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Encapsulation of Polypyrrole by Internal Domain Modification of Double-Cylinder-Type Copolymer Brushes

Koji Ishizu,* Keiichiro Tsubaki, and Satoshi Uchida

Department of Organic Materials and Macromolecules, International Research Center of Macromolecular Science, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: Double-cylinder-type copolymer brushes were synthesized by free-radical polymerization of vinylbenzyl-terminated poly(α-methylstyrene)-*block*-poly(2-vinylpyridine) (PMS-*block*-P2VP) diblock macromonomers. These copolymer brushes formed a single macromolecule even in good solvent due to crowded side chains. To design the encapsulation of conducting polymers, Cu^{2+} ions (oxidant) were introduced internal P2VP cylindrical domains by complexation based on the pyridine nitrogen interacting with metal ions. Encapsulation of conducting polymers was performed by the oxidation polymerization of double-cylinder-type copolymer brushes complexed with such an oxidizing agent being added to a mixture of pyrrole and water vapor. It was found from light scattering data that the encapsulation materials of polypyrrole (P2VP block 8 mol %) obtained after chemical modifications formed a single macromolecule in good solvent such as benzene.

Introduction

It is well-known that comb polymers with densely grafted side chains in a good solvent can adopt a wormlike cylinder brush conformations, in which the side chains are stretched in the direction normal to the backbone, owing to the excluded-volume interaction. The polymerization of macromonomers provides regular multibranched polymers with dense branching. Since both the degree of polymerization (DP) and the length of branches are varied, poly(macromonomer)s, often so-called "polymer brushes" , are interesting models for the study of branched polymers.[1−9] We have reported the synthesis and dilute-solution properties of poly(diblock macromonomer)s (double-cylinder-type copolymer brushes, see Figure 1) by free-radical polymerization of the corresponding diblock macromonomer: polystyrene-*block*-polyisoprene (PS-*block*-PI)[10] and poly(α-methylstyrene)-*block*-poly(2-vinylpyridine) (PMS-*block*-P2VP) copolymer brushes.[11] We also prepared such double-cylinder-type copolymer brushes by anionic one-shot polymerization of AB-type diblock macromonomers.[12] These types of copolymer brushes have the advantage of controlling the stiffness of the main chain parts by cross-linking internal PI or P2VP blocks. In fact, we derived the cylinder brushes by cross-linking internal P2VP domains of the diblock copolymer brushes with 1,4-diiodobutane.[11] Both the diblock copolymer brush and cross-linked cylinder brush formed a single macromolecule in the dilute solution. However, the semidilute solution properties of cross-linked cylinder brushes (P2VP block, 33 mol %) showed a clear plateau region in the rheological data, which originated from the entanglement effect. More recently, Matyjaszewski[13] and Muller[14] have also synthesized double-cylinder-type copolymer brushes by the "grafting from" approach, using atom transfer radical polymerization (ATRP).

More recently, Yoshida et al.[15] reported the formation of an insulated molecular wire, a conjugated conducting polymer covered by insulated cyclic molecules such as β-cyclodextrins. Anderson et al.[16] also synthesized water-soluble conjugated rotaxanes. Both synthetic strategies originate from an idea that a conjugated conducting polymer is covered by insulated cyclic molecules. More recently, Schmidt and co-workers[17] have synthesized the double-cylinder-type copolymer brushes (they called core−shell cylindrical brushes) by free-radical polymerization of methacryloyl-terminated polystyrene-*block*-P2VP diblock macromonomers. Subsequently, they prepared the molecular wires by forming a linear array of the gold clusters with the core of the cylinder brushes as templates.[18] On the other hand, we fabricated the conducting materials possessing high anisotropic conductivity by oxidation polymerization of pyrrole on the microphase-separated diblock copolymer films as template.[19] So, it can be expected that a new type of the encapsulations of conducting polymers will be created by oxidation polymerization of pyrrole on the internal cylindrical domain of double-cylinder-type copolymer brushes as a template. Modification steps for the encapsulation of polypyrrole (PPy) are shown in Figure 1.

