr followed by washing with fresh THF, toluene, and hexane three times each afforded the immobilized catalyst (1.15×10^{-3} mol of ligand/g of catalyst as determined by elemental analysis).

As comparative experiments, the polymerization of methyl methacrylate (MMA) with CuBr/PS-bpy or CuBr/Me_6TREN was performed.[16] As shown in experiments 1 and 2 in Table 1, a large difference between experimental and theoretical molecular weights was observed with a broad molecular weight distribution, indicating poor control over the polymerizations.

When $CuBr_2/Me_6TREN$ soluble catalyst was added to the reaction mixture along with CuBr/PS-bpy immobilized catalyst (3 mol % soluble catalyst relative to the immobilized catalyst), the control over the polymerization was improved significantly as shown in experiment 3 in Table 1. The conversion was 83% after 24 h with a narrow molecular weight distribution (M_w/

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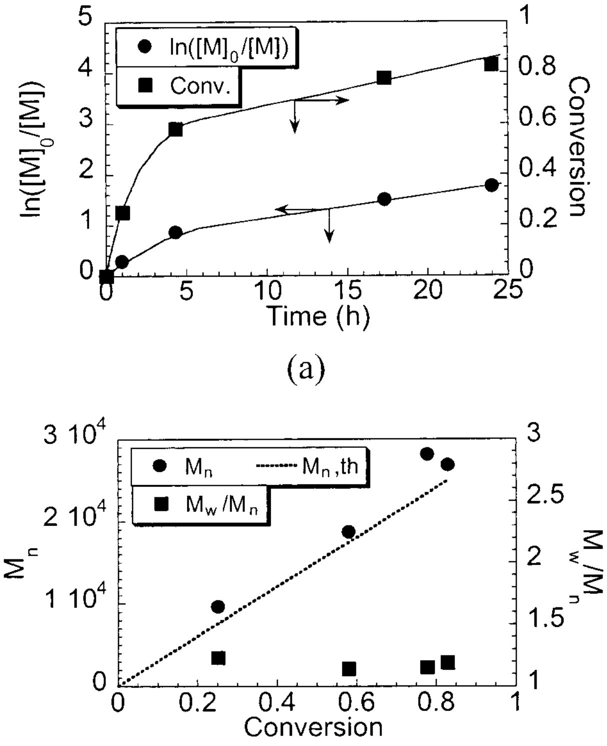
Table 1. Methyl Methacrylate and Methyl Acrylate Polymerization with Hybrid Catalysts[a]

expt no.	monomer	hybrid ratio[b] (mol %)	w_0(Cu)/ w_0(monomer)[c] (ppm)	polym time (h)	conv[d] (%)	M_n ($\times 10^3$)	M_n(th) ($\times 10^3$)	M_w/M_n	w(Cu)/ w(polymer)[e] (ppm)
1[f]	MMA	0	0	16	59.0	71.2	17.7	2.26	n.d.[g]
2[h]	MMA	100	2100	22	61.8	43.7	18.5	1.73	n.d.[g]
3[i]	MMA	3	63	24	83.0	26.8	25.0	1.19	107
4[i]	MMA	1	21	17	89.1	32.4	26.7	1.25	27
5[i]	MMA	0.3	6	24	96.9	35.5	29.0	1.29	15
6[i]	MA	1	25	51	84.7	21.5	22.6	1.09	n.d.[g]

