Amphiphilic, Thermosensitive Ruthenium(II)-Bearing Star Polymer Catalysts: One-Pot Synthesis of PEG Armed Star Polymers with Ruthenium(II)-Enclosed Microgel Cores via Metal-Catalyzed Living Radical Polymerization

Takaya Terashima,[†] Makoto Ouchi,[†] Tsuyoshi Ando,[†] Masami Kamigaito,[‡] and Mitsuo Sawamoto*,[†]

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan, Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Received October 23, 2006; Revised Manuscript Received March 1, 2007

ABSTRACT: Amphiphilic and thermosensitive star polymers with Ru(II) complex−encapsulating microgel cores were directly synthesized in high yield via $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization. For the solvo- and thermal responsiveness, the arms stem from a block copolymer of poly(ethylene glycol) methyl ether methacrylate (PEGMA) with a small amount of methyl methacrylate. For the metal encapsulation into the core, a phosphine-ligand monomer [$CH_2{=}CH(C_6H_4)PPh_2$] was "copolymerized" with a divinyl compound (linking agent); upon block polymer formation, in situ addition of these two components induced the linking reaction of the arm chains and, subsequently, the formation of Ru(II)-bearing microgels (cores) via ligand exchange between the triphenylphoshines in the original catalyst and the pendent phosphines in the core network. Thus, the hydrophobic catalyst [$RuCl_2(PPh_3)_3$] for polymerization was in situ transformed into an amphiphilic core-bound catalyst. The star polymers with different Ru(II) contents were prepared by changing the ratio of the ligand monomer to the living end (or the initiator). Even after isolation and exhaustive purification, the polymers colored dark red-brown and accordingly exhibited UV−vis absorptions similar to those of $RuCl_2(PPh_3)_3$, confirming the encapsulation of Ru(II) complexes into the core, from which the Ru(II) content was estimated in the range of 24−39 μmol/g of polymer, or 35−60 mol % of the originally added catalyst. The products were further characterized by SEC-MALLS in DMF: f (arm number) = 19−53 per polymer; $M_w = 7.7 \times 10^5$ to 2.2×10^6; and R_z (radius of gyration) = 15−22 nm. The PEG-armed star polymers were also found to be amphiphilic (soluble in both alcohols and water) and thermosensitive (UCST near 30 °C in 2-propanol).

Introduction

Recent advances in living polymerization have provided a wide variety of synthetic polymers with well-defined and complex architectures coupled with functionality.[2−4] Among them are included star polymers,[5] a class of multiarmed macromolecules that carry a few to tens of polymer "arm" chains radially connected onto a core. In particular, given a large number of functionalities to be implanted into their arms, cores, and surface (arm ends), these polymers are expected to provide unique and novel functionalized polymers of interesting spatial shape and multiple functions.

In living polymerization, star polymers may be obtained by a polymer linking reaction, or the "arm-first" method, in which linear living polymers (arms) are allowed to react with a linking agent (a bifunctional monomer such as dimethacrylate), to form a small, localized gel (microgel core) carrying the linear arm chains on its surface. Combination of this method with living radical polymerization[6] allows direct introduction of functionalities[7−9] without cumbersome protection/deprotection into arms and cores, in sharp contrast to ionic polymerizations.[10] In fact, we have developed the "arm-first" method[11,12] via ruthenium-catalyzed living radical polymerization to prepare various star polymers with block/random copolymer arms[13] and functionalized core[14]/surface.[15]

Apart from their three-dimensional shape and multiple functionality, these star polymers are unique in that the microgel core is an isolated and solubilized gel which may provide not only a supporting bed of arm chains but a interesting network space as well. In fact, we have recently synthesized "star-polymer catalysts", whose microgel core includes a large number of phosphine ligands to ligate a ruthenium complex [$RuCl_2(PPh_3)_3$]. Thus, in the living radical polymerization of methyl methacrylate (MMA) with $RuCl_2(PPh_3)_3$, a ligand monomer with phosphine is added along with a dimethacrylate as the linking agent.[16,17] It is copolymerized with the linking agent and concurrently or subsequently interacts with ruthenium catalysts and thereby form a microgel core incorporating a large number of the complexes in a single star polymer. Accordingly, the polymerization catalyst is in situ transformed into a "catalyst-supported star polymer".

The Ru(II)-bearing star polymer would be of interest as new catalysts, in view of their unique structure, possible enhancement of catalytic activity via concentrated and network embedded catalysts,[1b] tolerance against functional groups,[18] substrate selectivity,[1a−c] among others, besides solubility enhancement and facile catalyst removal already achieved by conventional polymer-supported catalysts.[19] Thus, the "star polymer catalysts"[16,17,20,21] would be distinct from hitherto known supported catalysts.

---

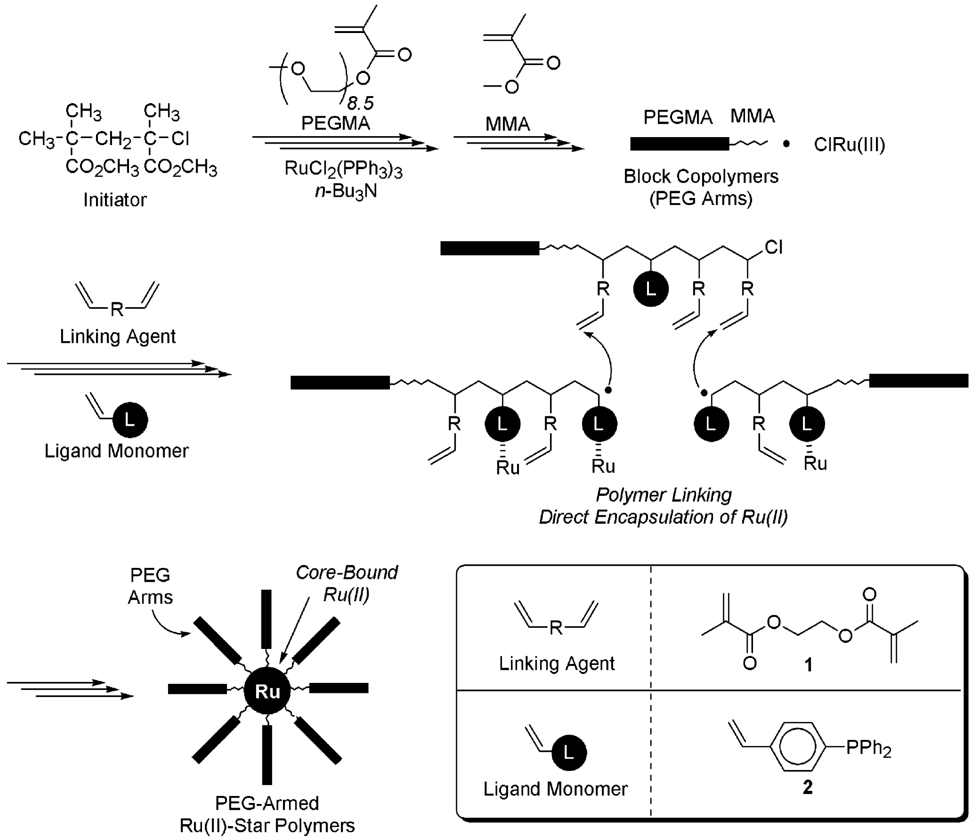
* Corresponding author. E-mail: sawamoto@star.polym.kyoto-u.ac.jp. Telephone: +81-383-2600. Fax: +81-383-2601. E-mail: sawamoto@star.polym.kyoto-u.ac.jp.