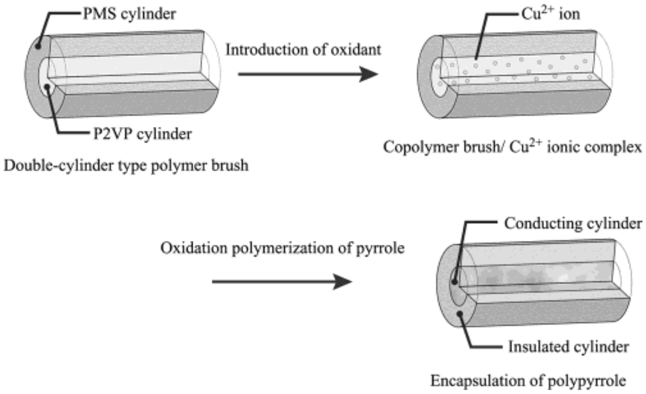

Figure 1. Modification steps for encapsulation of polypyrrole into double-cylinder-type copolymer brush.

In this article, double-cylinder-type copolymer brushes were synthesized by free-radical homopolymerization of vinylbenzyl-terminated PMS-*block*-P2VP diblock macromonomers. These copolymer brushes formed a single macromolecule even in good solvent such as benzene,

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Table 1. Characteristics of PMS-*block*-P2VP Diblock Macromonomers

no.	M_n[a]	M_w/M_n[b]	P2VP block[c] (mol %)	functionality[c]
MSV1	2700	1.19	23	0.92
MSV4	7100	1.35	25	0.91
MSV5	3000	1.15	8	0.91

[a] Determined by vapor pressure osmometer in benzene. [b] Determined by gel permeation chromatography (GPC) in THF. [c] Determined by ^{1}H NMR in $CDCl_3$.

Table 2. Dilute-Solution Properties of Double-Cylinder-Type Copolymer Brushes

no.	$10^{-6}M_w$[a]	DP[b]	R_g[a] (nm)	10^7D_0[c] (cm^2/s)	R_h[c] (nm)
PMSV1-406	1.29	406	31.0	1.91	19.1
PMSV4-87	0.84	87	14.1	3.82	10.2
PMSV5-460	1.37	460	21.6	2.02	18.0

[a] Determined by SLS in benzene at 25 °C. [b] Degree of polymerization. [c] Determined by DLS in benzene at 25 °C.

due to crowded side chains. Cu^{2+} ions (oxidant) were introduced into internal P2VP cylindrical domains by complexation based on the pyridine nitrogen interacting with metal ions. Encapsulation of PPys was performed by the oxidation polymerization of double-cylinder-type copolymer brushes complexed with such an oxidizing agent being added to a mixture of pyrrole and water vapor. Characterization of such encapsulation materials of PPys was carried out in detail.

Experimental Section

Synthesis of Double-Cylinder-Type Copolymer Brushes. Vinylbenzyl-terminated PMS-*block*-P2VP diblock macromonomers (MSV) were synthesized by the living anionic polymerization technique of coupling reaction of corresponding diblock lithium with a small excess amount of *p*-chloromethylstyrene (CMS) in a tetrahydrofuran (THF). Details concerning the synthesis and characterization of diblock macromonomers were given elsewhere.[11] Characteristics of diblock macromonomers are listed in Table 1.

Free-radical polymerizations of diblock macromonomers were carried out in benzene at 60 °C using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator in a sealed glass ampule under high vacuum. After polymerization, the solution was poured into an excess of hexane. The double-cylinder type copolymer brush (PMSV) obtained was fractionated stepwise by precipitation fractionation (benzene−hexane system) to perform narrow molecular weight distribution.

The weight-average molecular weight ($\bar{M}_w$) and the radius of gyration (R_g) of copolymer brushes were determined by static light scattering (SLS; Photal TMLS-6000HL: Otsuka Electronics, $\lambda_0 = 632.8$ nm) in benzene ($\eta = 0.654$ cP, $n_D = 1.498$) at 25 °C in the Berry mode. The diffusion coefficient (D_0) was determined by the extrapolation to zero concentration and zero angle on dynamic light scattering (DLS; Otsuka Electronics) data with cumulant method at 25 °C in 0.35−5.20 mg/mL benzene solution. The scattering angle was in the range 30°−150°. The hydrodynamic radius (R_h) is defined by the Stokes−Einstein equation: $R_h = kT/6\pi\eta_0D_0$, where k, T, and η_0 indicate the Boltzmann coefficient, absolute temperature, and viscosity of solvent, respectively. Details concerning the characterization and solution properties of copolymer brushes were also given elsewhere.[11] The dilute-solution properties of double-cylinder-type copolymer brushes are listed in Table 2.