[a] Polymerization conditions: initiator = 2-bromopropionitrile; for expt no. 1, 2, $[\mathrm{MMA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{catalyst}]_0$ = 300:1:1, $[\mathrm{MMA}]_0$ = 4.69 mol/L, MMA/toluene = 1/1 v/v; temperature = 90 °C; for expt no. 3, 4, $[\mathrm{MMA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuBr/PS\text{-}bpy}]_0$ = 300:1:1, $[\mathrm{MMA}]_0$ = 4.67 mol/L, MMA/toluene = 1/1 v/v, temperature = 90 °C; for expt no. 5, $[\mathrm{MMA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuBr/PS\text{-}bpy}]_0$ = 300:1:1, $[\mathrm{MMA}]_0$ = 4.67 mol/L, $CuBr_2/Me_6TREN$ from stock solution in acetone, MMA/toluene/acetone = 1/0.75/0.25 v/v/v, temperature = 90 °C; for expt no. 6, $[\mathrm{MA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuBr/PS\text{-}bpy}]_0$ = 300:1:1, $CuBr_2/Me_6TREN$ from stock solution in acetone, $[\mathrm{MA}]_0$ = 5.55 mol/L, MA/toluene/acetone = 1/0.87/0.13 v/v/v, temperature = 70 °C. [b] $[CuBr_2/Me_6TREN]_0/[CuBr/bpy$ immobilized on PS bead$]_0$ (mol %). [c] Initial copper (Cu) content as a soluble catalyst ($CuBr_2/Me_6TREN$ or $CuBr/Me_6TREN$) by weight in monomer. [d] Conversion determined by GC. [e] Residual copper (Cu) content in polymer by weight determined by inductively coupled plasma (ICP) analysis. [f] Polymerization with immobilized catalyst only; catalyst = CuBr/bpy immobilized on PS bead. [g] Not determined. [h] Polymerization with $Cu^{I/II}/Me_6TREN$ only; catalyst = $CuBr/CuBr_2/Me_6TREN$ (0.97/0.03/1.00). [i] Polymerization with hybrid catalyst; catalyst = (CuBr/bpy immobilized on PS bead)/($CuBr_2/Me_6TREN$) hybrid catalyst.



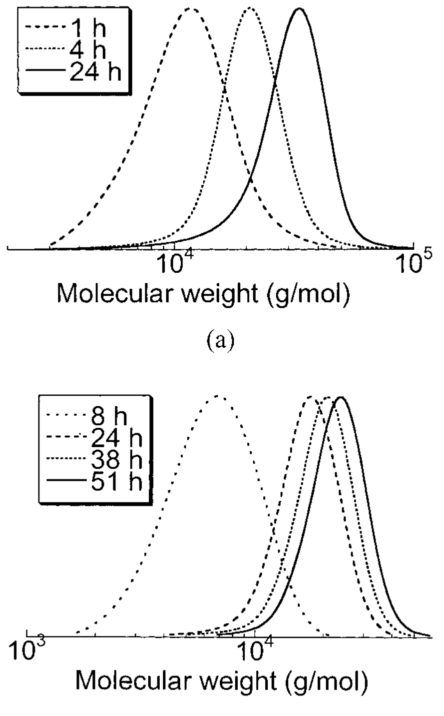
(a)

(b)

Figure 1. Kinetic plots (a) and evolution of M_n and M_w/M_n vs conversion (b) for the polymerization of MMA using (CuBr/PS-bpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system: $[\mathrm{MMA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuBr/PS\text{-}bpy}]_0$:$[CuBr_2/Me_6TREN]_0$ = 300:1:1:0.03, $[\mathrm{MMA}]_0$ = 4.67 mol/L, MMA/toluene = 1/1 v/v, initiator = 2-bromopropionitrile, temperature = 90 °C.

M_n = 1.19), and a good agreement between the experimental and theoretical molecular weight was attained, indicating a good control over the polymerization. A 3 mol % of $CuBr_2/Me_6TREN$ relative to the immobilized catalyst corresponded to 63 ppm of Cu vs monomer by weight.

The semilogarithmic kinetic plot and the evolution of M_n and M_w/M_n with conversion also confirm the control over polymerization as shown in Figure 1. The kinetics exhibited an initially faster rate, but then it followed first-order kinetics (Figure 1a). In Figure 1b, a good agreement between the experimental and theoretical molecular weight was observed throughout the whole conversion region. The molecular weight distribution (M_w/M_n) was around 1.1. Clear shifts of molecular weight distribution curves to the high molecular weight region with conversion were observed in GPC analysis as shown in Figure 2a, although some tailing in the low molecular region was noted. These observations suggest that the polymerization was well-controlled using the hybrid catalyst system.