[†] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University.

[‡] Department of Applied Chemistry, Graduate School of Engineering, Nagoya University.

10.1021/ma062446r CCC: $37.00

Scheme 1. PEG Armed Star Polymers with Ru(II)-Enclosed Microgel Core by Ru(II)-Catalyzed Living Radical Polymerization



This work is to focus attention on the arm functionalization of the ruthenium-bearing star polymers outlined as above, to enhance their catalyst performance in organic reactions. We are particularly interested in the introduction of poly(ethylene glycol) (PEG) to the arms to provide amphiphilicity and thermosensitivity. Poly(ethylene glycol) methyl ether methacrylate (PEGMA), a methacrylate with a PEG side chain, was employed for the arm synthesis via our ruthenium-mediated living radical polymerization.

Living radical polymerizations of PEGMA have recently been examined extensively,[22,23] because the polymer was attractive as not only amphiphilic and thermosensitive materials,[24−26] but also electrolytes[27] for batteries and biocompatible and medically useful polymers.[28,29] Additional advantages include possible applicability for aqueous organic reactions[1c] and ready catalyst removal and recycle,[30] thanks to the thermoresponsive solubility change in PEG. Importantly, unlike usual organometallic complexes, ruthenium catalysts are uniquely tolerant against the polyether functions in PEGMA and its polymers to allow controlled radical polymerization required in the star polymer synthesis via polymer linking.

Herein we report a novel synthetic pathway (Scheme 1) to PEG-armed star polymers with Ru(II)-enclosed microgel cores via one-pot transformation of "polymerization catalysts" into "amphiphilic, homogeneous star polymer catalysts". The living PEGMA arms were subsequently cross-linked with a dimethacrylate as a linking agent in the presence of a phosphine-ligand functionalized styrene, to produce the PEG-armed star polymers with Ru(II)-encapsulated microgel-core. The star polymers were characterized in terms of yield, molecular weight, size, and loaded amount of Ru(II) into the core. Furthermore, the amphiphilicity and thermosensitivity of the star polymers were also examined.

Experimental Section

Materials. Poly(ethylene glycol) methyl ether methacrylate (PEGMA; $M_n \approx 475$) was of commercial source (Aldich), was purified by passing it through an inhibitor removal column (Aldrich) and degassed by reduced pressure before use. Methyl methacrylate (Tokyo Kasei; purity>99%) was dried overnight over calcium chloride, and purified by double distillation from calcium hydride before use. $(MMA)_2Cl$ was prepared according to the literature.[31] Divinyl compound **1** (Aldrich, purity >98%) was purified by distillation from calcium hydride before use. Phosphine ligand monomer **2** was prepared according to the literature.[32]

$RuCl_2(PPh_3)_3$ (Aldrich, 97%) was used as received and handled in a glove box under a moisture- and oxygen-free argon atmosphere ($H_2O < 1$ ppm, $O_2 < 1$ ppm). n-Bu_3N (Tokyo Kasei; purity>98%) was bubbled with dry nitrogen for more than 15 min before use. Toluene (solvent) and internal standards for gas chromatography (n-octane for MMA, tetralin for **1**) from dried overnight over calcium chloride, distilled twice from calcium hydride. Hexane (Wako, dehydrated) for star polymer precipitation was used as received. The solvents were bubbled with dry nitrogen for more than 15 min before use.

Polymerization Procedures. The polymerization was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedures with $(MMA)_2Cl/RuCl_2(PPh_3)_3/n\text{-}Bu_3N/\mathbf{1}/\mathbf{2}$ follows: In a 50 mL round-bottomed flask was placed $RuCl_2(PPh_3)_3$ (0.09 mmol, 86.29 mg), toluene (6.45 mL), n-Bu_3N (0.18 mmol, 0.45 mL, 400 mM in toluene), PEGMA (4.5 mmol, 1.98 mL), and $(MMA)_2Cl$ (0.09 mmol, 0.12 mL, 773 mM in toluene) were added sequentially in this order at 25 °C under dry nitrogen. The total volume of the reaction mixture was thus 9 mL. Immediately after mixing, the mixture placed in an oil bath at 80 °C. After the polymerization had reached over ca.90% conversion in 10 h, MMA (0.9 mmol, 0.096 mL), n-octane (0.024 mL) were added to the unquenched solution. After the block polymerization had reached over ca. 78% conversion of MMA in 24 h, a solution of **1**(1.35 mmol, 0.63 mL,