Introduction of Oxidant into Internal P2VP Domains. The introduction of oxidant into internal P2VP domains was performed by following two methods. (1) The double-cylinder-type copolymer brush film (PMSV1 and PMSV4; P2VP block 23−25 mol %, 120 μm thick) was cast from 0.06 g/mL toluene solution on a Teflon sheet. The cast film was dried under vacuum for 2 days at room temperature. These films were soaked in a dioxane/water (3/7 v/v) mixture of copper(II) chloride ($CuCl_2$, 0.4 mol/L) for 2 days. The film was washed with water and was dried at 30 °C. The Cu^{2+} ion content introduced was determined by following titration.[20] After soaking the film, the residual $CuCl_2$ solution was reacted with an excess amount of potassium iodide (KI). The I_2 produced was titrated with aqueous sodium thiosulfate ($Na_2S_2O_3$) solution using 0.2 wt % of starch as an indicator. The element (Cl and Cu atoms) distributions on a vertical section of the ionic complex films were measured by energy-dispersive X-ray spectrometry (EDX; Philips EDAX 9900I). The K intensity was fitted with a Zn atom ($K\alpha = 8.628$ and $L\alpha = 1.019$ keV). The mass concentration of the elements was estimated using a ZAF correction [stopping power, absorption and fluorescence corrections: RT-11 SJ(S) V 5.01C] on a computer (LSI-11/23).

It was found from preliminary experiments that the introduction of oxidant was achieved insufficiently for the copolymer brush composed of low P2VP block composition by means of the method described above. Then, the introduction of oxidant for PMSV5 (P2VP block 8 mol %) was carried out as follows. PMSV5 was dissolved in THF and reacted with 1.5-fold of $CuCl_2$ (based on 2-vinylpyridine units) for 2 days in the solution. The solutions were placed in dialysis tubes and dialyzed against distilled water for 5 days to remove the unreacted $CuCl_2$. The ionic complex copolymer was recovered by solvent evaporation.

Oxidation Polymerization of Pyrrole. The reaction vessel was a 200 mL flask with a flat flange, lid, and stopcock. The ionic complex films (120 μm thick) were mounted on a glass plate with double-sided adhesive tape around the walls inside the reaction vessel. The mixture of pyrrole/water (1/1 v/v) was charged into the bottom of the reaction vessel. The vessel was evacuated by a vacuum pump at −78 °C and was held in thermostatically controlled baths at 60 °C for 2−24 h. The sketch of apparatus used for oxidation polymerization was given elsewhere.[19]

The existence of PPy in the encapsulation materials was characterized by a UV spectrometer (Jasco Ubest-35 UV/vis spectrometer) in chloroform and gel permeation chromatography (GPC). GPC measurements were carried out with a Tosoh high-speed liquid chromatograph HLC-8120 equipped with refractive index (RI) and UV (characteristic absorption of PPy at 336 nm), which was operated with using two TSK gel columns, GMH_{XL} and $G2000H_{XL}$, in series using THF as the eluent (flow rate 1.0 mL/min) at 38 °C.

Hydrodynamic dimensions of encapsulation materials of PPys were determined using DLS in benzene at 25°C with a cumulant analysis (scattering angle 90°).

Results and Discussion

It was made clear from the previous work[11] that the effective diffusion coefficient D_{eff} for double-cylinder-type copolymer brushes with various aspect ratios showed the almost constant value in the range of polymer concentration (0−5) × 10^3 g/L. These results indicated that the copolymer brushes formed a single macromolecule even in good solvent such as benzene due to crowded side chains. It was speculated from angular dependence measurements that copolymer brushes with large aspect ratios took geometrical anisotropic conformation such as cylinder. That is to say, the shape of such copolymer brushes changed from a sphere or an ellipsoid to a rodlike cylinder with increasing the aspect ratio.