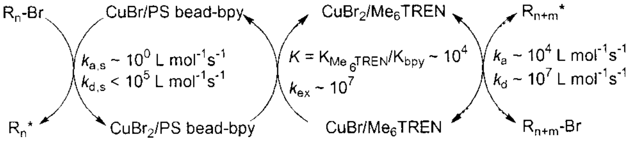
(a)

(b)

Figure 2. GPC traces from the polymerization of MMA (a, experiment 3 in Table 1) and MA (b, experiment 6 in Table 1) using (CuBr/PS-bpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system: for experiment 3, $[\mathrm{MMA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuBr/PS\text{-}bpy}]_0$:$[CuBr_2/Me_6TREN]_0$ = 300:1:1:0.03, $[\mathrm{MMA}]_0$ = 4.67 mol/L, MMA/toluene = 1/1 v/v, initiator = 2-bromopropionitrile, temperature = 90 °C; for experiment 6, $[\mathrm{MA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuBr/PS\text{-}bpy}]_0$:$[CuBr_2/Me_6TREN]_0$ = 300:1:1:0.01, $CuBr_2/Me_6TREN$ from stock solution in acetone, $[\mathrm{MA}]_0$ = 5.55 mol/L, MA/toluene/acetone = 1/0.87/0.13 v/v/v, initiator = 2-bromopropionitrile, temperature = 70 °C.

To reduce the amount of the soluble catalyst, the MMA polymerization with the hybrid catalyst containing 1 and 0.3 mol % of $CuBr_2/Me_6TREN$ vs immobilized

Scheme 2



CuBr/PS-bpy was conducted. The results are shown in experiments 4 and 5 in Table 1. A 1 and 0.3 mol % of $CuBr_2/Me_6TREN$ correspond to 21 and 6 ppm of Cu by weight vs monomer in solution phase. The conversion of the monomer reached over 90%, and good agreements between the experimental and theoretical molecular weight were observed in both cases. The molecular weight distributions were still narrow ($M_w/M_n \sim 1.3$).

The methyl acrylate (MA) polymerization was also attempted with the hybrid catalyst system containing 1 mol % of $CuBr_2/Me_6TREN$ to the CuBr/PS-bpy. The results are shown in experiment 6 in Table 1. A well-controlled polymerization was observed to high conversion (~85%). The experimental and theoretical molecular weights were essentially identical. A narrow molecular weight distribution ($M_w/M_n = 1.09$) was observed. The GPC traces shown in Figure 2b demonstrate symmetrical molecular weight distributions with clear shifts to the high molecular weight region with conversion.

The plausible overall action of the hybrid catalyst system is depicted in Scheme 2. Since the rate constant of activation with Cu^I/bpy is in the range of $k_a \sim 10^0$ L mol^{-1} s^{-1}, the activation of polymeric alkyl halide should not be significantly affected by a slow diffusion of the polymeric chains to the solid immobilized catalyst ($k_{diff} \sim 10^5$ L mol^{-1} s^{-1}).[8]

In the deactivation process, the diffusion of polymer to the immobilized catalyst ($k_d \gg k_{diff}$) is the rate-determining step. On the contrary, the homogeneous catalyst ($CuBr_2/Me_6TREN$) in the solution phase deactivates the growing radical efficiently without a diffusion limitation ($k_d \sim 10^7$ L mol^{-1} s^{-1}). The resulting CuBr/Me_6TREN rapidly reconverts to $CuBr_2/Me_6TREN$ by abstracting halogen from the immobilized catalyst ($CuBr_2$/PS-bpy) to accomplish the complete catalytic cycle. Overall, the soluble catalyst acts as a “shuttling” agent that delivers the halogen from the solid immobilized catalyst to growing polymeric radicals, thus facilitating an effective deactivation process.

