Synthesis and Characteristics of Poly(macromonomers) and Graft Copolymers Composed of Poly(phenylacetylene) Main Chain and Poly(ethylene oxide) Side Chains

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ABSTRACT: New amphiphilic water-soluble poly(macromonomers), poly(**1**) and poly(**2**), consisting of a poly(phenylacetylene) [poly(**3**)] main chain and poly(ethylene oxide) (PEO) side chains, were synthesized by the homopolymerization of PEO macromonomers, while poly(**3**)-based graft copolymers, poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**), with PEO side chains were prepared by the copolymerization of the PEO macromonomers with phenylacetylene (**3**). Two PEO macromonomers **1** ($DP_{PEO} \sim 16$) and **2** ($DP_{PEO} \sim 45$) possessing **3** as an end group were prepared by the esterfication of *p*-ethynylbenzoic acid with commercial PEO monomethyl ethers. The macromonomers **1** and **2** homopolymerized in the presence of a binary Rh catalyst to yield poly(**1**) (DPs up to 55) and poly(**2**) (DPs up to 18), respectively. They also copolymerized with **3** to give graft copolymers poly(**1**-*co*-**3**) (M_n 37 500−93 800, **1** 0.3−22 mol %) and poly(**2**-*co*-**3**) (M_n 44 900−177 800, **2** 0.5−13 mol %). Poly(**1**) and poly(**2**) were a brown liquid and solid, respectively, while poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**) were yellow solids. These polymers were soluble not only in relatively nonpolar solvents such as toluene and $CHCl_3$ but also in polar solvents such as DMSO and MeOH. The side-chain crystallinity was observed in the solid state in poly(**2**-*co*-**3**) with PEO contents above 9 mol % according to DSC analysis.

Introduction

Poly(macromonomers), graft polymers, and branched polymers exhibit unique properties, which are generally not observed in their linear counterparts.[1] For example, highly grafted polymers exhibit different modes of organization and assembly both in solution and in bulk as compared to their linear counterparts.[2] The synthesis of graft polymers has been achieved so far by three main methods: grafting-onto, in which side chains are first synthesized and then attached to a multifunctional linear backbone;[3] grafting-from, which involves the grafting of monomer from a linear macroinitiator;[4] and grafting-through (macromonomer method), in which the macromonomers are copolymerized with low molecular weight comonomers to result in loosely grafted copolymers.[5] As a particular case, homopolymerization of macromonomers provides comb polymers or polymer brushes.[6−15] The macromonomer method presents a convenient and effective route to access graft polymers and polymer brushes by one-step polymerization compared to the other methods.

Substituted polyacetylenes have attracted considerable interest because of their unique properties such as semiconductivity, high gas permeability, helix formation, and nonlinear optical properties.[16] While numerous studies have focused on polyacetylenes bearing a variety of functional groups, there have been only a few reports so far on the synthesis of polyacetylene-based graft polymers. The macromonomer method involves the construction of main chain in the final step and thus is the most suitable route for the synthesis of polyacetylene-based graft polymers as polyacetylenes gradually decompose in solution. Moreover, polyacetylene-based graft polymers and polymer brushes may be more stable due to the protection of the main chain by bulky side chains. Our group has reported the synthesis of helical substituted polyacetylenes with helical polypeptide side chains by the copolymerization of the *N*-propargylamide-terminated peptide-based macromonomer with the alanine-derived *N*-propargylamide.[17] Yashima and co-workers have prepared a series of optically active, stereoregular poly(phenylacetylene)s [poly(**3**)s] bearing polypeptide grafts by the homopolymerization of poly(γ-benzyl-L-glutamate)-based macromonomers having a phenylacetylene (**3**) chain end.[18] Otsuka et al. have prepared a poly(**3**) carrying polycarbohydrate ionophores as graft chains by the copolymerization of end-functionalized (1→6)-2,5-anhydro-3,4-di-*O*-ethyl-D-glucitol with a 4-ethynylbenzoyl group with **3**.[19] We have recently reported the synthesis of polyacetylenes grafted with polystyrene chain by the copolymerization of a propargyl-terminated polystyrene macromonomer with low molecular weight comonomers (**3** or propargyl 2-bromopropionate).[20] Furthermore, novel cylindrical polymer brushes composed of a poly(**3**) main chain and either polystyrene or poly(methyl methacrylate) side chains have recently been synthesized by the homopolymerization of **3**-ended macromonomers based on either polystyrene or poly(methyl methacrylate).[21]

Poly(ethylene oxide) (PEO) is a cheap, neutral, water-soluble, semicrystalline, and biocompatible polymer and is probably one of the most widely applied synthetic polymers in biotechnology and medical science.[22] On the other hand, PEO-based polymers are gaining attention because of their utility and potential for the applications in secondary lithium or lithium ion batteries.[23] Polyacetylene-based graft polymers with PEO side chains are interesting candidates as new amphiphilic polymer electrolytes, which may find potential applications in medicare system and high-performance batteries. Eder et al. have demonstrated that poly(3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}propyne) ($DP_{PEO} = 4$) was able to dissolve a large amount of lithium salts.[24]

