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Polymer 47 (2006) 1946–1952
polymer
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Preparation of poly(*N*-isopropylacrylamide) grafted silica bead using hyperbranched polysiloxysilane as polymer brush and application to temperature-responsive HPLC

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Received 8 November 2005; received in revised form 4 January 2006; accepted 11 January 2006
Available online 7 February 2006

Abstract

Hyperbranched polysiloxysilane (HBPS) terminated by the vinyl functional group was synthesized by the self polymerization of AB_2 monomer, 1,5-divinyl-1,1,3,5,5-pentamethyltrisiloxane, in the presence of the platinum catalyst. The terminal vinyl group was converted to 2-hydroxyethyl by the reaction with 9-BBN as the hydroboration reagent. The terminal function was then modified to the 2-bromoisobutyryl group by the reaction of hydroxyl group with 2-bromoisobutyryl bromide. The obtained HBPS possessing the 2-bromoisobutyryl terminal group was immobilized on the silica surface by mixing the silica bead and HBPS in hexane. Block copolymer of HBPS and poly(*N*-isopropylacrylamide) (PIPAAm) was synthesized by the atom transfer radical polymerization (ATRP) using 2-bromoisobutyryl terminated HBPS as a macroinitiator. The molecular weight of the block copolymer was $M_n = 23{,}500$ and $M_w/M_n = 1.31$. Graft polymerization of *N*-isopropylacrylamide on the silica surface was carried out on the 2-bromoisobutyryl terminated HBPS immobilized silica bead using ATRP. The PIPAAm grafted silica bead was applied to the column packed material for temperature-responsive HPLC. Two kinds of steroids, hydrophilic and hydrophobic, were successfully separated by the HPLC system.

Keywords: Polymer brush; Hyperbranched polysiloxysilane; Temperature-responsive HPLC

1. Introduction

Silica beads especially modified by grafting polymers on the surface have been applied to the stationary phase for HPLC [1]. Okano et al. have demonstrated a new system of temperature-responsive HPLC using thermo-responsive poly(*N*-isopropylacrylamide) (PIPAAm)-modified silica as a column packing material [2–8]. In the system, the physical properties of the stationary phase can be controlled by changing the external temperature, because PIPAAm on the silica surface exhibits thermally reversible hydrophilic–hydrophobic changes across a lower critical solution temperature (LCST) at 32 °C in aqueous solution [9,10].

Hyperbranched polymers have continuous branching structure as well as a number of terminal functional groups that can be easily designed. The use of hyperbranched polymers to modify silica surface is one of the polymer brush techniques that can introduce a large quantity of functionalities to the silica surface [11–26]. We found that hyperbranched polysiloxysilanes (HBPS) possess strong affinity with silica surface. In addition, various functional groups can be introduced on the terminal position of HBPS. Therefore HBPS seem to be suitable materials for the polymer brushes on the silica surface. Although several papers concerning HBPS synthesis have been presented [27–30], there is no report for positive application of HBPS.

Herein, we present the method for immobilization of HBPS having the 2-bromoisobutyryl terminal group as a initiator for atom transfer radical polymerization (ATRP) on the silica surface to graft PIPAAm (Scheme 1). ATRP is one of the most convenient methods for modification of silica, because molecular weight and dispersity of grafted polymers can be well controlled [31–34]. We also investigated resulting

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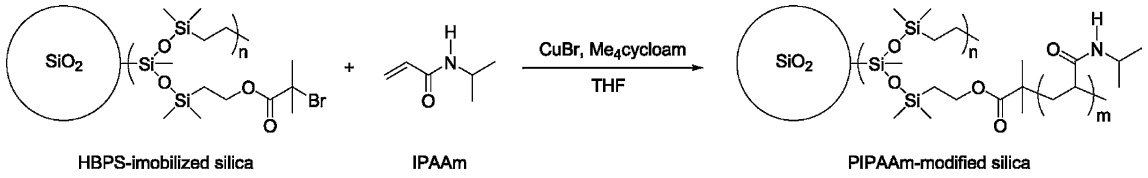
doi:10.1016/j.polymer.2006.01.027



Scheme 1.