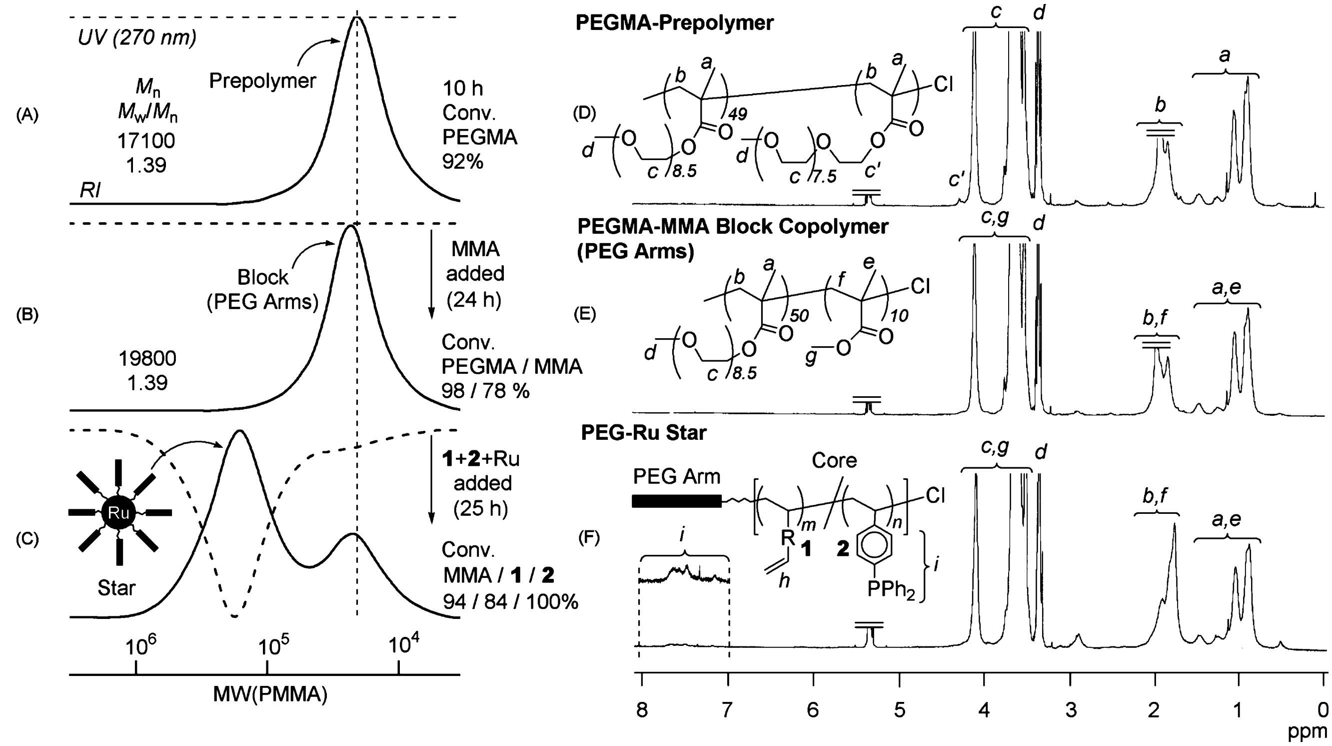


Figure 1. MWD and ^{1}H NMR spectra of the products obtained from the reaction of living PEGMA-MMA block copolymer with divinyl compound **1** and phosphine ligand monomer **2** in toluene at 80 °C. Prepolymer: $[\text{PEGMA}]_0/[(\text{MMA})_2\text{Cl}]_0/[\text{RuCl}_2(\text{PPh}_3)_3]_0/[n\text{-Bu}_3\text{N}]_0 = 500/10/10/20$ mM. Block copolymer: $[\text{MMA}]_{\text{add}} = 100$ mM (neat). Linking: $[\mathbf{1}]_{\text{add}}/[\mathbf{2}]_{\text{add}}/[\text{RuCl}_2(\text{PPh}_3)_3]_{\text{add}} = 300/25/20$ mM; prepolymer solution/linking solution = 2/1 v/v (the final molar ratio of used compounds PEGMA/$(\text{MMA})_2\text{Cl}$/MMA/**1**/**3**/$\text{RuCl}_2(\text{PPh}_3)_3$ = 50/1/10/15/1.25/1). (A) PEGMA-prepolymer, (B) PEGMA-MMA block copolymer (PEG arms) recovered after addition of MMA in 24 h, and (C) PEG−Ru star obtained after addition of **1**, **2**, and $\text{RuCl}_2(\text{PPh}_3)_3$ in 25 h. ^{1}H NMR spectra in CD_2Cl_2 at room temperature: (D−G) samples (A−C), respectively.

2159 mM in toluene), **2**(0.11 mmol, 0.11 mL, 1000 mM in toluene), tetralin (0.09 mL), and $\text{RuCl}_2(\text{PPh}_3)_3$ (86.29 mg) in toluene (3.68 mL) was added to the unquenched arm-polymer solution. The reaction was terminated by cooling the mixture to −78 °C. The conversion of PEGMA and **2** was determined from the ratio of the peak areas of olefin groups derived from PEGMA and **2** respectively to those of tetralin by ^{1}H NMR spectra. The conversion of the MMA and **1** was determined from the concentrations of the residuals measured by gas chromatography with the internal standards as *n*-octane (MMA) and tetralin (**1**). Finally, PEGMA, MMA, **1**, and **2** were consumed ca. 98%, 94%, 84%, and 100% respectively after addition of **1**, **2**, and Ru (25 h). The quenched reaction mixtures were diluted with toluene (ca. 40 mL) and rigorously shaken with an absorbent [kyowaad-2000G-7 ($\text{Mg}_{0.7}\text{Al}_{0.3}\text{O}_{1.15}$); Kyowa Chemical] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature.

Star Polymers Purification for Characterization (SEC-MALLS, UV—Vis, ICP-AES). The quenched reaction mixtures of star polymers were precipitated into hexane under dry nitrogen for the purpose of removing unreacted monomers and amine (additive). The red-brown polymers precipitated were filtered off, and dried under vacuum. The polymers were dissolved in toluene and passed through silica . gel (Wako Gel 200) column under dry nitrogen, which could achieve the removal of free Ru(II)-catalysts. The polymer solutions were evaporated under vacuum before analysis.

Polymer Characterization. The MWD, M_n, and M_w/M_n ratios of the polymers were measured by SEC in DMF containing 10 mM LiBr at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L; exclusion limit = 5×10^6; pore size = 20−1000 Å; 0.8 cm i.d. ×30 cm) that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV-970 UV/vis detector set at 270 nm. The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; $M_n = 200-1200000$; $M_w/M_n = 1.06-1.22$) as well as MMA monomer.

^{1}H NMR spectra were recorded in CD_2Cl_2 at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymer samples for ^{1}H NMR were fractionated by preparative SEC (column: α-gel α-3000) and those for MALLS analysis were written above.

The absolute weight-average molecular weight (M_w) of the polymers was determined by multiangle laser light scattering (MALLS) in DMF containing 10 mM LiBr at 40 °C on a Dawn E instrument (Wyatt Technology; Ga−As laser, $\lambda = 690$ nm). The refractive index increment (d*n*/d*c*) was measured in DMF at 40 °C on Optilab DSP refractometer (Wyatt Technology; $\lambda = 690$ nm, $c < 8.0$ mg/mL).

UV−vis spectra were analyzed in $\text{CH}_2\text{ClCH}_2\text{Cl}$ at room temperature on a Shimadzu MultiSpec-1500. The core-bound Ru(II) was calculated by using the absorbance at 475 nm and calibration plot made for $\text{RuCl}_2(\text{PPh}_3)_3$ (0.10−2.0 mM solution) at the same wavelength. Ruthenium content in the polymers was also measured by ICP-AES (Jarrell-Ash IRIS AP).

AFM measurements were performed by SPI3800 probe station and SPA300 unit system of the scanning probe microscopy system (Seiko Instruments). The cantilever was made of silicon (Olympus), and its spring constant was 20 N/m. The measurements were performed in a dynamic force mode (noncontact mode). For sample preparation, a 0.3 wt % star polymer solution in DMF was dropped and spread on a micro slide glass (IWAKI). The sample was dried in a horizontal position in a desiccator under vacuum for 6 h.

Results and Discussion

1. Synthetic Feasibility of PEG-Armed Star Polymers with Ru(II)-Bearing Microgel Core.

Star polymers with microgel cores have been synthesized by the linking reactions of living linear polymers (arms) with certain divinyl compounds.[11−17] These studies have revealed that the yield depends on various

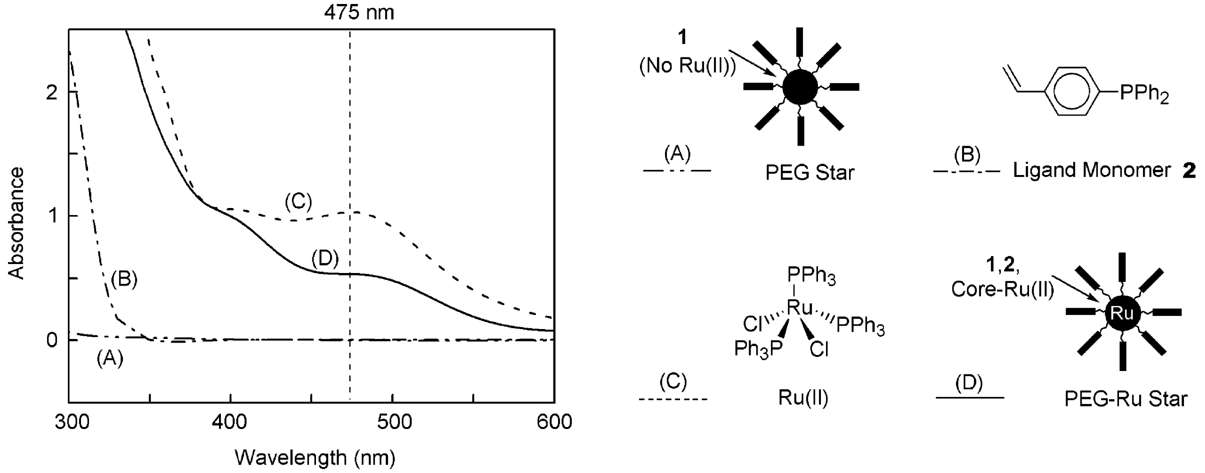


Figure 2. UV−vis spectra in CH_2ClCH_2Cl at room temperature. (A) PEG star obtained in Figure 3A = 12.5 mg/mL. (B) Ligand monomer **2** = 1.0 mM. (C) Polymerization catalyst $RuCl_2(PPh_3)_3$ = 0.98 mM. (D) PEG−Ru star = 12.5 mg/mL.