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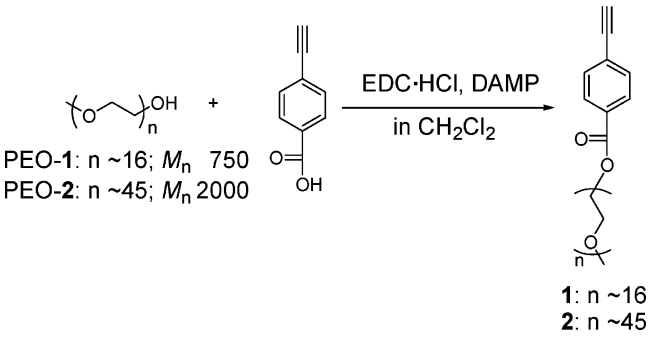
Recently, Chen et al. have reported the synthesis of a group of amphiphilic poly(**3**)s bearing oligo(ethylene oxide)s (DP_{PEO} = 2 and 3) with organorhodium complexes.[25]

Here we report homo- and copolymerizations of new PEO macromonomers, **1** and **2** (DP_{PEO} ~16 and 45, respectively) bearing **3** as a terminal group (Scheme 1). The homopolymerization of **1** and **2** yielded amiphiphilic, water-soluble poly(macromonomers), while their copolymerization with **3** resulted in graft copolymers. The structure elucidation of the resulting polymers was carried out by ^{1}H NMR, IR, and UV−vis spectroscopic techniques, and their properties were studied.

Scheme 1. Synthesis of Macromonomers 1 and 2



Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded in chloroform-*d* ($CDCl_3$) using tetramethylsilane as internal reference (δ = 0) on a JEOL EX-400 spectrometer. Infrared spectra (IR) were recorded on a JASCO FTIR-4100 spectrophotometer. Number- and weight-average molecular weights (M_n and M_w, respectively) and molecular weight distributions (MWD) (M_w/M_n) were determined by gel permeation chromatography (GPC) with a Jasco Gulliver System (PU-980, CO-965, RI-930, and UV-1570) equipped with a series of polystyrene gel columns (KF805L × 3, bead size: 10 μm, molecular weight range up to 4 × 10^6, flow rate 1 mL/min), using tetrahydrofuran (THF) as an eluent and a polystyrene calibration at 40 °C. UV−vis spectra were recorded on a Shimadzu UV-2200 spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA thermal analyzer (TGA-7). Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer Pyris I thermal analyzer. Heating and cooling runs were carried out under nitrogen at a rate of 10 °C/min.

Materials. Poly(ethylene oxide) monomethyl ethers with DP_n ~ 16 (M_n = 750) and DP_n ~ 45 (M_n = 2000) (Aldrich; denoted as PEO-**1** and PEO-**2**, respectively), 4-(dimethylamino)pyridine (DMAP) (Wako, 98%), triethylamine (Et_3N) (Wako, 98%), and H_2O (polymerization solvent) (Wako, distilled water) were used without further purification. Phenylacetylene (**3**) (Aldrich, 98%) was distilled from CaH_2 under reduced pressure and stored under argon at −15 °C. All the organic solvents used in the polymerization were purified by the standard methods. *p*-Ethynylbenzoic acid[26] and $[(nbd)RhCl]_2$ (nbd = 2,5-norbornadiene)[27] were synthesized according to the literature. 1-(3-(Dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) was purchased from Eiweiss Chemical Corp. (Japan) and used as received.

Other reagents were commercially obtained and used without further purification.

Synthesis of Macromonomer 1. 1 was synthesized by somewhat modifying the literature method.[5f] *p*-Ethynylbenzoic acid (1.76 g, 12.0 mmol) and DMAP (0.14 g, 1.15 mmol) were added to a solution of PEO-**1** (6.60 g, 3.3 mmol) and EDC·HCl (2.10 g, 11.0 mmol) in CH_2Cl_2 (30 mL) under argon at −20 °C and further stirred at room temperature for 24 h. The mixture was filtered, and the filtrate was washed with saturated Na_2CO_3 solution and concentrated. The product was dissolved in water (40 mL), washed with a hexane/ethyl acetate (v/v: 50/50) mixture (50 mL), and extracted with CH_2Cl_2 twice (40 mL for each). The solution was washed with brine (50 mL), dried over $MgSO_4$, and concentrated. The obtained product was kept under vacuum until constant weight to afford 6.12 g of **1** as a colorless viscous liquid in 86% yield. ^{1}H NMR ($CDCl_3$, δ): 8.05 (d, 2H, aromatic H), 7.54 (d, 2H, aromatic H), 4.44 (t, 2H, $COOCH_2$), 4.00−3.50 (broad m, 62H, OCH_2CH_2), 3.39 (s, 3H, CH_3), 3.34 (s, 1H, ≡C−H). ^{13}C NMR ($CDCl_3$, δ): 165.73 (C═O), 131.34 (aromatic), 129.44 (aromatic), 128.82 (aromatic), 126.24 (aromatic) 82.02 (HC≡*C*), 80.35 (H*C*≡C), 71.25 (*C*H_2OCH$_3$), 69.88 (O*C*H_2CH$_2$ and OCH$_2$*C*H_2), 68.41 (COOCH$_2$*C*H_2), 63.65 (COO*C*H_2), 58.18 (CH_3). IR (neat, cm^{-1}): 3233 (≡C−H), 2871, 2102 (C≡C), 1718 (C═O), 1106, 950, 860.

Synthesis of Macromonomer 2. Macromonomer **2** was synthesized from PEO-**2** in a similar way to **1** and obtained as a white solid; yield 39%.

