

Shuttling Catalyst for Living Radical Miniemulsion Polymerization: Thermoresponsive Ligand for Efficient Catalysis and Removal

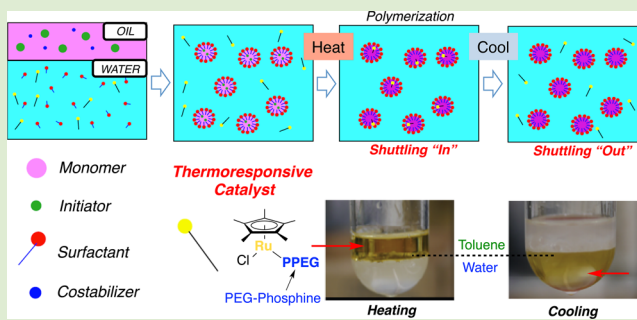
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S Supporting Information

ABSTRACT: In this report, we demonstrate the use of a thermoresponsive ligand for the ruthenium-catalyzed living radical polymerization of butyl methacrylate (BMA) in miniemulsion. A phosphine-ligand-functionalized polyethylene glycol chain (PPEG) in conjunction with a Cp^{*}-based ruthenium complex (Cp^{*}: pentamethylcyclopentadienyl) provided thermoresponsive character as well as catalysis for living polymerization: the complex migrated from the water phase to the oil phase for polymerization upon heating and then migrated from the oil to water phase when the temperature was decreased to quench polymerization. Consequently, simple treatment (i.e., water washing or methanol reprecipitation) yielded metal-free polymeric particles containing less than 10 μg/g (by ICP-AES) of ruthenium residue.



Aqueous dispersed radical polymerizations have been practically used to produce latex or particles in industry. Using water as a continuous phase and adding surfactant allows polymerization of hydrophobic monomers in the dispersed oil phase. These processes are highly favorable for polymer production because they generally have much lower viscosities and better heat transfer than comparable bulk or solution polymerizations. More importantly, they are environmentally benign: additional volatile organic compounds (VOCs) such as organic solvents are unnecessary.

Living radical polymerization (LRP), which allows precise control of polymer structures, has been adapted to aqueous dispersed systems.^{1–3} Among LRP systems, metal-catalyzed living radical polymerization (Mt-LRP) or atom transfer radical polymerization (ATRP)^{4,5} has been most widely employed due to the simple procedure and multiplicity of the initiator design. Ligands of the catalyst in Mt-LRP often play critical roles for catalyst solubility as well as the catalysis by controlling the electron passage to promote the catalytic cycle. Thus, various ligand designs have allowed emulsions,^{6–13} miniemulsions,^{14–22} and microemulsions.^{23,24}

Despite the good usability, Mt-LRP incurs a serious issue: metal residue could contaminate the final product. The issue is especially serious with dispersed systems since as-polymerized polymers generally become products for particle or emulsion applications. One solution is extreme reduction of the catalyst concentration²⁵ through use of highly active catalysts²⁶ or in combination with reducing agents,^{27,28} and extensive investigations on this subject have been done in homogeneous solution polymerization as well as in dispersed systems.

However, there has been little real progress achieved in developing an ideal system satisfying all requirements such as controllability, reproducibility, production stability, and removability of metal.

With these objectives in mind, we focused on the development of thermoresponsive ligands for miniemulsion Mt-LRP to achieve “shuttling” of the catalyst in the dispersed system as follows (Scheme 1). Before polymerization at room temperature, the catalyst is soluble in the water phase because of the hydrophilicity of the ligand. However, upon heating to start the polymerization, the hydrophilicity of the ligand is significantly decreased, causing the complex to migrate into the oil phase, i.e., monomer droplet. Finally, through the cooling process to quench the polymerization, the catalyst is transferred back to the water phase. To realize such a shuttling process, we hypothesized polyethylene glycol (PEG) chains might be promising candidates for the thermoresponsive feature²⁹ since we have used designed PEG-decorated triphenyl phosphine for ruthenium³⁰ or iron³¹ catalyst in solution Mt-LRP.