Cu^{2+} ions were introduced into internal P2VP domains of copolymer brush PMSV1-406 and PMSV4-87 films by soaking in a dioxane/water (3/7 v/v) mixture. The amount of introduced ionic complex increased with increasing the soaking time and reached a plateau after 30 h (Cu^{2+}/2VP = 0.33 mol/mol). Therefore, we set 2 days as the soaking time in the following experiments.

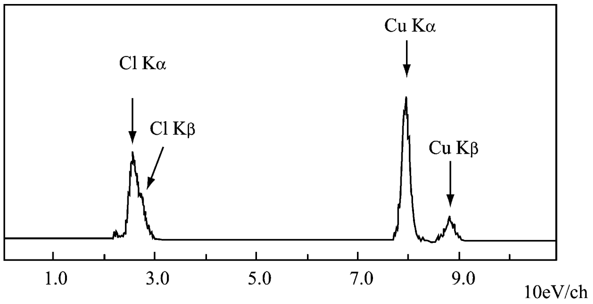

Figure 2. EDX spot analysis of PMSV4-87/Cu^{2+} ionic complex film.

Table 3. Oxidation Polymerization Conditions and Results of PMSV1-406/Cu^{2+} Ionic Complex with Pyrrole

no.	polymerization time (h)	polymerization product $(D_h)_z$ (nm), [LS %]
PMSV1-406P1	2	36.5 [100]
PMSV1-406P2	6	37.6 [63.2], 168.8 [36.8]
PMSV1-406P3	12	39.8 [16.9], 175.0 [83.1]
PMSV1-406P4	24	39.0 [5.2], 163.3 [94.2]

Both films showed a blue color, which was characteristic of Cu^{2+} ions. A typical EDX spot analysis of PMSV4-87/Cu^{2+} ionic complex film is shown in Figure 2. Peaks at 8.0 and 8.9 (10 eV/ch) correspond to Cu Kα and Cu Kβ, respectively. Spot analyses of other places also showed the almost same peak intensities. It seems from the Cu atom distribution that the introduction of Cu^{2+} ions to internal P2VP domains was performed homogeneously.

On the other hand, the introduction of oxidant was not achieved sufficiently for the copolymer brush PMSV5-460 composed of low P2VP composition (P2VP block 8 mol %) using this method. So, Cu^{2+} ions were introduced in THF solution of PMSV5-460. The introduction of oxidant depends strongly on the diffusion effect of $CuCl_2$ through the PMS matrix.

The oxidation polymerization of pyrrole was carried out by exposing the PMSV/Cu^{2+} ionic complex film (120 μm thick) to pyrrole vapor. The blue color of the PMSV/Cu^{2+} ionic complex film changed to black on exposure to pyrrole vapor after 1 h. It was found from the previous work[11] that the growth of PPy film proceeded with a fast rate in the initial stage of polymerization for PS-*block*-P2VP diblock copolymer film (100 μm thick), and a 5 h exposure time was enough for complete diffusion of pyrrole vapor through the matrix polymer. To investigate the encapsulation of PPy (PMSV−P), experiments were carried out varying the polymerization time of exposure to pyrrole/water vapor, and their hydrodynamic diameters $(D_h)_z$ (z-distribution) were measured in benzene by DLS. All the polymerization products dissolved in benzene. Parts a and b of Figure 3 show the hydrodynamic diameter distributions of PMSV1-406P2 (polymerized for 6 h) and PMSV1-406P4 (polymerized for 24 h), respectively, in benzene. Benzene is a good solvent for PMS chains and is nonsolvent for P2VP/PPy composite. In both size distribution profiles, two peaks are observed at around 38 and 160 nm. The peak appearing at the larger D_h suggests the presence of aggregates in the system. The peak at 38 nm seems to correspond to the encapsulation material of PPy (starting copolymer brush PMSV1-406: P2VP block = 23 mol %, R_h = 19.1 nm). Table 3 lists the oxidation polymerization conditions and results of PMSV1-406/Cu^{2+} ionic complex with pyrrole. The size distribution of PMSV1-406P1 (polymerization time = 2 h) appeared unimodal. Oxidation polymerization of the PMSV4-87 (P2VP block 25 mol %)/Cu^{2+} ionic complex film with pyrrole gave similar results after 6 h of polymerization time. We checked the hydrodynamic diameter distribution of the PMSV1-406/Cu^{2+} ionic complex in benzene. The size distribution profile showed a unimodal pattern. It can be speculated from these results that the aggregates were formed by intermolecular polymerization of pyrrole between internal P2VP/Cu^{2+} domains due to the thinness of external PMS cylinders. Such aggregates increase with increasing the introduced amounts of PPy in internal P2VP domains.