^{1}H NMR ($CDCl_3$, δ): 8.00 (d, 2H, aromatic H), 7.54 (d, 2H, aromatic H), 4.46 (t, 2H, $COOCH_2$), 4.00−3.50 (broad m, 178H, OCH_2CH_2), 3.37 (s, 3H, CH_3), 3.28 (s, 1H, ≡C−H). ^{13}C NMR ($CDCl_3$, δ): 164.90 (C═O), 131.27 (aromatic), 129.34 (aromatic), 128.83 (aromatic), 126.19 (aromatic), 82.00 (HC≡*C*), 80.35 (H*C*≡C), 71.12 (*C*H_2OCH$_3$), 69.85 (O*C*H_2CH$_2$ and OCH$_2$*C*H_2), 68.58 (COOCH$_2$*C*H_2), 63.60 (COO*C*H_2), 58.24 (CH_3). IR (KBr, cm^{-1}): 3234 (≡C−H), 2890, 2104 (C≡C), 1720 (C═O), 1115, 963, 842.

Homopolymerization of Macromonomers 1 and 2. All the polymerizations were carried out in a glass tube equipped with a three-way stopcock under argon. In a typical polymerization reaction (run 11, Table 1), a MeOH (2.0 mL) solution of **1** (0.053 g, 0.25 mmol) was added to a MeOH (0.50 mL) solution of $[(nbd)RhCl]_2$ (0.58 mg, 1.25 μmol; this means [Rh] = 1.0 mM) and Et_3N (2.5 mg, 25 μmol), and the solution was vigorously stirred and then kept at 30 °C for 24 h. After polymerization, the solution was poured into a large amount of hexane to precipitate the product, which was washed by hexane for several times and dried under reduced pressure to constant weight. The conversions of the macromonomers were determined by GPC of an aliquot of the polymerization mixture before workup.

Copolymerization of Macromonomers 1 and 2 with 3. All the polymerizations were carried out in a glass tube equipped with a three-way stopcock under argon. In a typical copolymerization reaction (run 2, Table 3), a toluene (4.0 mL) solution of **1** (0.047 g, 0.053 mmol) and **3** (0.10 g, 1.0 mmol) was added to a toluene (1.0 mL) solution of $[(nbd)RhCl]_2$ (2.3 mg, 5.0 μmol) and Et_3N (10 mg, 0.10 mmol), and the mixture was vigorously stirred and then kept at 30 °C for 24 h. The solution was poured into a large amount of hexane to precipitate the product, dissolved in toluene, and reprecipitated in hexane twice. The product was then collected by filtration and dried under reduced pressure to constant weight. The yields and compositions of the formed copolymers were determined by gravimetry and ^{1}H NMR, respectively.

Results and Discussion

Synthesis of Macromonomers 1 and 2. 3-terminated macromonomers **1** (M_n = 880) and **2** (M_n = 2130) were prepared by esterfication of *p*-ethynylbenzoic acid with PEO monomethyl ether PEO-**1** (M_n = 750, DP_{PEO} ~ 16) and PEO-**2** (M_n = 2000, DP_{PEO} ~ 45), respectively, using EDC·HCl as compensating agent in the presence of DMAP (Scheme 1). The macromonomers **1** and **2** were characterized by spectroscopic methods, and both of them showed similar patterns in ^{1}H and ^{13}C NMR spectra. For example, the ^{1}H NMR spectrum of **2** showed signals for acetylenic proton at δ 3.28 ppm (signal a), for the aromatic protons at δ 8.00−7.54 ppm (signals b and c), and for those of PEO backbone at δ 4.00−3.50 ppm (signals e, f, and g) (Figure 1). The ^{13}C NMR spectrum of **2** also corresponds well to the macromonomer structure (Figure 2). Moreover, the characteristic peak due the methylene adjacent to the hydroxyl group (H_3-CO−PEO−*C*H_2−OH) at δ 61.9 ppm was absent, thus confirming the absence of the residual PEO monomethyl ether. IR

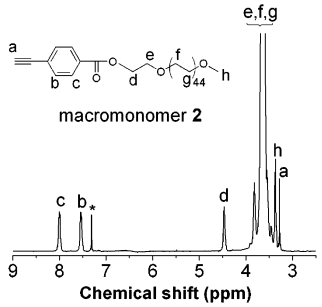


Figure 1. ^{1}H NMR spectrum of macromonomer **2** (*: $CDCl_3$ solvent).

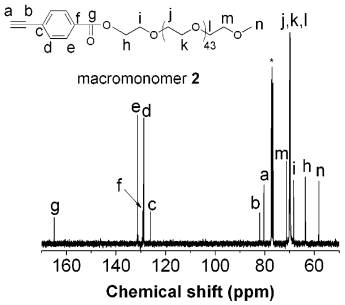


Figure 2. ^{13}C NMR spectrum of macromonomer **2** (*: $CDCl_3$ solvent).

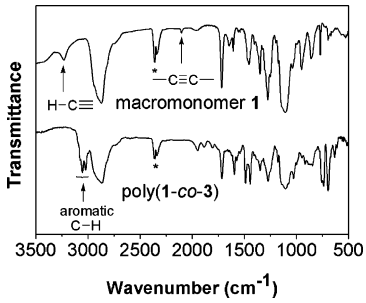


Figure 3. IR spectra of macromonomer **1** and poly(**1**-*co*-**3**) (run 3, Table 3) (*: CO_2).