PIPAAm-modified silica as a column packing material in temperature-responsive HPLC for steroids.

2. Experimental section

2.1. Materials

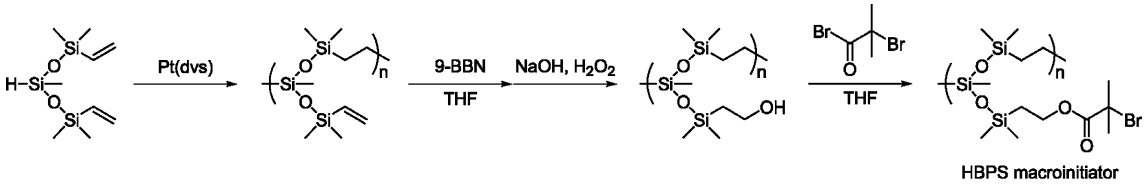
Nucleosil 300-5 (Macherey-Nagel, Inc., Germany) having particle size of 5 μm and pore size of 300 Å was used as silica bead. It was dried in vacuum at 80 °C for 3 h before use. An AB_2 monomer, 1,5-divinyl-1,1,3,5,5-pentamethyltrisiloxane (Kozima Chemical, Inc., Japan), was purified by distillation. Platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Pt[dvs]) 0.1 M solution in xylene and 9-borabicyclo[3.3.1]-nonane (9-BBN) 0.5 M solution in THF were purchased from Aldrich. *N*-Isopropylacrylamide (IPAAm) was purified by recrystallization from hexane. Copper bromide (CuBr) was purified by stirring over 24 h in acetic acid. After filtration, it was washed with ethyl alcohol and diethyl ether and then dried in vacuum. 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cycloam) was purchased from Aldrich. Tetrahydrofuran (THF) was used after distillation from sodium. Other solvents and reagents were used without further purification.

2.2. Measurements

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-AL 300 spectrometer. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Molecular weights were determined by gel permeation chromatography (GPC) with polystyrene calibration using a Shodex GPC-101 system with RI detector and Shodex KF-803 and 804 columns using THF as an eluent. Light transmittance of polymer solution (5 mg/mL) was measured at 500 nm using a JASCO V-550 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was measured with an ULVAC-PHI Model 5500 MT. Differential scanning calorimetry (DSC) was measured with a Seiko DSC 6200 at a heating rate of 10 °C/min under nitrogen. Thermogravimetric analysis (TGA) was carried out with a Seiko TGA 6200 at a heating rate of 10 °C/min under air. Scanning electron microscopy (SEM) was taken on a Hitachi FE-SEM S-800. Energy-filtering transmission electron microscope (EFTEM) was taken on a LEO 912. The sample was embedded in a curable epoxy resin (Quetol 812, Nissin EM, Inc., Japan), and was microtomed with a diamond knife to give sections. The sections were collected into a cupper grid and served for the EFTEM measurement. High performance liquid chromatography (HPLC) was performed on a Hitachi Lachrom Elite L-2000 with a stainless-steel column (length: 150 mm × 4.6 mm i.d.) packed with the PIPAAm-modified silica in water as an eluent. The column oven was an Aquaway Gradienter (Cell Seed, Inc., Japan). The elution behaviors of the steroids were recorded at a flow rate 1 mL/min at various temperatures.