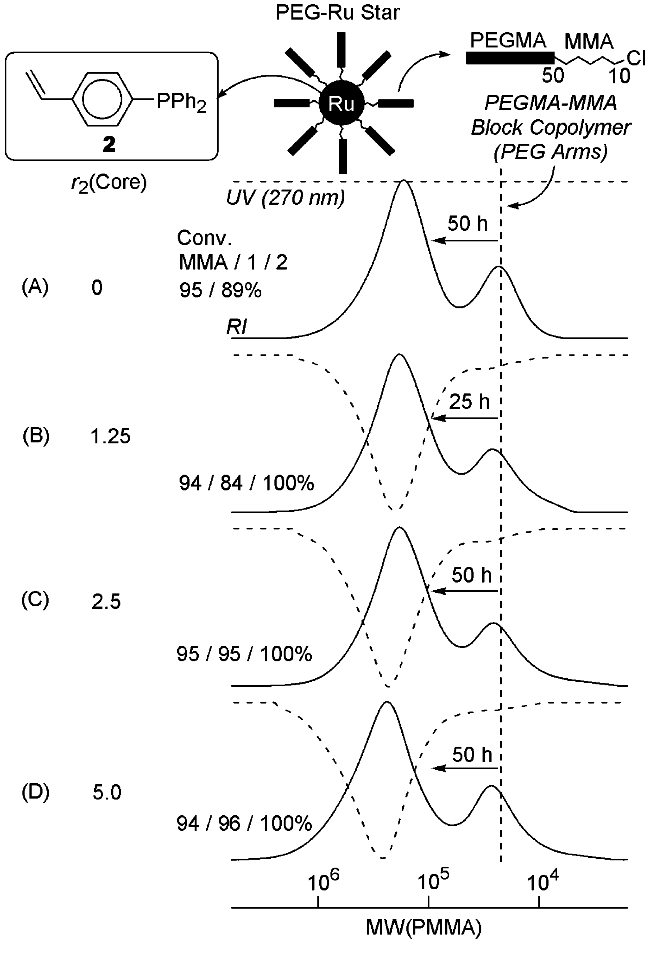


Figure 3. PEG armed Ru(II)-star polymers obtained from living PEG Arms with linking agents **1** and ligand monomer **2** in toluene at 80 °C: $[P^*] = 10$ mM; DP (arm) = 60; r_1 (core) = $[\mathbf{1}]_0/[P^*]_0 = 15$; r_2 (core) = $[\mathbf{2}]_0/[P^*]_0$. (A−D) Linking agent **1**, $r_2 = 0-5$.

factors such as the relative concentrations of monomer, initiator (living end), and linking agent, along with catalytic activity. Furthermore, the steric hindrance of arm chains (i.e., the bulkiness of the monomer substituent) might be also important for efficient linking reactions. Thus, the PEGMA linear polymers with long and bulky PEG side chains were predicted to interfere with the arm linking processes. Actually, the living linear PEGMA-prepolymers (arms) could not afford the effective linking reactions under the condition used previously (support information Figure 1),[33] where just a divinyl compound (**1**) was added into polymerization solution via $RuCl_2(PPh_3)_3$-based system with the optimized mole ratio for PMMA-armed star polymers.[11,16,17]

On the basis of preliminary experiments, we added a small amount of MMA to a solution of living poly(PEGMA) before the linking reaction, to generate block copolymers. As a result, the steric hindrance around the growing end of the arms would be reduced and similar to that of living PMMA, which have already been demonstrated to undergo relatively efficient linking reactions.[11] To verify the synthetic strategy, we analyzed the products obtained in successive individual steps by size-exclusion chromatography (SEC), ^{1}H NMR, and UV−vis spectroscopy.

(a) Size-Exclusion Chromatography (SEC) Analysis. Poly(ethylene glycol) methyl ether methacrylate (PEGMA; M_n = 475; 8.5 equiv of PEG units to the methacrylate group; i.e., $n = [-CH_2CH_2O-]_0/[PEGMA]_0 = 8.5$) was polymerized with $(MMA)_2Cl$[31] (initiator) coupled with $RuCl_2(PPh_3)_3$[33] (catalyst) and n-Bu_3N[34] (additive) in toluene at 80 °C (Scheme 1). The polymerization smoothly reached 92% conversion in 10 h to give a linear PEGMA-prepolymer (P*) with a relatively narrow molecular weight distribution (MWD) [$M_n = 1.70 \times 10^4$ (PMMA standard), $M_w/M_n = 1.39$] (Figure 1A).

At this point, a small amount of MMA (10 equiv to living end P*; $[MMA]_0/[P^*]_0 = 10$) was added into the unquenched prepolymer (P*) solution maintained at 80 °C. In an additional 24 h, the obtained products showed an unimodal SEC curve of slightly higher molecular weight than that of P* [$M_n = 1.98 \times 10^4$ (PMMA standard), $M_w/M_n = 1.39$, conversion of PEGMA/MMA: 98%/78%] (Figure 1B). This would indicate the small amount of MMA was polymerized from the end group of the PEGMA prepolymer to produce a PEGMA-MMA block copolymer (less hindered "PEG arms"). Note that, at the end of this block polymerization, PEGMA had almost quantitatively been consumed.

In the subsequent linking reaction, a toluene solution of **1**[11] (linking agent), **2**[16,17,31] (phosphine ligand monomer), and $RuCl_2(PPh_3)_3$ ($r_1 = [\mathbf{1}]/[P^*] = 15$, $r_2 = [\mathbf{2}]/[P^*] = 1.25$) was added into the solution of the prepolymer ("PEG arm"). An efficient polymer linking and microgel core formation ensued, with the concurrent encapsulation of the Ru catalysts, as observed for the corresponding MMA-based star polymers.[16,17]

The products obtained after 25 h (Figure 1C) exhibited a bimodal SEC curve. The peak of higher molecular weight was derived from star polymers, and the other was for unlinked linear

Table 1. Ru(II)-Bearing Microgel Star Polymers with Various Phosphine Ligand Densities

entry	arm	r_2[c](core)	$M_{w,arm}$(SEC)[d]	$M_w/M_{n,arm}$(SEC)	$M_{w,arm}$(MALLS)[e]	$M_{w,star}$(SEC)	$M_{w,\ star}$(MALLS)[e]	d*n*/dc_{star}[f] (mL/g)	no. of arms[g]	R_z[h] (nm)	yield[i] (%)
A	PEGMA[a]	0	35 300	1.46	41 000	216 000	803 000	0.0507	18	16.1	74
B	PEGMA[a]	1.25	34 800	1.47	40 900	207 000	772 000	0.0540	16	15.1	76
C	PEGMA[a]	2.5	34 800	1.47	40 900	208 000	1 190 000	0.0559	25	17.3	75
D	PEGMA[a]	5	34 800	1.47	40 900	302 000	2 220 000	0.0574	45	21.6	74
E	MMA[b]	1.25	9 800	1.19		286 000	600 000	0.0815	40	11.6	88