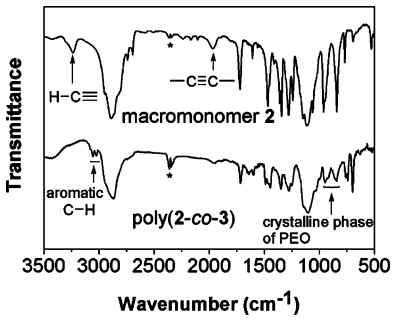
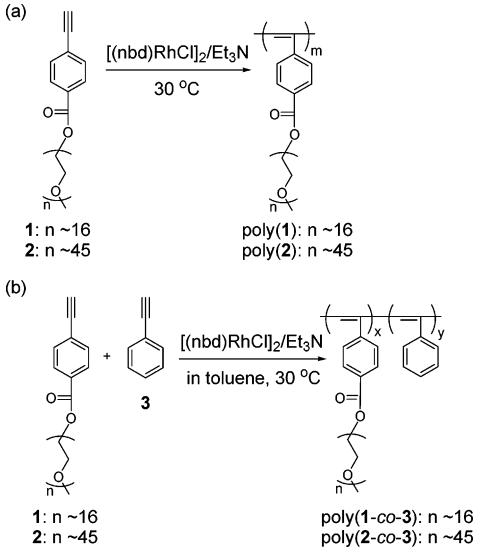


Figure 4. IR spectra of macromonomer **2** and poly(**2**-*co*-**3**) (run 3, Table 4) (*: CO_2).

spectra of **1** (Figure 3) and **2** (Figure 4) display absorption peaks around 3230 and 2100 cm^{-1} attributable to ≡C−H and C≡C stretchings of the terminal acetylene group.

Homopolymerization of Macromonomers 1 and 2. Homopolymerization of **1** and **2** was performed at 30 °C using a binary Rh catalyst system [(nbd)RhCl]$_2$/Et$_3$N, which is well-known as a very active catalyst for the polymerization of **3** and its ring-substituted derivatives (Scheme 2a).[28] Table 1 lists results for the polymerization of **1** at different macromonomer and catalyst concentrations in various solvents. Poly(**1**) was obtained in high conversions (80−92%) in toluene, whose

Scheme 2. Synthesis of Poly(1), Poly(2), Poly(1-*co*-3), and Poly(2-*co*-3)



apparent M_n values based on GPC were 7000−15 700 (M_w/M_n = 1.71−2.23) (runs 1−3). An increase in the concentration of **1** from 0.2 to 0.5 M led to the gel formation (run 4). Changing the solvent to $CHCl_3$ and CH_2Cl_2 did not enhance the molecular weight and conversion (runs 5−9), and no polymer was obtained in THF (run 10). On the other hand, use of MeOH as a solvent resulted in a polymer with M_n = 21 800 in a good conversion (80%) (run 11). Poly(**1**) obtained in the above solvents showed bimodal GPC traces composed of a major high molecular weight fraction (95%; see Table 1 for M_n) and a minor low molecular weight fraction (5%; DP ∼ 3−5), suggesting the presence of two propagating species in the polymerization. In contrast, the polymerization using H_2O as a solvent gave poly(**1**) with unimodal GPC traces (Figure 5). The polymerization at a monomer concentration of 0.1 M gave the highest molecular weight (M_n = 47 200) with M_w/M_n = 1.62 (run 14). The DPs of poly(**1**) were in the range 6−55 according to GPC. It should be pointed out that the GPC analysis using linear polystyrenes as calibration standards often underestimates the molecular weight of poly(macromonomers) due to their graft structures. The true DPs of poly(**1**) thus should probably be several times higher than those of the GPC values.

The polymerization of **2** was carried out at lower macromonomer concentrations (0.01−0.05 M) because of its lack of solubility at higher concentrations (≥0.1 M), as shown in Table 2. Polymerization in toluene gave poly(**2**) with M_n = 12 400 and a relatively broad MWD (M_w/M_n = 2.08) in a good conversion (94%) (run 1). When $CHCl_3$ was used as a solvent, a polymer having the highest molecular weight (M_n = 38 700) and a narrower MWD (M_w/M_n = 1.66) was produced in a good conversion (95%) (run 2). Use of CH_2Cl_2 also afforded a higher M_n value of 20 500 and a fairly narrow MWD (M_w/M_n = 1.27), although the conversion was somewhat lower (65%) (run 3). The increase of the macromonomer concentration from 0.02 to 0.05 M ended up with the formation of a gel (run 4). A protic solvent, MeOH, also worked well in the polymerization, producing poly(**2**) (M_n = 26 000, M_w/M_n = 1.32) in a good conversion (75%) (run 5). However, the GPC traces of poly(**2**) obtained in the above solvents consisted of high (∼95%) and low (∼5%) molecular weight fractions (Figure 6). Again, H_2O as a polymerization solvent provided poly(**2**) (M_n = 15 500, M_w/M_n = 1.48) with a unimodal GPC trace in a good conversion (70%) (run 6). The macromonomer concentration in water