2.3. Hyperbranched poly(siloxysilane) (HBPS) macroinitiator

In a 500 mL flask, Pt(dvs) solution (0.1 M in xylene) (1 mL, 0.1 mmol, 0.1 mol%) was added to 1,5-divinyl-1,1,3,5,5-pentamethyltrisiloxane (24.65 g, 0.1 mol) under argon, and the reaction mixture was stirred at room temperature for 3 h. 9-BBN solution (0.5 M in THF) (250 mL, 0.125 mol) was slowly added to the reaction mixture diluted with THF (50 mL) at 0 °C, and then was stirred at 40 °C for 17 h. After cooling to 0 °C, sodium hydroxide aqueous solution (6 M, 25 mL, 0.15 mol) and hydrogen peroxide solution (35%, 50 mL) were added dropwise in turn, and the reaction mixture was stirred at the same temperature for 1 h. The THF solution was diluted with diethyl ether and washed with water, dried over magnesium sulfate, and evaporated to remove the solvents. In a 300 mL flask, the product mixture, triethylamine (20.24 g, 0.2 mol), and THF (100 mL) were placed. 2-Bromoisobutyryl bromide (34.49 g, 0.15 mol) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 1 h. The THF solution was diluted with diethyl ether and washed with water, and dried over magnesium sulfate, and evaporated. After reprecipitation from diethyl ether into acetonitrile, the precipitate was collected and dried in vacuum to give HBPS (10.17 g, yield 25%). $M_n = 8800$, $M_w/M_n = 1.68$ (GPC). T_g: −43 °C (DSC). T_d: 224 °C (TGA). ^{1}H NMR: δ −0.11 (br, $Si(CH_3)C\mathit{H}Si$), 0.05 (br, $OSi(C\mathit{H}_3)_2C$), 0.14 (m, $O_2Si(C\mathit{H}_3)C$), 0.42 (br, $SiC_2\mathit{H}_4Si$), 1.01 (m, $Si(C\mathit{H}_3)CHSi$),



Scheme 2.

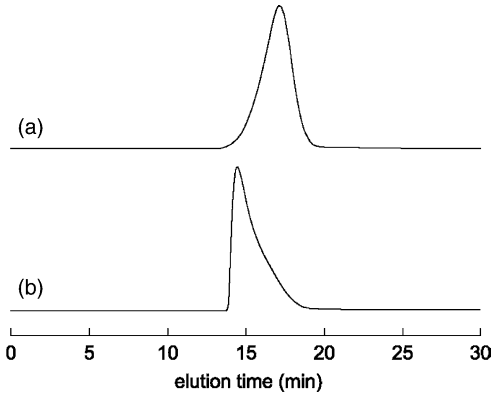


Fig. 1. GPC of HBPS (a) and PIPAAm–HBPS (b).

1.08 (m, SiCH_2CH$_2$O), 1.90 (s, BrC(CH_3)2C), 4.25 (t, SiCH$_2$CH_2O, J = 9.0 Hz). ^{13}C NMR: δ −1.16 to 1.58 (SiCH$_3$), 7.92 (Si(CH$_3$)CHSi), 8.94 (SiCH$_2$), 9.45 (SiCH$_2$), 11.75 (Si(CH$_3$)CHSi), 18.77 (SiCH$_2$CH$_2$O), 30.71 (BrC(CH$_3$)$_2$C), 55.90 (SiCH$_2$$CH_2$O), 63.83 (Br$C$(CH$_3$)$_2$C), 171.61 ($C$=O). ^{29}Si NMR: δ −20.84 (CSiMeO$_2$), 4.68 (BrC(CH$_3$)$_2$CO$_2$C$_2$H$_4$$SiMe_2$O), 7.96 (C$SiMe_2$O). IR (neat, cm^{-1}): 1736 (C=O), 1045 (Si–O).