[a] Reaction conditions: $[P^*] = 10$ mM; DP(arm) = $[\text{monomer}]_0/[P^*]_0 = 60$ (A−D, PEGMA-*b*-MMA; E, MMA); $r_1(\text{core}) = [\mathbf{1}]_0/[P^*]_0 = 15$ with $RuCl_2(PPh_3)_3$, *n*-Bu_3N and **2** (phosphine ligand monomer) in the mixture of toluene at 80 °C. [b] Reaction conditions: $[P^*] = 20$ mM; DP(arm) = $[\text{monomer}]_0/[P^*]_0 = 60$ (A−D, PEGMA-*b*-MMA; E, MMA); $r_1(\text{core}) = [\mathbf{1}]_0/[P^*]_0 = 15$ with $RuCl_2(PPh_3)_3$, *n*-Bu_3N and **2** (phosphine ligand monomer) in the mixture of toluene at 80 °C. [c] Mole ratio of phosphine ligand monomer to P* ($r_2 = [\mathbf{2}]_0/[P^*]_0$). [d] Size-exclusion chromatography. [e] Multiangle laser light scattering. [f] Refractive index increment. [g] Arm numbers per molecule = (mole fraction of arm monomer) × $M_{w,star}$(MALLS)/$M_{w,arm}$ (A−D, MALLS; E, SEC). [h] Mean radius of gyration by MALLS. [i] Calculated from the areas of SEC curves.

polymers, because the position was almost the same as that of the PEG arms. The star polymer yield was ca. 76%, calculated from the area ratio of the two peaks. The main peak was accompanied by intensive UV absorptions (broken line) derived from **2**, which was not seen for PEG arms. These indicate that the linking reaction of PEG arms (PEGMA-MMA block copolymers) and introduction of phosphine ligand into the core occurred simultaneously to form PEG-armed star polymer with a microgel core carrying phosphine ligands.

(b) ^{1}H NMR Analysis. Figure 1, parts D−F, shows the ^{1}H NMR spectra of PEGMA prepolymer, PEGMA-MMA block copolymer (PEG arm), and the final products (star polymer); the three polymer samples correspond to the samples whose SEC traces are shown in parts A, B, and C of Figure 1, respectively.

Figure 1D shows a small characteristic signal (c') of the ester methylene protons adjacent of the chlorine atom at the ω-end near the large absorptions (c) of the methylene protons of poly(ethylene glycol) pendent units, with the backbone PEGMA repeat unit (a, b) and the pendent ester methyl protons (d). The products obtained after addition of MMA (Figure 1E) exhibited the disappearance of the small signal (c'). This indicates that the first-born growing PEGMA terminal was converted into a MMA counterpart to give PEGMA-MMA Block copolymer (PEG arm). The backbone MMA repeat unit (e, f) could not be observed due to the quite close structure to that of PEGMA (a, b). There were also no olefinic protons originated from loss of halogens via side reactions.

In Figure 1F, a new signal (i) derived from the aromatic groups of **2** appeared and virtually no olefin peaks (h: 5.5−6.5 ppm) from **1** were detected. The series of ^{1}H NMR spectra thus showed PEGMA-MMA block copolymer (PEG arm) reacted with the divinyl compound **1** and phosphine ligand monomer **2** to form PEG-armed star polymers with phosphine ligand microgel core.

(c) UV—Vis Analysis. The prepared star polymer was further analyzed by UV−vis to confirm direct encapsulation of ruthenium catalysts into the microgel core. Figure 2 shows the spectra of the product (D), along with the PEG-armed star (PEG star) (A), phosphine ligand monomer **2** (B), and $RuCl_2(PPh_3)_3$ (C). As described in previous literature,[17] both star polymer samples were purified by a precipitation into hexane and column chromatography on silica gel using toluene as the eluent. The product exhibited a broad absorption between 350 and 600 nm, which was almost the same as that of $RuCl_2(PPh_3)_3$ (Figure 2, parts C and D). On the other hand, no signal was observed in the PEG star (Figure 2A), synthesized by the linking reaction of PEGMA-MMA block copolymers ("PEG arm") with only a divinyl compound **1** (GPC curves is shown in Figure 3A). Additionally, **2** (Figure 2B) showed the absorptions of the aromatic groups below 350 nm. These results demonstrate the products include the ruthenium complex in the core, which was directly encapsulated by a ligand exchange reaction with phosphine ligands **2** during the linking reaction of arms.

2. Effects of Ligand Monomer Concentration on Star Polymer Yield. To investigate effects of ligand monomer (**2**) concentration on the star polymer yield, we synthesized PEG-armed star polymers with various ligand concentrations in the core. Figure 3, parts A−D, shows SEC curves of the products that were respectively prepared with 0, 1.25, 2.5, and 5.0 r_2 (= $[\mathbf{2}]/[P^*]$: ratio of **2** to PEGMA-prepolymer). As seen in Figure 3, the star polymer was obtained under every condition and the yield was independent of the phosphine ligand concentration (about 75% for every case), which is similar tendency to the PMMA armed counterpart.[17] The effects on other factors were discussed below.

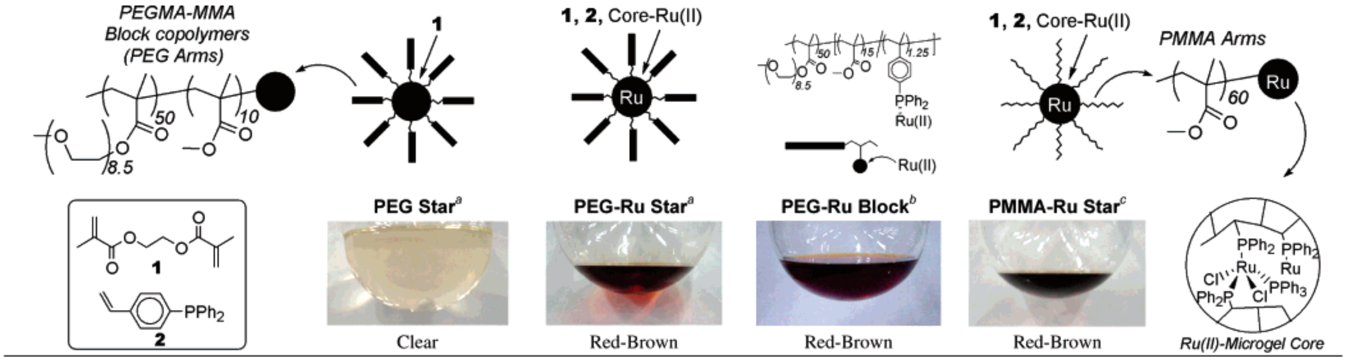
3. Polymer Characterization. (a) SEC-MALLS Analysis. The absolute weight-average molecular weights (M_w), the arm numbers (f), and the gyration radius (R_z) of the star polymers (given in Figure 3) were characterized by using multiangle laser light scattering (MALLS)[14] coupled with SEC in DMF (Table 1). The purification of star polymers was the same way as stated in UV−vis analysis part.

The obtained star polymers had M_w of 7.7×10^5 to 2.2×10^6 and R_z of 15 − 22 nm. The average number (f) of arms per star polymer was then calculated from M_w by MALLS/SEC. Consequently, the star polymers have 16−45 arms/molecule. The M_w determined by SEC was lower than that by MALLS, which indicates that the star polymers were more compact than the linear counterparts with the same molecular weights. $M_{w,star}$(MALLS), f, and R_z increased with r_2 (core), although they were almost the same for r_2 of 0 (entry A) and 1.25 (entry B). Especially, the star polymer, synthesized by a large amount of phosphine ligand monomer ($r_2 = 5$; entry D), had quite large M_w (2.2×10^6) and many arms (45) in comparison to the others.