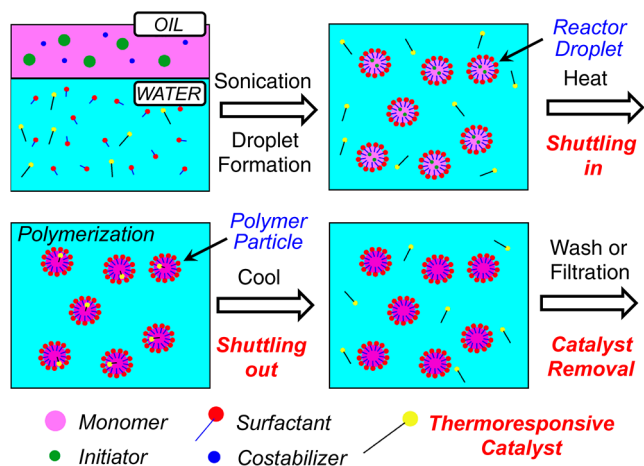
Triphenylphosphine-terminated PEG (PPEG) was synthesized through the reaction of tosylated PEG and (4-hydroxyphenyl)diphenylphosphine (Supporting Information Figure S1). The thermoresponsive catalyst was synthesized through aging of the Cp^{*}-ruthenium complex precursor ([Cp^{*}Ru(μ₃-Cl)]₄, Cp^{*} = pentamethylcyclopentadienyl) with 2 equiv of PPEG in toluene at 80 °C. ³¹P NMR analyses

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Scheme 1. Miniemulsion Mt-LRP with Thermoresponsive Shuttling Catalysts



indicated formation of one phosphine-ligated complex $[\text{RuCp}^*\text{Cl}(\text{PPEG})]$, unlike with triphenylphosphine (PPh_3) giving two-ligated, probably due to the bulkiness of PEG (Figure S2, Supporting Information³⁰). Such a coordinatively unsaturated complex (i.e., 16e) of $\text{RuCp}^*\text{Cl}(\text{PPEG})$ might show higher catalytic activity than 18e saturated. The peak from the ligated phosphine was broad, promising high activity due to the dynamic coordination of the phosphine ligand.

The aged complex was perfectly soluble in water at rt to give yellow homogeneous solution, which also supported the PEG ligation to the ruthenium complex. Thus, the yellow solution in water was combined with toluene to prepare bilayer solution for simple demonstration of the thermoresponsive character (Figure 1A). Upon heating to 95 °C, the upper layer (i.e., toluene) became yellow, while the lower layer (i.e., water) became colorless, indicating the complex became hydrophobic and soluble in toluene rather than water. Afterward, cooling to

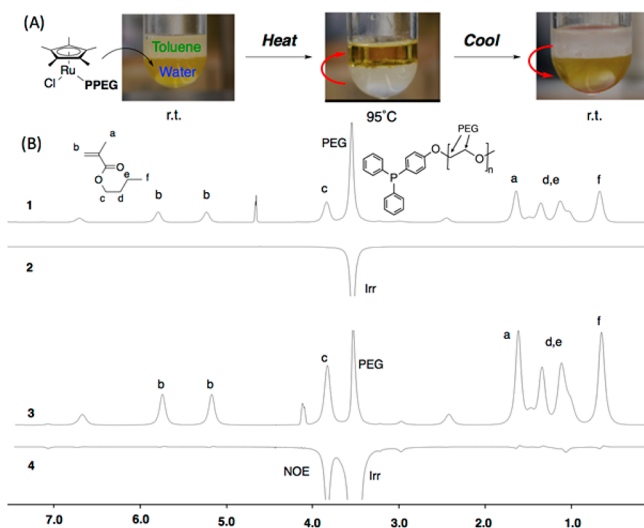


Figure 1. (A) Pictures for phase transfer of the thermoresponsive catalyst on heating (from rt to 95 °C) and cooling (from 95 °C to rt). (B) Normal ^1H NMR and the NOE spectrum at 25 °C (1, 2) and 80 °C (3, 4), respectively. The PEG peak was chosen for irradiation at both temperatures with a strong NOE observed at 80 °C between the BMA proton and the PEG proton while no NOE was observed after cooling to 25 °C.

room temperature gave the original colored bilayer appearance. Thus, the PEG-ligated complex indeed showed temperature-responsive property suitable for the concept in Scheme 1.