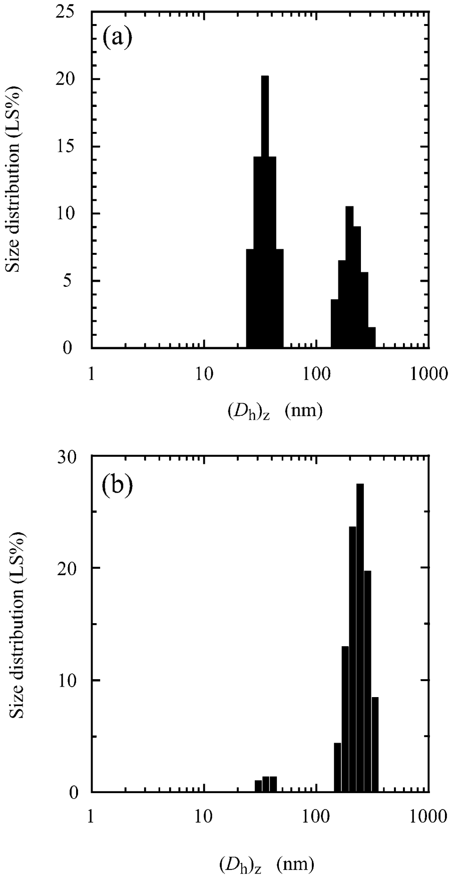

Figure 3. Hydrodynamic diameter $(D_h)_z$ distributions of PMSV1-406P2 and PMSV1-406P4: (a) PMSV1-406P2, polymerized for 6 h; (b) PMSV1-406P4, polymerized for 24 h.

The PMSV5-460 (P2VP block, 8 mol %)/Cu^{2+} ionic complex film also showed a slight blue color. EDX spot analysis of this film indicated the characteristic peaks of Cu Kα and Cu Kβ. The oxidation polymerization of pyrrole was carried out by exposing the ionic complex film (120 μm thick) to pyrrole/water vapor for 6 h. The slight blue color of the ionic complex film also changed to slight black on exposure to pyrrole vapor. Figure 4 shows the hydrodynamic diameter distribution of the polymerization product PMSV5-460P in benzene. The size distribution profile appears unimodal at around 30 nm. It indicates that the encapsulation product of PPy forms a single macromolecule in solution. The same result was obtained when the exposure to pyrrole vapor was longer (24 h) than 6 h.

Figure 5 shows UV−vis spectra of the encapsulated brush of PPy PMSV5-460P and the corresponding copolymer brush PMSV5-460 in chloroform. The spectrum of the copolymer brush (Figure 5b) indicates the

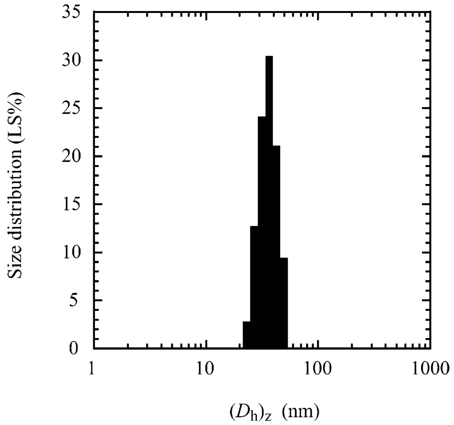

Figure 4. Hydrodynamic diameter $(D_h)_z$ distribution of PMSV5-460P.