These structure-factors of the star polymers with PEG arms (characterized above) were compared to that with poly(MMA) arms prepared under a similar condition, where DP of arms, r_1, and r_2 were uniform (entry B vs E, in Table 1). The higher $M_{w,star}$(MALLS) is likely caused by the higher molecular weight of a monomer unit of arm-polymer. The lower arm number (f) would be attributed to the larger excluded volume of PEG arms due to steric hindrance between the neighboring arms, which might be also concerned with the lower yield. The larger mean radius of gyration would be responsible for the difference of chain dimension between the two arms in DMF solvent. Poly(PEGMA) ("PEG-arms") would be more stretched because of the bulkier substitute than MMA.

(b) AFM Analysis: Direct Observation of PEGMA Star Polymers. We have already reported the direct observation of

Table 2. Calculation of Core-Bound Ru(II) by UV−Vis and ICP-AES Analysis



	PEG Star[a]	PEG-Ru Star[a]			PEG-Ru Block[b]	PMMA-Ru Star[c]
r_2 (core)[d]	0	1.25	2.5	5.0	1.25	1.25
Ru (obsd; UV)[e], μmol/g	0.56	24	30	39	17	29
Ru (obsd; ICP-AES)[f], μmol/g	1.1	27	24	52	–	–
Ru (calcd)[g], μmol/g	–	68	67	65	80	99
Ru (UV) Incorporation[h], %	–	35	45	60	21	30

[a] Reaction conditions: PEGMA (DP = $[\text{PEGMA}]_0/[\text{P*}]_0 = 50$), MMA (DP = $[\text{MMA}]_0/[\text{P*}]_0 = 10$), linking agent **1** ($r_1 = [\mathbf{1}]_0/[\text{P*}]_0 = 15$), and phosphine ligand monomer **2**. [b] Reaction conditions: PEGMA (DP = $[\text{PEGMA}]_0/[\text{P*}]_0 = 50$), MMA (DP = $[\text{MMA}]_0/[\text{P*}]_0 = 15$), and **2** ($r_2 = [\mathbf{2}]_0/[\text{P*}]_0 = 1.25$). [c] Reaction conditions: MMA (DP = $[\text{MMA}]_0/[\text{P*}]_0 = 60$), **1** ($r_1 = [\mathbf{1}]_0/[\text{P*}]_0 = 15$), and **2** ($r_2 = [\mathbf{2}]_0/[\text{P*}]_0 = 1.25$), with $(\text{MMA})_2\text{-Cl/RuCl}_2(\text{PPh}_3)_3/n\text{-Bu}_3\text{N}$ in the mixture of toluene at 80 °C. [d] Mole ratio of phosphine ligand monomer **2** to P* ($r_2 = [\mathbf{2}]_0/[\text{P*}]_0$). [e] Determined by UV absorption at 475 nm. [f] Measured by ICP-AES (Jarrell-Ash IRIS AP). [g] The calculated value assuming that all Ru catalysts introduced into the star polymers. [h] Mole percent of core-bound Ru(II) to Ru(calcd) (=100 [Ru(obsd; UV)]/[Ru(calcd)]).

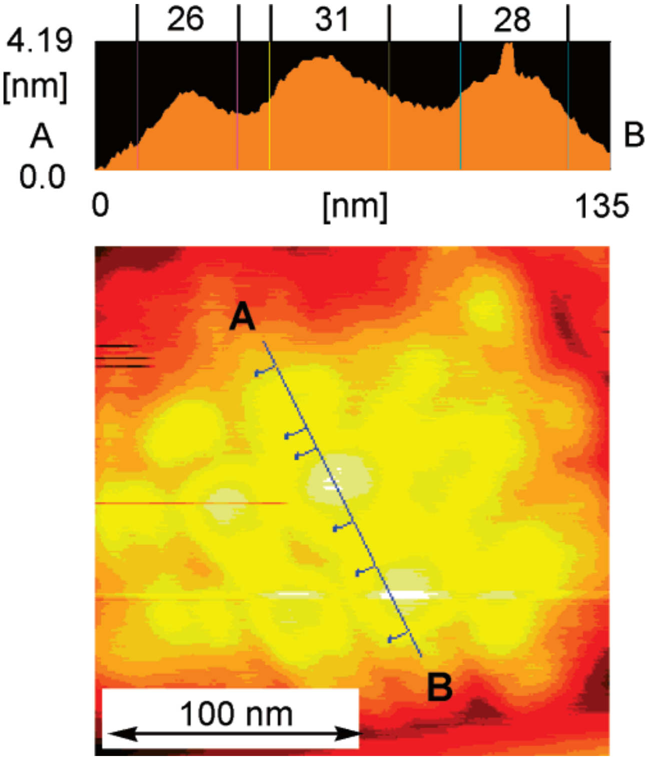


Figure 4. AFM images of PEG−Ru star (Table 1B) cast on a glass plate from 0.3 wt % DMF solution.

star polymers cast on the glass plate by atomic force micrograph (AFM).[16,17] From this observation, it revealed that the cast PMMA-armed star polymers exhibited semicircular structure and smaller than the conformation in DMF solution. Thus, the solid-state structures of PEGMA-armed star polymers were also analyzed by AFM.

Figure 4 shows the atomic force micrograph of Ru(II)-functionalized star polymers with PEG-arms (Table 1. entry B), cast from a 0.3 w% DMF solution on a glass plate. The star polymers were observed as individual star polymer molecules (yellow circles) to reveal semicircular images with ≈ 30 nm diameters and ≈ 4 nm heights. The height value in solid state might show the diameter of the microgel core due to relatively hard cross-linked structure.[12] These diameters and heights were very close to those of the PMMA-armed star polymers. However, as already shown in Table 1, the MALLS analyses in DMF solution indicated that the diameters of PEG-armed star polymers considerably larger than those of the PMMA-armed. These results would be due to the different conformation between in bulk and in solution.

(c) UV−Vis and ICP-AES Analysis: Calculation of Core-Bound Ru(II). The PEG-armed star polymers were analyzed by UV−vis and IPC-AES to determine the amount of loaded Ru(II) catalysts into the microgel core (Table 2). When the phosphine ligand **2** was not added at the linking stage (PEG star), the toluene solution of final products after purification was almost colorless indicating little ruthenium catalysts were contained. The amount was quite low, 0.56 μmol Ru/g of polymer by UV−vis analysis with calibration plot for $\text{RuCl}_2(\text{PPh}_3)_3$ at 475 nm. In contrast, the star polymers with an introduction of phosphine ligand **2** into the core (PEG−Ru star) exhibited a red-brown color originating from ruthenium complexes in toluene even after purification, and the bound amount was estimated as 24−39 μmol Ru/g of polymer. These values were in approximate agreement with those by ICP-AES (24−52 μmol/g). The loaded ruthenium catalysts into the core increased with increasing the ratio r_2.[17]

To examine the effects of polymer-conformation, the linear block copolymer (PEG−Ru linear block)[35] was also prepared in the similar way except for no addition of linking agent. The composition is almost same as "PEG−Ru star" and therefore it corresponds to "cut-out" from "PEG−Ru star". The solution also exhibited a red-brown color even after purification, which suggested that ruthenium was bound by the phosphine side chain. However, the percentage of Ru loaded into the polymer was smaller than that for PEG−Ru star. The star type would more efficiently incorporate ruthenium by virtue of microgel formation than the linear type.