2.4. HBPS–PIPAAm block copolymer (HBPS–PIPAAm)

HBPS (0.414 g, 1 mmol bromine) and THF (25 mL) were placed in a 100 mL flask under argon. A solution of IPAAm (11.3 g, 0.1 mol), CuBr (0.144 g, 1 mmol), and Me$_4$Cycloam (0.256 g, 1 mmol) in THF (15 mL) was added, and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with THF and passed throughout a column of aluminum oxide. Removal of the solvent afforded crude product, which was precipitated from acetone into diethyl ether. The precipitate was collected and dried in vacuum to give HBPS–PIPAAm (6.31 g, yield 54%). M_n = 23,500, M_w/M_n = 1.31 (GPC). T_g: 14, 136 °C (DSC). T_d: 329 °C (TGA). ^{1}H NMR: δ 0.03 (br, OSi(CH_3)$_2$C), 0.10 (br, O$_2$Si(CH_3)C), 1.19 (s, CH(CH_3)$_2$), 1.62–2.38 (br, CH_2CH), 3.98 (br, CH(CH$_3$)$_2$), 6.41 (br, NH). ^{13}C NMR: δ −0.77 (O$_2$Si(CH_3)C), 0.42 (OSi(CH_3)$_2$C), 22.30 (CH(CH_3)$_2$), 35.53 (CH_2CH), 40.98 (CH(CH$_3$)$_2$), 41.79 (CH$_2$CH), 173.87 (C=O). IR (KBr, cm^{-1}): 1652 (C=O), 1550 (N–H), 1460 (C–N), 1047 (Si–O).

2.5. HBPS–immobilized silica (HBPS–silica)

In a 200 mL flask, as the suspension prepared silica (10 g) and hexane (80 mL) was gently stirred under argon, a solution of HBPS (1.24 g) in hexane (20 mL) was slowly added. The reaction mixture was stirred at room temperature for 12 h. The product was filtered and rinsed twice with 50 mL of hexane. The sample was dried at 80 °C for 3 h in vacuum to give HBPS–silica (10.27 g). IR (KBr, cm^{-1}): 1107 (Si–O). Elemental analysis: C, 3.44; H, 0.65.

2.6. PIPAAm–modified silica (PIPAAm–HBPS–silica)

HBPS–silica (5 g) and THF (25 mL) were placed in a 100 mL flask under argon. As the suspension was gently stirred, a solution of IPAAm (11.3 g, 0.1 mol), CuBr (0.144 g, 1.0 mmol), and Me$_4$Cycloam (0.256 g, 1 mmol) in THF (15 mL) was added, and the reaction mixture was stirred at room temperature for 12 h. The product was filtered and rinsed repeatedly with methanol and acetone. The sample was dried at 80 °C for 3 h in vacuum to give PIPAAm–HBPS–silica (5.60 g). IR (KBr, cm^{-1}): 1655 (C=O), 1549 (N–H), 1461 (C–N), 1107 (Si–O). Elemental analysis: C, 13.29; H, 2.26; N, 2.41.

3. Results and discussion

3.1. Synthesis and characterization of HBPS macroinitiator

HBPS macroinitiator was synthesized according to Scheme 2. HBPS with the vinyl terminal group was prepared by the hydrosilylation of 1,5-divinyl-1,1,3,5,5-pentamethyltrisiloxane (AB$_2$ monomer) in the presence of 0.1 mol% of Pt(dvs) as a catalyst. The hydroboration of the vinyl group with 9-BBN followed by treatment with hydrogen peroxide gave