Table 1. Polymerization of PEO-Based Macromonomer 1 (DP of PEO ~ 16) with [(nbd)RhCl]$_2$/Et$_3$N[a]

					poly(**1**)		
run	solvent	$[M]_0$ (M)	[Rh] (mM)	conv (%)[b]	M_n[c]	M_w/M_n[c]	DP[d]
1	toluene	0.10	1.0	87	15700[e]	2.23	18
2	toluene	0.10	5.0	80	8000[e]	1.80	9
3	toluene	0.20	5.0	92	7000[e]	1.71	8
4	toluene	0.50	5.0	93[f]	gel	gel	
5	$CHCl_3$	0.05	1.0	87	10200[e]	1.33	12
6	$CHCl_3$	0.10	1.0	15	23900[e]	1.20	28
7	$CHCl_3$	0.10	5.0	74	6900[e]	1.44	8
8	CH_2Cl_2	0.05	1.0	75	12800[e]	1.92	15
9	CH_2Cl_2	0.10	5.0	7	5400[e]	1.10	6
10	THF	0.10	5.0	0[g]			
11	MeOH	0.10	1.0	80	21800[e]	1.80	25
12	MeOH	0.20	1.0	64[f]	gel	gel	
13	H_2O	0.05	1.0	68	12600[h]	1.22	15
14	H_2O	0.10	1.0	54	47200[h]	1.62	55

[a] Polymerization conditions: [Rh]/[Et$_3$N] = 1/10, 30 °C, 24 h. [b] Conversion of macromonomer (determined by GPC). [c] Determined by GPC using a polystyrene calibration. [d] Degree of polymerization (calculated by M_n/880, where 880 is the number-average molecular weight of **1**). [e] For the main peak of bimodal GPC traces. [f] Determined by gravimetry. [g] No polymerization. [h] Unimodal GPC traces.

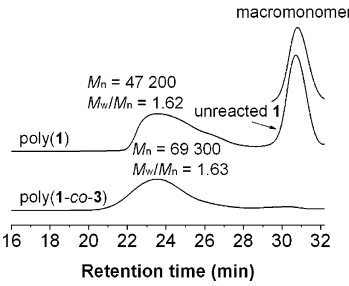


Figure 5. GPC curves of macromonomer **1**, poly(**1**) (run 14, Table 1), and poly(**1**-*co*-**3**) (run 3, Table 3).

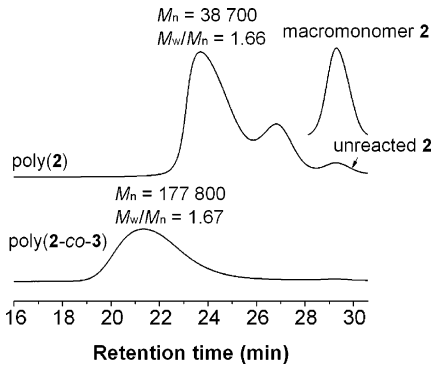


Figure 6. GPC curves of macromonomer **2**, poly(**2**) (run 2, Table 2), and poly(**2**-*co*-**3**) (run 3, Table 4).

should be kept up to 0.01 M because of the gel formation at higher macromonomer concentrations of 0.02 and 0.05 M (runs 7 and 8). The DPs of poly(**2**) were in the range 6−18, and lower than those of poly(**1**), which can be attributed to the steric hindrance of too long and bulky PEO chain in **2**.

Copolymerization of Macromonomers 1 and 2 with Phenylacetylene (3). The copolymerization of macromonomers **1** and **2** with **3** was examined by using [(nbd)RhCl]$_2$/Et$_3$N as a catalyst in toluene at 30 °C for 24 h (Scheme 2b). The copolymerization of **1** with **3** ($[\mathbf{3}]_0$ = 0.50 M; **1**:**3** = 10:90 mole ratio) instantaneously gave a red gel. When the concentration of **3** was decreased to 0.20 M, a gel-free graft copolymer poly(**1**-*co*-**3**) was obtained. The GPC curve of poly(**1**-*co*-**3**) showed a unimodal peak shifted to a higher molecular weight region (M_n = 69 300) as compared to **1**, while possessing a similar MWD (M_w/M_n = 1.63) (Figure 5).

Poly(**1**-*co*-**3**) was characterized spectroscopically, and satisfactory spectral data were obtained. For instance, the IR spectrum of poly(**1**-*co*-**3**) displayed no C−H stretching vibration of ethynyl group appearing at 3292 cm^{-1} in **1** but showed aromatic C−H stretching derived from the unit of **3** at 3053−3022 cm^{-1} (Figure 3). The ^{1}H NMR spectrum exhibited resonances at δ 4.00−3.50 ppm (signals c, d, and e) due to the protons on the PEO backbone and a sharp singlet peak at δ 3.39 ppm (signal f) due to the protons of the methyl group at the PEO chain end (Figure 7). In addition, the ^{1}H NMR spectrum clearly showed signals at δ 5.83 and 5.70 ppm (signals a and a′) assigned to the cis olefinic proton of the unit of **3** and **1**, respectively, indicating that the backbone of poly(**1**-*co*-**3**) possesses a cis-transoidal structure.

The mole composition of **1**:**3** was calculated by comparing the areas of the peaks of PEO backbone protons ($A_{c,d,e}$) and aromatic protons (A_{arom}), as shown in eq 1:

$$\text{composition } \mathbf{1{:}3} \text{ (mole ratio)} = \frac{A_{c,d,e}}{63} : \frac{A_{arom} - \dfrac{A_{c,d,e}}{62} \times 4}{5} \quad (1)$$

where $A_{c,d,e}$ and A_{arom} represent the areas of CH_2 of PEO chain (4.00−3.50 ppm) and of aromatic protons (8.00−6.25 ppm), respectively. The copolymerization was performed at several macromonomer-to-comonomer feed ratios in order to obtain copolymers with different compositions. As shown in Table 3, when the **1**/**3** mole ratios were 21:79 and 50:50, gels were formed during the copolymerization; otherwise, the reactions proceeded homogenously.