As compared with PMMA-arm star (PMMA−Ru star) prepared under similar conditions (r_2 = 1.25), the loaded ruthenium proportion was almost the same, which shows that the arm-structure does not affect the ruthenium incorporation.

Table 3. Solubility of Amphiphilic PEGMA Polymers[a]

			solvent						
entry	shape	polymer structure[b]	hexane	toluene	$CHCl_3$	DMF	1-propanol	MeOH	H_2O[c]
A	PEG prepolymer	$(PEGMA)_{50}$	−	+	+	+	+	+	+
B	PEG-MMA block (arm)	$(PEGMA)_{50}$-$(MMA)_{10}$	−	+	+	+	+	+	+
C	PEG−Ru block	$(PEGMA)_{50}$-$[(MMA)_{15}$-/-$(\mathbf{2}\text{-Ru})_{1.25}]$	−	+	+	+	+	+	+
D	PEG star	$(PEGMA)_{50}$-$(MMA)_{10}$-$(\mathbf{1})_{15}$	−	+	+	+	+	+	+
E	PEG−Ru star	$(PEGMA)_{50}$-$(MMA)_{10}$-$[(\mathbf{1})_{15}$-/-$(\mathbf{2}\text{-Ru})_{1.25}]$	−	+	+	+	+	+	+
F	PMMA−Ru star	$(MMA)_{60}$-$[(\mathbf{1})_{15}$-/-$(\mathbf{2}\text{-Ru})_{1.25}]$	−	+	+	+	−	−	−

[a] Key: (+) soluble; (−) insoluble, at room temperature in 3 wt % solution. [b] The segment compositions (DP_n) are the calculated values. The characterization data of the samples: (A) Figure 1A; (B) Figure 1B; (C) M_n = 23 100 (PMMA calcd.), M_w/M_n = 1.48; (D) Table 1A; (E) $M_{n,arm}$(SEC) = 23 000 (PMMA calcd), $M_w/M_{n,arm}$(SEC) = 1.50, $M_{w,star}$(MALLS) = 1 040 000; (F) Table 1E. [c] From room temperature to 100 °C.

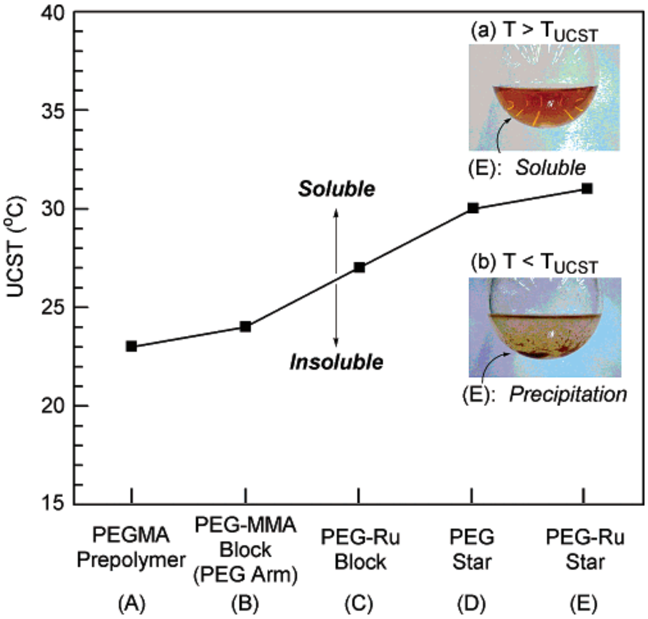


Figure 5. UCST of various PEGMA polymers in 3 wt % 2-propanol solutions: samples A−E correspond to Table 3A−E, respectively. Inset pictures: (a) PEG−Ru star (E) in 2-propanol above UCST; (b) PEG−Ru star (E) in 2-propanol under UCST.

Importantly, this would also indicate that PEG−Ru star bears ruthenium only at the microgel core and not at the arm-chain.

4. Solubility. As is well-known, the PEG segments have the amphiphilic and thermosensitive properties.[23a,24−26] Actually, "PEG−Ru star" showed amphiphilic property for wide rage of solvents including water (Table 3E). In contrast, PMMA−Ru star was obviously hydrophilic and soluble in limited solvents (Table 3F). Thus, the PEG−Ru star would allow various applications as a catalyst. On the other hand, the star-form and presence of ruthenium had little effects on solubility since all the PEGMA-based polymers showed the same solubility regardless of composition, structure, and incorporation of ruthenium (Table 3, parts A−E).

Furthermore, the "PEG−Ru star" showed thermosensitive solubility for 2-propanol solvent and upper critical solution temperature (UCST) was observed, where it was soluble (homogeneous) at above the UCST (~31 °C) and precipitated at below it (Figure 5). The phase separation was quite sensitive and reversible on heating and cooling. In comparison with other PEGMA-based polymers, the UCST depended on the structure and the composition. The star polymers (D, E) have higher UCST than the linear polymers (A, B, and C), which would be caused by higher contents of hydrophobic segments; MMA, phosphine, and linking agent. Introduction of ruthenium catalyst also increased UCST in either case of linear- (B vs C) and star-structure (D vs E).

As seen in these results, amphiphilicity and thermosensitivity of the "PEG−Ru star" were demonstrated. It is noteworthy that it possesses such properties in spite of the hydrophobic microgel structure at the core. These would be attributed to the unique structure where the core is separated from external environment by lots of PEG-based arms.

Conclusions

We have demonstrated that PEG-armed star polymers with a Ru(II)-bearing microgel core were synthesized via Ru(II)-catalyzed living radical polymerization of PEGMA and subsequent linking reaction of the living polymers with divinyl compounds and phosphine ligand monomers. Importantly, even such a bulky monomer with a polymeric side chain allowed star polymer formation, as proved by a series of analyses such as NMR, SEC, MALLS, and AFM giving various structure factors. The ruthenium encapsulation was confirmed by not only the appearance of solution color but also the UV−vis and ICP-AES analysis. The proportion of bound ruthenium was adjustable depending on the amount of phosphine ligand without disturbing star polymer formation. These PEG-armed star polymers were soluble in various solvents due to their amphiphilic arms and also exhibited unique thermosensitive properties, UCST-type phase separation in 2-propanol at ambient temperature. The catalytic functions of these Ru(II)-bearing microgel cores in PEGMA armed star polymers will be the subjects of our forthcoming articles.

Acknowledgment. T.T. is grateful to the Japan Society for the Promotion of Sciences (JSPS) for a Grant-in-Aid for JSPS Fellows (No. 16-1205). We thank Prof. H. Matsuoka and Dr. K. Matsumoto (Kyoto Univ.) for AFM and Mr. H. Sakai and Mr. T. Ono (Kurarey Co. Ltd.) for IPC-AES.

Supporting Information Available: Figure showing SEC data of PEG-armed star polymers synthesized by the linking reaction of PEGMA prepolymers without a short MMA segment and text discussing the synthesis of PEG-armed star polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) This work was presented in part at the following meeting: (a) The 52th Symposium on macromolecules, Yamaguchi, Japan, September 2003; paper IIB15: Terashima, T.; Ando, T.; Sawamoto, M.; Kamigaito, M. *Polym. Prepr. Jpn.* **2003**, *52* (8), 1530. (b) The 53th Annual Meeting on the Society of Polymer Science, Kobe, Japan, May 2004; paper IIC13: Terashima, T.; Ando, T.; Sawamoto, M.; Kamigaito, M. *Polym. Prepr. Jpn.* **2004**, *53* (1), 166. (c) The 53th Symposium on macromolecules, Hokkaido, Japan, September 2004; paper I D12: Terashima, T.; Ando, T.; Sawamoto, M.; Kamigaito, M. *Polym. Prepr. Jpn.* **2004**, *53* (2), 2604.