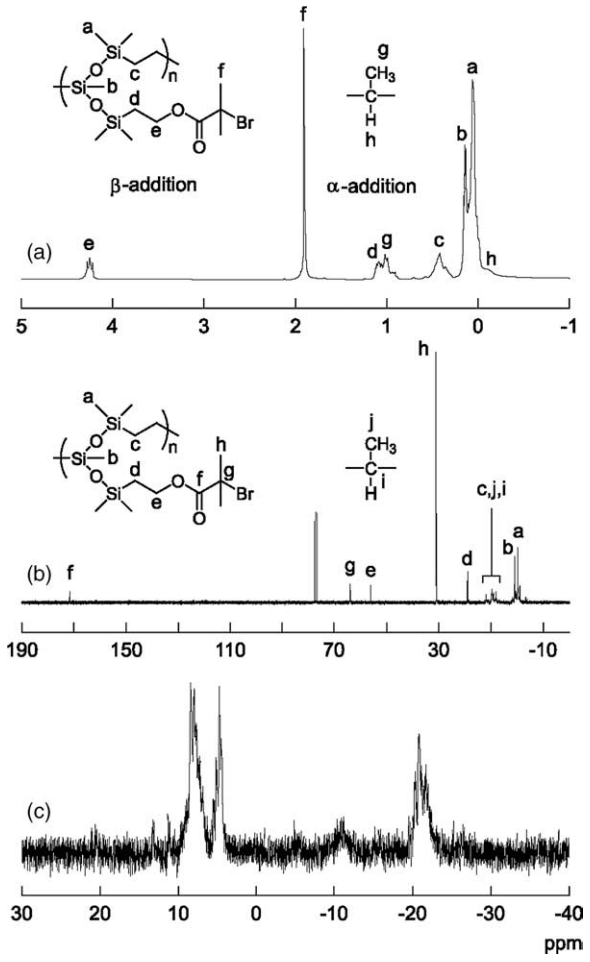


Fig. 2. ^{1}H (a), ^{13}C (b), and ^{29}Si (c) NMR spectra of HBPS.

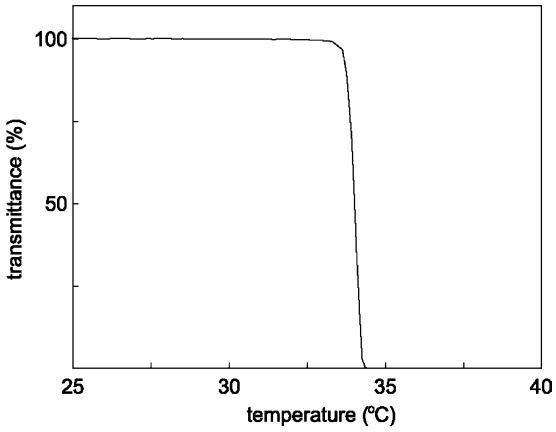


Fig. 3. Temperature dependence of light transmittance of HBPS–PIPAAm solution.

HBPS having the hydroxyl terminal group without cleavage of siloxane bond. The reaction for conversion of the terminal group from vinyl to 2-hydroxyethyl was quantitatively proceeded judging from the fact that there was no vinyl peak in the ^{1}H NMR spectrum. HBPS macroinitiator was prepared by the esterification of the hydroxyl terminal group with 2-bromoisobutyryl bromide. The GPC of HBPS macroinitiator indicated $M_n = 8800$ and $M_w/M_n = 1.68$ as shown in Fig. 1(a).

The chemical structure of HBPS macroinitiator was characterized by NMR and IR spectra. In the IR spectrum, the absorption of ester group was observed at 1736 cm^{-1}. In the ^{1}H NMR spectrum (Fig. 2(a)), the sharp signal of methyl proton of $C(CH_3)_2Br$ was observed at 1.90 ppm. The signals of ethylene proton connected with ester group were observed at 1.08 and 4.25 ppm. The signal at 0.42 ppm is assigned to ethylene proton of β-addition, and those at −0.11 and 1.01 ppm are methine and methyl protons of α-addition by the help of ^{1}H–^{13}C COSY spectrum. The signals of methyl protons of $OSi(CH_3)_2C$ and $O_2Si(CH_3)C$ were observed at 0.05 and 0.14 ppm, respectively. In the ^{13}C NMR spectrum (Fig. 2(b)), the carbon signals of 2-bromoisobutyryl group were observed at 30.71, 63.83, 171.61 ppm. The signals at 18.77 and 55.90 ppm are assigned to ethylene carbon connected with ester group. The signals at 7.92, 8.94, 9.45, and 11.75 ppm are ethylene and methyl methylene carbons in the main chain. Methyl carbon of $SiCH_3$ appeared as complicated signals at −1.86 to 1.58 ppm, because HBPS probably contained cyclic moiety in the main chain formed by intermolecular cyclization of the vinyl group with the SiH group. The ^{29}Si NMR spectrum (Fig. 2(c)) exhibited three kinds of signals at −20.36, 4.68 and 7.96 ppm, which were ascribed to silicons of $CSiMeO_2$, $BrC(CH_3)_2CO_2C_2H_4SiMe_2O$ and $CSiMe_2O$.