On the basis of the mole composition of **1** to **3**, the cis content of poly(**1**-*co*-**3**) was determined by eq 2, which was derived from Percec's equation:[29]

$$\text{cis (\%)} = \frac{A_a(4M_1 + 5M_3)}{A_{arom}} \times 100 \quad (2)$$

where A_a and A_{arom} stand for the relative areas of the cis olefinic protons (signals a and a′) and the aromatic protons, respectively, and M_1 and M_3 are the mole percentages of **1** and **3** in poly(**1**-*co*-**3**), respectively. The values of yield, composition, molecular weight, and cis content for a series of poly(**1**-*co*-**3**) are listed in Table 3. Copolymerizations whose content of macromonomer **1** was 10 mol % and below produced soluble poly(**1**-*co*-**3**)s having M_n and M_w/M_n in the ranges 37 500−93 800 and 1.63−2.82, respectively. These copolymers possessed high cis contents in the range 72−99%. The mole percentages of **1**

Table 2. Polymerization of PEO-Based Macromonomer 2 (DP of PEO ~ 45) with [(nbd)RhCl]$_2$/Et$_3$N[a]

					poly(**2**)		
run	solvent	$[M]_0$ (M)	[Rh] (mM)	conv (%)[b]	M_n[c]	M_w/M_n[c]	DP[d]
1	toluene	20	1.0	94	12400[e]	2.08	6
2	$CHCl_3$	20	1.0	95	38700[e]	1.66	18
3	CH_2Cl_2	20	1.0	65	20500[e]	1.27	10
4	CH_2Cl_2	50	1.0	98[f]	gel	gel	
5	MeOH	20	1.0	78	26000[e]	1.32	12
6	H_2O	10	2.0	70	15500[g]	1.48	7
7	H_2O	20	1.0	98[f]	gel	gel	
8	H_2O	50	1.0	97[f]	gel	gel	

[a] Polymerization conditions: [Rh]/[Et_3N] = 1/10, 30 °C, 24 h. [b] Conversion of macromonomer (determined by GPC). [c] Determined by GPC using a polystyrene calibration. [d] Degree of polymerization (calculated by M_n/2130, where 2130 is the number-average molecular weight of **2**). [e] For the main peak of bimodal GPC traces. [f] Determined by gravimetry. [g] Unimodal GPC traces.

Table 3. Copolymerization of Macromonomer 1 (DP of PEO ~ 16) with Phenylacetylene (3) by [(nbd)RhCl]$_2$/Et$_3$N[a]

		poly(**1**-*co*-**3**)					
run	feed ratio **1**:**3** (mol ratio)	yield (wt %)[b]	composition **1**:**3** (mol ratio)[c]	EO (mol %)[d]	M_n[e]	M_w/M_n[e]	cis (%)[c]
1	1:99	60	0.3:99.7	3	93800	2.82	95
2	5:95	43	4:96	39	37500	2.24	>99
3	10:90	62	22:78	78	69300	1.63	72
4	21:79	100			gel	gel	
5	50:50	100			gel	gel	

[a] Polymerization conditions: $[\mathbf{3}]_0$ = 0.20 M, [Rh] = 2.0 mM, [Et_3N] = 20 mM, in toluene, 30 °C, 24 h. [b] Hexane-insoluble product. Determined by gravimetry. [c] Determined by ^{1}H NMR. [d] EO content (mol %) against the total of EO and **3** units. [e] Determined by GPC using polystyrene calibrations.

Table 4. Copolymerization of Macromonomer 2 (DP of PEO ~ 45) with Phenylacetylene (3) by [(nbd)RhCl]$_2$/Et$_3$N[a]

		poly(**2**-*co*-**3**)					
run	feed ratio **2**/**3** (mol ratio)	yield (wt %)[b]	composition **2**:**3** (mol ratio)[c]	EO (mol %)[d]	M_n[e]	M_w/M_n[e]	cis (%)[c]
1	0.5:99.5	92	0.5:99.5	18	106400	2.41	96
2	2:98	81	2:98	47	113500	1.87	91
3	5:95	55	9:91	80	177800	1.67	90
4	10:90	76	13:87	85	44900	1.67	81
5	30:70[f]						

[a] Polymerization conditions: $[\mathbf{3}]_0$ = 0.20 M, [Rh] = 2.0 mM, [Et_3N] = 20 mM, in toluene, 30 °C, 24 h. [b] Hexane-insoluble product. Determined by gravimetry. [c] Determined by ^{1}H NMR. [d] EO content (mol %) against the total of EO and **3** units. [e] Determined by GPC using polystyrene calibrations. [f] Could not be carried out because **2** was incompletely soluble in toluene at the present concentration.

in poly(**1**-*co*-**3**) were in the range 0.3−22% and relatively close to those in the feed. It is noteworthy that the ethylene oxide (EO) content (mol %) in the poly(**1**-*co*-**3**) (run 3, Table 3) based on the total of EO and **3** units reached 78%.