Furthermore, to confirm the expected thermoresponsive shuttling behavior on the colloidal scale, the interaction between PEG and butyl methacrylate (BMA) under miniemulsion conditions similar to the actual polymerization (see below) was observed with a 1D nuclear Overhauser effect (NOE) difference NMR. In general, the NOE spectrum can provide the location of chemical species from its interactions with nearby species (≤ 5 Å) and has shown to be effective in providing insight on the chemical microenvironment within an emulsion,³² allowing for the measurement of phase transfer on the colloidal scale.

The heterogeneous solution in D_2O containing PPEG, BMA, hexadecane (HD, stabilizer), and hexadecyltrimethylammonium bromide (CTAB, surfactant) was sonicated to make a milky NMR sample. For the NOE measurement, the peak from methylene PPEG at around 3.6 ppm was chosen as the “target”. Figure 1 shows the normal NMR and the NOE spectrum at 25 °C (1, 2) and 80 °C (3, 4), respectively. At 25 °C no correlation peak was observed between PPEG and BMA, indicating they do not exist close to each other in the dispersed medium. This would make sense since PPEG is rather hydrophilic at lower temperature but BMA is hydrophobic. On the other hand, upon heating to 80 °C, clear correlation peaks were observed between the two compounds, suggesting PPEG became hydrophobic and recognized by the BMA. Interestingly, peaks from methylene protons (c) neighboring the oxygen showed a strong correlation peak, which may be due to the highest polarity of the protons among others in BMA. Since this model experiment was started at 80 °C and then cooled we believe the PPEG chain can be shuttled from the hydrophobic phase in the miniemulsion to the hydrophilic (water) phase simply by changing temperature.

We thus conducted living radical miniemulsion polymerizations of butyl methacrylate (BMA) with the PEG-ligated Ru catalyst $[\text{RuCp}^*\text{Cl}(\text{PPEG})]$, in conjunction with ethyl-2-chloro-2-phenylacetate (ECPA, initiator), HD, and CTAB. These components were dispersed into water in either the presence or absence of toluene, followed by ultrasonication under argon to make a highly dispersed solution. The system without toluene is more practical due to fewer amounts of VOCs. As the standard condition, $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ was employed as the catalyst for the miniemulsion with toluene as it is not soluble in bulk monomer. Note that polymerization was done without amine cocatalysts, which are commonly required for effective catalysis of ruthenium-mediated polymerizations in solution,³³ though water may act as an activator or cocatalyst for this catalyst.³⁴

The polymerizations were carried out at 80 °C. As shown in Figure 2A, using the temperature-sensitive catalyst $[\text{RuCp}^*\text{Cl}(\text{PPEG})]$ in the presence of toluene, the monomer was smoothly consumed to reach nearly 85% conversion at 15 h. The rate was much higher than that with $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$, resulting in limited conversion ($\sim 40\%$). A similar rate profile was also seen for the toluene-free miniemulsion polymerization.

The $\text{RuCp}^*\text{Cl}(\text{PPEG})$ -catalyzed polymerization exhibits a much higher polymerization rate than with $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$, which can be accounted for by the structure. The PEG-containing triphenyl phosphine derivative has an electron-donating group in the para position that the triphenyl phosphine does not have. The introduction of the electron-