The NMR analysis indicated that almost all the vinyl terminal groups were converted to 2-bromoisobutyryl groups. The integral ratio of the methyl protons of $BrC(CH_3)_2$ in the terminal groups to $SiCH_3$ in the main chain was found to be 1/4.9 from ^{1}H NMR spectrum. The content of the terminal groups is smaller than theoretical value (1/2.5). It is considered that the terminal groups were decreased by the intermolecular cyclization in the polymerization process mentioned above. The average number of terminal groups was about 13 per polymer molecule from calculation based on the molecular weight of the GPC and integral ratio of ^{1}H NMR spectrum.

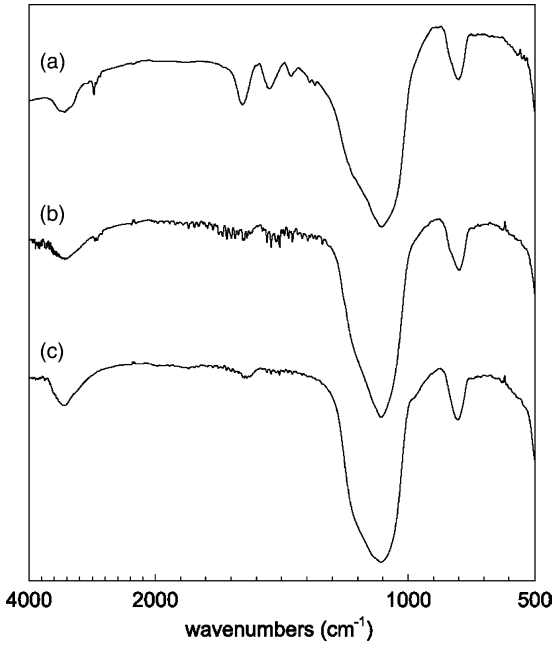


Fig. 4. IR spectra of PIPAAm–HBPS–silica (a), HBPS–silica (b), and original silica (c).

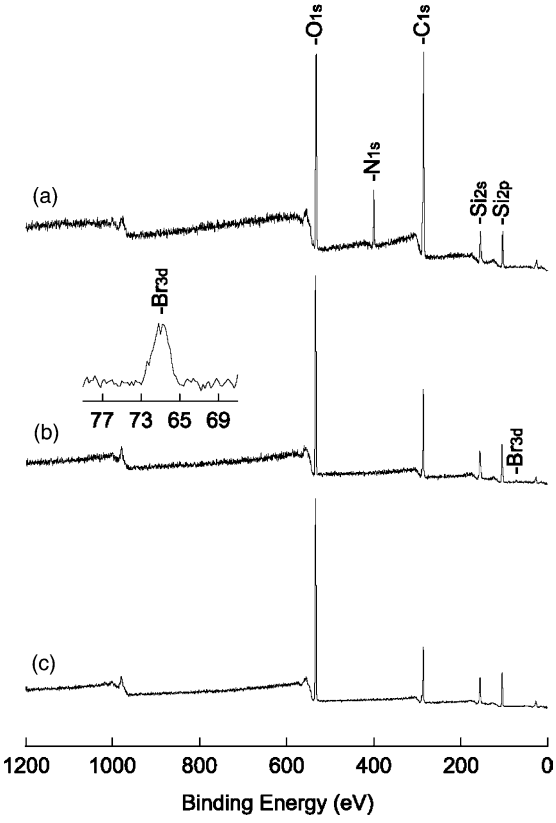


Fig. 5. XPS spectra of PIPAAm–HBPS–silica (a), HBPS–silica (b), and original silica (c).