Copolymerization of **2** with **3** was also carried out to give graft copolymer poly(**2**-*co*-**3**) under the same conditions as for the **1**/**3** copolymerization. The GPC curve of poly(**2**-*co*-**3**) (run 3, Table 4) showed a unimodal peak without any tails in a high molecular weight region (Figure 6). Other samples of poly(**2**-*co*-**3**) in Table 4 exhibited similar patterns in GPC curves. The IR spectrum of poly(**2**-*co*-**3**) did not display the acetylenic C−H stretching vibration, either, while it appeared in macromonomer **2** (Figure 4). The compositions and cis contents of poly(**2**-*co*-**3**) were determined by ^{1}H NMR in a manner similar to the case of poly(**1**-*co*-**3**). When the content of **2** in the feed was 10 mol % and below, soluble copolymers were obtained in good yields of 55 wt % and above (runs 1−4, Table 4). These copolymers possessed compositions similar to those of the monomer feeds, fairly high molecular weights above 4×10^5, and high cis contents of 81−96%. Since the DP of EO in **2** is as large as ~45, the poly(**2**-*co*-**3**) (run 4, Table 4) has a high EO content up to 85 mol %, although the content of **2** is no more than 13 mol %.

It can be seen from Tables 3 and 4 that similar or even larger amounts of macromonomers **1** and **2** were usually incorporated in the corresponding graft copolymers compared to those of **1** and **2** in the feed, although the macromonomers should suffer large steric hindrance than **3** does. This finding indicates that the polymerizability of **1** and **2** is similar to or even slightly higher than that of **3** in copolymerization, which can be attributed to the presence of the electron-withdrawing ester group in **1** and **2**. The MWDs became narrower as the content of the present macromonomers in the feed was increased, although the reason is not clear. As the feed ratio of either **1** or **2** to **3** was increased, the cis content of the resulting copolymers tended to decrease. Further, neither poly(**1**) nor poly(**2**) displayed the cis olefinic proton in the main chain in ^{1}H NMR. These results indicate either that the homo- and copolymers containing **1** and **2** have lower cis contents owing to the steric reason or that the ^{1}H NMR signal of the cis-olefinic proton of the macromonomer unit simply becomes small owing to the lower mobility of the unit.

Polymer Properties. Because of their amphiphilic nature, poly(**1**) and poly(**2**) were quite soluble in a wide range of nonpolar and polar solvents such as benzene, toluene, $CHCl_3$, CH_2Cl_2, acetone, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and MeOH but insoluble in hexane, cyclohexane, and diethyl ether. Furthermore, these polymer brushes were soluble even in water owing to the presence of hydrophilic PEO side chains. Poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**) also dissolved readily in common organic solvents such as benzene, toluene, $CHCl_3$, CH_2Cl_2, and DMF. Interestingly, samples of poly(**1**-*co*-**3**) (PEO: 22 mol %) (run 3, Table 3) and poly(**2**-*co*-**3**) (PEO: 13 mol %) (run 4, Table 4) became partly soluble in

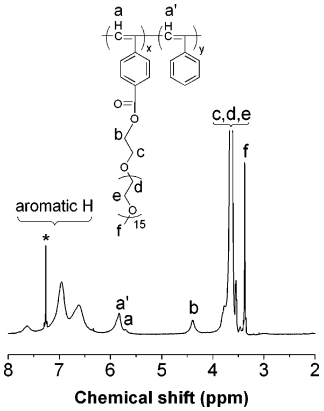


Figure 7. ^{1}H NMR spectrum of poly(**1**-*co*-**3**) (run 3, Table 3) (*: $CDCl_3$ solvent).

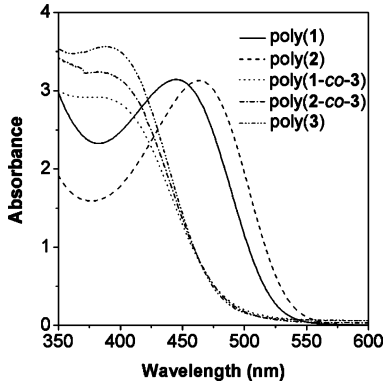


Figure 8. UV−vis spectra of poly(**1**) (run 12, Table 1), poly(**2**) (run 2, Table 2), poly(**3**) (sample obtained with $[(nbd)RhCl]_2/Et_3N$ in toluene at 30 °C; $M_n = 350\,000$, $M_w/M_n = 2.0$), poly(**1**-*co*-**3**) (run 3, Table 3), and poly(**2**-*co*-**3**) (run 3, Table 4) measured in $CHCl_3$. Solution concentration: 0.15 mg/mL.

H_2O and completely soluble in acetone, DMSO, and MeOH, which are known to be poor solvents of poly(**3**).

Homopolymers poly(**1**) and poly(**2**) were brown liquid and solid, respectively, while copolymers poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**) were yellow solids. Figure 8 illustrates the UV−vis spectra of poly(**1**), poly(**2**), poly(**1**-*co*-**3**), poly(**2**-*co*-**3**), and poly(**3**) for comparison. Poly(**1**) and poly(**2**) exhibited absorption peaks in the range of 375−575 nm with maxima at 456 and 485 nm, respectively, and cutoffs at 550 nm, while poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**) showed the absorptions with shoulder peaks at around 375 nm and cutoff wavelengths at around 525 nm, like the case of poly(**3**). This result indicates that poly(**1**) and poly(**2**) have longer conjugation lengths in the main chain than poly(**1**-*co*-**3**), poly(**2**-*co*-**3**), and poly(**3**). It has been reported that the absorption peak of a poly(**3**) derivative shifts to longer wavelength as the steric effect of ring substituents increases. For example, poly[(*o*-methylphenyl)acetylene] exhibits an absorption at 440 nm,[30] while poly{[*o*-(trimethylsilyl)phenyl]-acetylene}, which possesses a bulkier trimethylsilyl substituent, does it at 520 nm. Yashima et al. have observed that para-substituted poly(**3**) derivatives with bulkier substituents absorb at longer wavelengths.[31] Grubbs and co-workers have proposed an idea that the steric requirements of the substituents impose a planar conformation on the polymer backbone.[32] The bulky PEO side chain of poly(**1**) and poly(**2**) should prevent the polyacetylene backbone from bending and twisting and force the main chain to take a more straight conformation. In the case of poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**), the main chain could take a more bent conformation like poly(**3**) because the PEO chains are loosely grafted. This seems to be the reason why poly(**1**) and poly(**2**) absorb at longer wavelength regions than do poly-(**1**-*co*-**3**) and poly(**2**-*co*-**3**). Furthermore, poly(**2**) displayed a bathochromic shift of 29 nm in comparison with poly(**1**), which can be attributed to the longer and bulkier PEO side chain of poly(**2**) than that of poly(**1**).