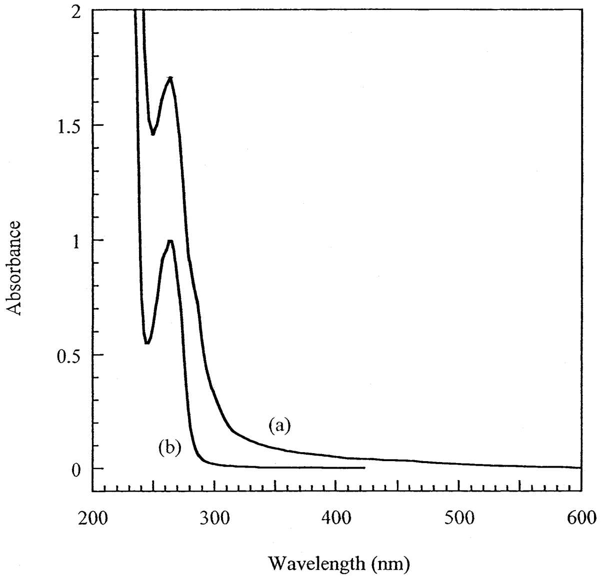

Figure 5. UV−vis spectra of PMSV5-460P (a) and corresponding copolymer brush PMSV5-460 (b) in chloroform.

expected absorptions for the MS ring (260 nm) and the pyridine ring (280−350 nm). It is well-known that the PPy exhibits characteristic broad absorptions at around 350 and 600 nm.[21] The spectrum of PMSV5-460P (Figure 5a) also indicates broad absorptions in the range of 300−600 nm, in addition of the MS ring absorption. To make clear the double-cylinder structure of encapsulation material of PPy, we carried out the GPC measurements of PMSV5-460P and copolymer brush PMSV5-460 equipped with RI and UV (characteristic absorption of PPy at 336 nm) double detectors in THF (see Figure 6). The GPC elution pattern of PMSV5-460P is identical with that of the copolymer brush in the RI monitor. Moreover, it is foud from the UV monitor that the intensity of UV absorption for PMSV5-460P appears strong as well as the elution pattern observed in the RI monitor. Internal PPy phases are stabilized sterically by highly branched PMS chains in solution.

We performed transmission electron microscopy (TEM) of PMSV5-460P because PPy has a higher electron density than P2VP. However, the clear image could not be obtained due to the extremely narrow size of the PPy phase. As mentioned in the Introduction, we prepared the conducting materials possessing high anisotropic conductivity by oxidation polymerization of pyrrole on the PS/P2VP lamellar microdomains of diblock copolymers as the template.[19] The cross-sectional TEM image of this specimen showed the clear PS/PPy alternating lamellar morphology. Both PS and PPy domains sizes were the almost same as those of starting diblock copolymers. The conductivity parallel to the film plane was 10^{-1} S cm^{-1}, and this film had a high anisotropic conductivity. The methodology for encapsulation of PPys employed in this work originates from our previous studies. Oxidation polymerization conditions were almost the same as previous ones. It seems that the PPy phase may be continuous within the brush because PMSV5-460P had broad UV absorptions (300−600 nm) of π-conjugated PPy. It is evident by dual-detector GPC that PPy has formed within internal P2VP cylinders and does not grow from one copolymer brush to the next. Terao et al.[22] investigated the solution properties of polymer brushes and made clear that the intramolecular excluded-volume interactions between the main chain and side chains and between neighboring side chains played an important role in the global conformation or structure of a polymer brush in solution. Even in bulk film of double-cyliner copolymer brushes, it seems that both terminal ends of the internal P2VP cylinder are shielded with neighboring PMS side chains and cannot aggregate with those of other brushes. Unfortunately, clear-cut evidence for the formation of the continuous PPy phase was not obtained in this work.

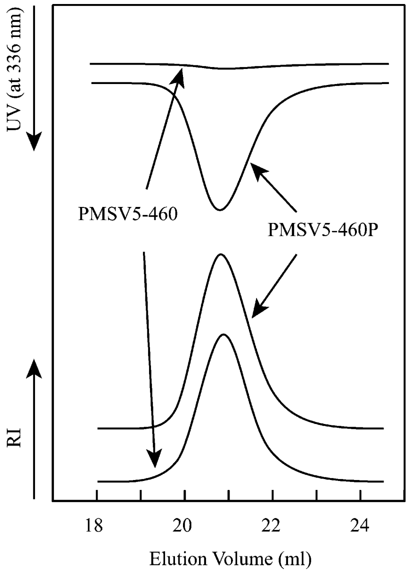

Figure 6. GPC profiles of PMSV5-460P and copolymer brush PMSV5-460.