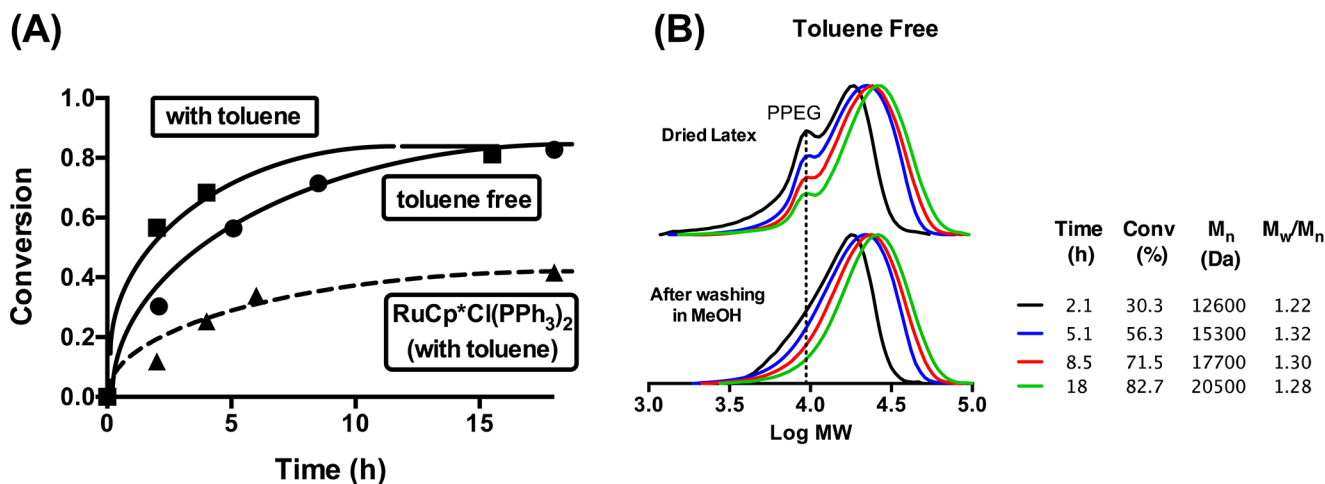


Figure 2. (A) Conversion versus time plots of miniemulsion polymerizations of BMA with RuCp*Cl(PPEG) or RuCp*Cl(PPh₃)₂ at 80 °C: [BMA]₀:[ECPA]₀:[Ru Catalyst]₀ = 100:1:0.05 with [CTAB]/[hexadecane] = 4.3/5.2 wt % vs BMA and [CTAB]/[hexadecane] = 4.3/5.2 wt % vs BMA. RuCp*Cl(PPEG) was prepared through aging of [Ru(Cp*)Cl]₄ with PEG-ligand ([Ru(Cp*)Cl]₄:[PEG-ligand] = 1:2) before polymerization, followed by use as it was. For the miniemulsion polymerizations in the presence of toluene, the solution was prepared for the volume ratio of organic/water to be 1/5 v/v%. (B) The GPC traces for the “toluene-free” miniemulsion polymerization with RuCp*Cl(PPEG): just dried latex (as they are (top)) and after washing in MeOH (bottom).

donating PEG group has been shown to produce a more active catalyst in reports investigating the effect of ligand (PEG and methoxy) substitutions.^{26,29,35,36} In addition, the coordinatively unsaturated complex (i.e., 16e) of RuCp*Cl(PPEG) and the dynamic coordination would also contribute to the higher activity.

The upper part of Figure 2B shows the GPC traces of the latex samples with RuCp*Cl(PPEG) (without toluene). The main peaks shifted to higher molecular weight as the polymerization proceeded. They are definitely from obtained poly(BMA)s, and the peak shift would indicate controlled propagation in the miniemulsion polymerization. The M_n values from these samples increased linearly with respect to conversion, although they were slightly above the theoretical values (Supporting Information, Figure S5). Along with the peaks from the controlled polymers, motionless peaks, whose elution time was almost the same as that of PPEG, were observed at lower molecular weight region. This would be reasonable since the macromolecular ligand and the complex still exist in the latex.

The z-average diameter of obtained polymer particle (82% conversion, prewashing) was 168 nm, as measured by dynamic light scattering. Interestingly, a polymerization was induced at a reaction temperature of 40 °C, significantly below the cloud point, indicating that the catalyst may be surface-bound or surface-active while mediating the polymerization (Supporting Information Figure S4).

The obtained latexes were cooled in an ice bath to quickly stop the polymerizations before washing with methanol, leaving a colorless polymer. The unmoved peaks disappeared, indicating removal of the catalyst residue. The removal process allowed exact determination of the molecular weights and its molecular weight distributions, revealing the polymerization was certainly controlled: linear relationship between M_n and conversion; low PDI (M_w/M_n ~ 1.3).

Finally, the residual ruthenium concentration in the washed polymer (at 82% conversion) was measured with ICP-AES and compared before the washing process (dried latex). It was less than 10 ppm, which was much lower than that for the just-dried

sample (360 ppm). The rough estimation indicates that more than 98% of the ruthenium catalyst was removed from the product.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, GPC of toluene-containing miniemulsion polymerizations, ³¹P NMR of catalysts, and photographs of catalyst phase transfer on macroscale. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00286.

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Notes

The authors declare no competing financial interest.

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