Activation of polymeric alkyl halide can partially occur by a homogeneous CuBr/Me_6TREN catalyst, regenerating soluble deactivator ($CuBr_2/Me_6TREN$). The relative values of the equilibrium constants ($K = [Cu^{II}_{Me_6TREN}][Cu^{I}_{bpy}]/[Cu^{I}_{Me_6TREN}][Cu^{II}_{bpy}] \sim 10^4$) (eq 1) suggest the following distribution of immobilized and soluble Cu species, when the total concentration of Cu species is 10^{-2} M, 1 mol % of $CuBr_2/Me_6TREN$ is added, and total 2% Cu^{II} species is present.

$$\underset{\sim 10^{-4}\ \mathrm{M}}{\mathrm{Cu^{II}Br_2/PS\text{-}bpy}} + \underset{\sim 10^{-6}\ \mathrm{M}}{\mathrm{Cu^{I}Br/Me_6TREN}} \rightleftarrows \underset{\sim 10^{-2}\ \mathrm{M}}{\mathrm{Cu^{I}Br/PS\text{-}bpy}} + \underset{\sim 10^{-4}\ \mathrm{M}}{\mathrm{Cu^{II}Br_2/Me_6TREN}} \qquad (1)$$

Using the aforementioned concentrations of Cu species and the individual activation rate constant of CuBr/Me_6TREN ($k_a \sim 10^3$ L mol^{-1} s^{-1}) and CuBr/dNbpy ($k_a \sim 0.085$ L mol^{-1} s^{-1}),[13] it has been calculated that approximately half of the activation process should occur with homogeneous CuBr/Me_6TREN (($R_{a,CuBr/Me_6TREN})/(R_{a,CuBr/Me_6TREN} + R_{a,CuBr/PS-bpy}) = 10^{-6}$ M × 10^3 L mol^{-1} s^{-1})/(10^{-6} M × 10^3 L mol^{-1} s^{-1} + 10^{-2} M × 0.085 L mol^{-1} s^{-1}) = 0.54). Nevertheless, the presence of the immobilized catalyst improves control of the polymerization, since only poorly defined PMMA in low yield was obtained with $Cu^{I/II}/Me_6TREN$ alone (experiment 1 in Table 1 and ref 16).

After sedimentation or simple filtration of the polymerization medium through a Gelman Acrodisc 0.2 μm PTFE filter, the immobilized catalyst was removed efficiently to afford a clear, colorless polymer solution. Solvent casting of the polymer solution afforded a clear, transparent polymer film with an average thickness of 0.3 mm measured by micrometer. The residual amounts of Cu in the polymer films were measured by the inductively coupled plasma (ICP) analysis, and the results are shown in Table 1. The residual amounts of Cu were as low as 15 ppm, with a good agreement with the calculated value. However, caution should be paid not to keep the catalyst under the solution for an extended time, which may cause extra leaching of the catalyst from the immobilized catalyst.

In conclusion, a hybrid catalyst system composed of an immobilized catalyst and a small amount of soluble catalyst was developed for ATRP. The control over the ATRP of both MA and MMA was significantly improved. A high conversion of monomer was achieved, leading to polymers with a predetermined molecular weight and narrow molecular weight distributions. The immobilized catalyst was removed by simple filtration or sedimentation, affording a colorless transparent polymer solution. The hybrid catalyst system enabled the synthesis of well-defined polymers using ATRP with a salient reduction of the residual transition metal in the final polymer products.

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(15) Qiu, J.; Matyjaszewski, K.; Thouin, L.; Amatore, C. *Macromol. Chem. Phys.* **2000**, *201*, 1625: $\ln K = nFE/RT$, $E = 0.06 \log K$ at room temperature, $\Delta E = E_{1/2}(\mathrm{Cu^{II}/bpy}) - E_{1/2}(\mathrm{Cu^{II}/Me_6\text{-}TREN}) = 0.335$ V, where $E_{1/2}$ is redox potentials; from the above equation $K = 10^{5.6}$.

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