Conclusions

We have explored the scope of the approach to encapsulation of conducting polymers shown in Figure 1. Double-cyliner-type copolymer brushes formed a single macromolecule even in good solvent due to crowded side chains. Encapsulation of conducting polymers was performed by the oxidation polymerization of double-cylinder-type copolymer brushes complexed with an oxidizing agent (Cu^{2+} ions) being added to a mixture of pyrrole/water vapor. Encapsulation material of PPy (P2VP block, 8 mol %) obtained after chemical modifications formed a single macromolecule in good solvent such as benzene. The conformation of P2VP/PPy nanocomposites is confined to a rodlike structure. PPy phases are isolated from each other by insulated PMS external cylinders. If such PPy phase is continuous, the modification procedure employed in this work seems to be one of the best methods for the architecture of molecular wires.

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References and Notes

(1) Wintermantel, M.; Fischer, K.; Gerle, M.; Ries, R.; Schmidt, M.; Kajiwara, K.; Urakawa, H.; Wataoka, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1606.
(2) Wintermantel, M.; Gerle, M.; Fischer, K.; Schmidt, M.; Wataoka, I.; Urakawa, H.; Kajiwara, K.; Tsukahara, Y. *Macromolecule* **1996**, *29*, 978.
(3) Wintermantel, M.; Schmidt, M.; Tsukahara, Y.; Kajiwara, K.; Kohjiya, S. *Macromol. Raapid Commun.* **1994**, *15*, 279.
(4) Tsukahara, Y.; Kohjiya, S.; Tsutsumi, K.; Okamoto, Y. *Macromolecules* **1994**, *27*, 1662.
(5) Nemoto, N.; Nagai, M.; Koike, A.; Okada, S. *Macromolecules* **1995**, *28*, 3854.
(6) Wataoka, I.; Urakawa, H.; Kajiwara, K.; Schmidt, M.; Wintermantel, M. *Polym. Int.* **1997**, *44*, 365.
(7) Terao, K.; Nakamura, Y.; Norisuye, T. *Macromolecules* **1999**, *32*, 711.
(8) Kawaguchi, S.; Imai, G.; Suzuki, J.; Miyahara, A.; Kitano, T.; Ito, K. *Polymer* **1997**, *38*, 2885.
(9) Kawaguchi, S.; Matsumoto, H.; Iriany, H.; Ito, K. *Polym. Prepr. Jpn.* **1998**, *47*, 1694.
(10) Ishizu, K.; Tsubaki, K.; Ono, T. *Polymer* **1998**, *39*, 2935.
(11) Tsubaki, K.; Ishizu, K. *Polymer* **2001**, *42*, 8387.
(12) Ishizu, K.; Shimomura, K.; Saito, R.; Fukutomi, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 607.
(13) Borner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **2001**, *34*, 4375.
(14) Cheng, G.; Boker, A.; Zhang, M.; Kraush, G.; Muller, A. H. E. *Macromolecules* **2001**, *34*, 6883.
(15) Yoshida, K.; Shimomura, T.; Ito, K.; Hayakawa, R. *Langmuir* **1999**, *15*, 910.
(16) Anderson, S.; Aplin, R. T.; Claridge, T. D. W.; Goodson III, T.; Maciel, A. C.; Rumbles, G.; Ryan, J. F.; Anderson, H. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2383.
(17) Djalali, R.; Hugenberg, N.; Fischer, K.; Schmidt, M. *Macromol. Rapid Commun.* **1999**, *20*, 444.
(18) Djalali, R.; Li, S.-Y.; Schmidt, M. *Macromolecules* **2002**, *35*, 4282.
(19) Ishizu, K.; Honda, K.; Kanbara, T.; Yamamoto, T. *Polymer* **1994**, *35*, 4901.
(20) JISM 8121, 1977. In *Bunseki Kagaku Binran* (*Handbook of Analytical Chemistry*); Maruzen: Tokyo, 1991; p 206.
(21) Radhakrishnan, S.; Deshpande, S. D. *Mater. Lett.* **2001**, *48*, 144.
(22) Terao, K.; Nakamura, Y.; Norisuye, T. *Macromolecules* **1999**, *32*, 3690.

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