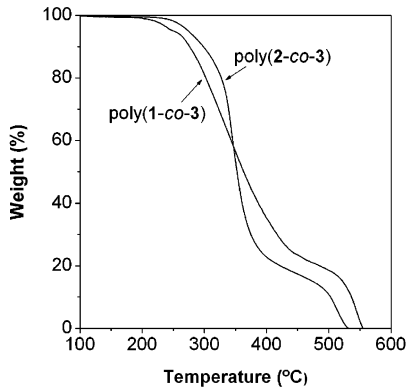


Figure 9. TGA thermograms of poly(**1**-*co*-**3**) (run 3, Table 3) and poly(**2**-*co*-**3**) (run 3, Table 4) measured in air at a heating rate of 10 °C /min.

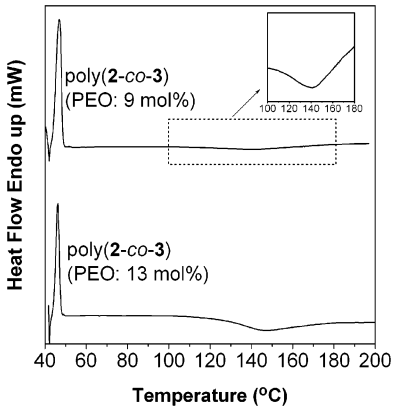


Figure 10. DSC traces of poly(**2**-*co*-**3**) (up: run 3, Table 4; down: run 4, Table 4) measured under nitrogen at a heating rate of 10 °C /min.

The thermal properties of poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**) were studied by TGA and DSC measurements. Figure 9 depicts the TGA thermograms, showing that the temperatures for 5% weight loss in poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**) were 250 and 280 °C, respectively, higher than that of poly(**3**) (225 °C).[33] These results indicate that the grafting of PEO chains increases the thermal stability of poly(**3**) main chain.

The DSC analysis was examined in the region below under 200 °C, since no degradation occurred below this temperature according to TGA. The DSC curves of poly(**2**-*co*-**3**) with **2** contents of 9 and 13 mol % (samples from runs 3 and 4, Table 4, respectively) in the first run of heating up to 200 °C at 10 °C/min exhibited sharp melting transitions at 46.2 and 46.9 °C, respectively, due to the crystalline structure of the PEO chains (Figure 10). When the samples were cooled at the same rate, the PEO side chains did not have enough time to organize. Therefore, no melting point appeared in the second run of heating in the DSC trace. A similar behavior has been reported in other graft copolymers having rigid main chains and PEO side chains, where no crystallization was observed upon cooling the samples at 10 °C/min.[34] No melting peaks were observed in the DSC curves of graft copolymers poly(**1**-*co*-**3**) containing

PEO with $M_n = 750$ and poly(**2**-*co*-**3**) with 0.5 and 2 mol % PEO. Consequently, these graft copolymers should be in a crystalline state only when the PEO side chain has a relatively high M_n of 2000 and its content is 9 mol % or above. This was further confirmed by the presence of absorption peaks at 961 and 844 cm^{-1} characteristic of the crystalline phase of PEO in the IR spectrum of poly(**2**-*co*-**3**) (run 3, Table 4) (Figure 4).[35] These results appear reasonable because crystallization often occurs above a critical side chain length and/or above a certain content of PEO side chains in graft copolymers.[36] It should be noted that the melting points of the crystalline poly(**2**-*co*-**3**) were lower than that of PEO ($M_n = 2000$) (53.4 °C) by ~7 °C,[37] presumably because of the crystal defects induced by incomplete phase separation of the backbone polymer. The graft copolymers also showed exothermic peaks at 140−150 °C, which is possibly correlated to the cis−trans isomerization of the poly(**3**) main chain.[38]

Conclusions

New water-soluble amphiphilic poly(**1**) and poly(**2**) were obtained by the Rh-catalyzed homopolymerization of PEO macromonomers having a phenylacetylene (**3**) end group, **1** ($DP_{PEO} \sim 16$) and **2** ($DP_{PEO} \sim 45$), respectively. These poly(macromonomers) possessed a polymer-brush structure composed of a poly(**3**) main chain and PEO side chains. The PEO macromonomers were copolymerized with **3** to produce graft copolymers, poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**), which consisted of a poly(**3**) main chain and loosely grafted PEO chains. The UV−vis absorption maxima of poly(**1**) and poly(**2**) were much red-shifted than those of poly(**1**-*co*-**3**) and poly(**2**-*co*-**3**), which is attributed to steric effects of the dense grafts in the poly(macromonomers). Crystallization of the graft copolymers was found to depend on the mole percentages and chain lengths of PEO grafts.

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