(2) Matyjaszewski, K. *Polym. Int.* **2003**, *52*, 1559.

(3) Mori, H.; Muller, A. H. E. *Prog. Polym. Sci.* **2003**, *23*, 1403.

(4) Hawker, C. J.; Wooley, K. L. *Science* **2005**, *309*, 1200.

(5) For reviews on star polymers, see: (a) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *51*, 406. (b) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 90. (c) Marsalkó, T. M.; Majoros, I.; Kennedy, J. P. *Pure Appl. Chem.* **1997**, *A34*, 775. (d) Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857. (e) Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A.; Higashihara, T. *Prog. Polym. Sci.* **2005**, *30*, 111.

(6) For recent reviews on living radical polymerization, see: (a) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (c) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661. (d) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rec.* **2004**, *4*, 159. (e) Perrier, S.; Takolpuckdee, P. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5347. (f) Matyjaszewski, K., Ed. *ACS Symposium Series 854*; American Chemical Society: Washington, DC, 2003.

(7) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 8005.

(8) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromol. Symp.* **2000**, *157*, 193.

(9) Fuji, Y.; Watanabe, K.; Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2055.

(10) For reviews on synthesis of star polymers by cationic living polymerization, see: (a) Sawamoto, M. In *Cationic polymerization*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 412−420. (b) Sawamoto, M.; Kamigaito, M. In *New Methods of Polymer Synthesis*; Ebdon, J. R., Eastmond, G. C., Eds.; Blackie: Glasgow, Scotland, 1995; Vol. 2, pp 37−68. (c) Sawamoto, M.; Kanaoka, S.; Higashimura, T. In *Hyper-Styructured Molecules I: Chemistry, Physics and Application*; Sasabe, H., Ed.; Gordon and Breach Science Publishers: Amsterdam, 1999; pp 43−61.

(11) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 215.

(12) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2245.

(13) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 633.

(14) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 7629.

(15) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1972.

(16) Terashima, T.; Kamigaito, M.; Baek, K.-Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2003**, *125*, 5288.

(17) Terashima, T.; Ouchi, M.; Ando, T.; Sawamoto, M.; Kamigaito, M. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4966.

(18) Terashima, T.; Ouchi, M.; Ando, T.; Sawamoto, M. *Polym. Prepr. Jpn.* **2005**, *54* (2), 2810.

(19) For recent reviews on polymer-supported catalysts, see: (a) Toy, P. H.; Janda, K. D. *Acc. Chem. Res.* **2000**, *33*, 546. (b) Clapham, B.; Reger, T. S.; Janda, K. D. *Tetrahedron* **2001**, *57*, 4637. (c) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217. (d) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345. (e) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401. (f) Kobayashi, S.; Akiyama, R. *Chem. Commun.* **2003**, 449.

(20) Bosman, A. W.; Vestberg, R.; Heumann, A.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 7.

(21) Helms, B.; Guillaudeu, S. J.; Xie, Y.; McMurdo, M.; Hawker, C. J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6384.

(22) For recent articles on living radical polymerization of PEGMA, see: (a) Armes, S. P.; Wang, X.-S. *Macromolecules* **2000**, *33*, 6640. (b) Neugebauer, D.; Zhang, Y.; Pakula, T.; Sheiko, S. S.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 6746. (c) Chen, Y.; Ying, L.; Yu, W.; Kang, E. T.; Neoh, K. G. *Macromolecules* **2003**, *36*, 9451. (d) Mantovani, G.; Lecolley, F.; Haddleton, D. M.; Clerx, J.; Cornelissen, J. J. L. M.; Velonia, K. *J. Am. Chem. Soc.* **2005**, *127*, 2966. (e) Oh, J. K.; Min, K.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 3161.

(23) For recent articles on star polymers with amphiphilic arms carrying PEGMA, see: (a) Ali, M. M.; Stöver, H. D. H. *Macromolecules* **2003**, *36*, 1793. (b) Dichtel, W. R.; Baek, K.-Y.; Fréchet, J. M. J.; Rietveld, I. B.; Vinogradov, S. A. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4939. (c) Gao, H.; Ohno, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 15111.

(24) Saraiva, A.; Persson, O.; Fredenslund, A. *Fluid Phase Equilib.* **1993**, *91*, 291.

(25) Gil, E. S.; Hudson, S. M. *Prog. Polym. Sci.* **2004**, *29*, 1173.

(26) Aoshima, S.; Sugihara, S.; Shibayama, M.; Kanaoka, S. *Macromol. Symp.* **2004**, *215*, 151.

(27) Chandrasekhar, V. *Adv. Polym. Sci.* **1998**, *135*, 139.

(28) Veronese, F. M. *Biomaterials* **2001**, *22*, 405.

(29) Torchilin, V. P. *J. Controlled Release* **2001**, *73*, 137.

(30) Terashima, T.; Ando, T.; Sawamoto, M.; Kamigaito, M. *Polym. Prepr. Jpn.* **2005**, *54* (1), 1491.

(31) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6708.

(32) Rabinowitz, R.; Marcus, R. *J. Org. Chem.* **1961**, *26*, 4157.

(33) Synthesis of PEGMA-armed star polymers without a short MMA segment is shown in Figure 1 of the Supporting Information. The small amount of **1** (100 and 200 mM) produced a low yield (53−67 %) of star polymers, probably due to the steric hindrance of PEG side chains during linking reactions of the arms. The large amount of **1** (400 mM) gave a relatively high yield (74 %) of star polymers but, however, also generated star−star coupling.

(34) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

(35) Hamasaki, S.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2002**, *35*, 2934.

(36) Synthesis of PEGMA-*b*-MMA/**2** copolymer: Prepolymer $[\mathrm{PEGMA}]_0/[(\mathrm{MMA})_2\mathrm{Cl}]_o/[\mathrm{RuCl}_2(\mathrm{PPh}_3)_3]_o/[n\text{-}\mathrm{Bu}_3\mathrm{N}]_o = 500/10/10/20$ mM in toluene at 80 °C; Block $[\mathrm{MMA}]_{\mathrm{add}}/[\mathbf{2}]_{\mathrm{add}} = 300/25$ mM in toluene; prepolymer solution/block solution = 2/1 v/v (the final molar ratio of used compounds PEGMA/$(\mathrm{MMA})_2\mathrm{Cl}$/MMA/**2**/$\mathrm{RuCl}_2(\mathrm{PPh}_3)_3$ = 50/1/15/1.25/1). Polymerization and characterization: a toluene solution of MMA and **2** was directly added into living PEGMA solution [PEGMA conversion 90% (10 h), $M_n = 21400$ (PMMA calibration), $M_w/M_n = 1.45$] to give PEGMA-b-MMA/**2** block copolymer [MMA/**2** conversion 75/100% (+24 h), $M_n = 23100$ (PMMA calibration), $M_w/M_n = 1.48$]. The obtained block polymer was bound 17 μmol of Ru(II)/g of polymer by UV−vis analysis.

MA062446R