3.2. Synthesis and characterization of HBPS–PIPAAm block copolymer

In advance of ATRP initiated by the HBPS immobilized on the silica surface, the reactivity of HBPS as the macroinitiator was investigated in a silica free system. The ATRP of IPAAm was carried out at rt for 12 h in the presence of copper bromide with Me_4cycloam in THF ($[M]_0$:$[I]_0$:$[CuBr]_0$:$[Me_4cycloam]_0$ = 100:1:1:1) [35–37]. The resulting polymer was purified by reprecipitation from acetone to ether. The GPC showed that molecular weight of obtained block copolymer HBPS–PIPAAm was M_n = 23,500 and M_w/M_n = 1.31 (Fig. 1(b)). The chemical structure of HBPS–PIPAAm was characterized by NMR and IR spectra. In the NMR spectra, the signals of PIPAAm were observed with those of methyl groups of HBPS. IR spectrum of HBPS–PIPAAm showed the characteristic absorptions of amide groups of PIPAAm and siloxane bonds of HBPS. According to the results of GPC, the molecular weight of PIPAAm moiety in HBPS–PIPAAm was 14,700, which subtracted the molecular weight (8800) of HBPS from that (23,500) of HBPS–PIPAAm. The molecular weight of each grafted PIPAAm chain was about 1100 (14,700/13) from calculation based on the molecular weight and the number of terminal groups described above.

Fig. 3 shows the temperature dependence of the light transmittance of HBPS–PIPAAm dissolved in aqueous solution. HBPS–PIPAAm was highly soluble in water under low temperature. The turbidity change took place at 34 °C as the temperature was raised, indicating that HBPS–PIPAAm has a LCST in the aqueous solution. The solution became transparent again when the temperature was decreased below the LCST. These findings indicate that HBPS–PIPAAm exhibits thermally reversible behavior for temperature-responsive HPLC.

3.3. Preparation and characterization of PIPAm–HBPS–silica

Immobilization of HBPS on the silica bead was conducted by mixing HBPS and silica bead in hexane. It is assumed that HBPS was connected to the silica surface by the chemical or physical adsorption between siloxane segment in the main chain and silica surface. ATRP of IPAAm on the silica surface was carried out by the similar procedure described above. After ATRP, the product was washed with acetone and methanol throughly to remove free attachable polymer and unreacted monomer. The structure of PIPAAm–HBPS–silica was confirmed by IR spectrum. Fig. 4 shows IR spectra of PIPAAm–HBPS–silica, HBPS–silica, and original silica. Compared with the spectrum of original silica, the spectrum of PIPAAm–HBPS–silica showed characteristic absorptions of the amide of PIPAAm at 1655, 1549 and 1461 cm^{-1}, that were also observed in the IR spectrum of HBPS–PIPAAm. The broad absorption around 1100 ppm is assigned to Si–O bonds of HBPS and silica bead.

Characterization of the silica surface was carried out by XPS. Fig. 5 shows XPS spectra of PIPAAm–HBPS–silica, HBPS–silica, and original silica. In the spectrum of PIPAAm–HBPS–silica (Fig. 5(a)), the signal of nitrogen of PIPAAm was observed, and the relative integral ratio of the signal of carbon was higher than those of the spectra of HBPS–silica (Fig. 5(b)) and original silica (Fig. 5(c)). The spectrum of HBPS–silica showed the almost similar signal as original silica, but the relative integral ratio of the signal of carbon was slightly higher and the small signal of bromine of HBPS was observed. These results supported that HBPS macroinitiator was immobilized on the silica bead and PIPAAm was grafted on the silica surface.

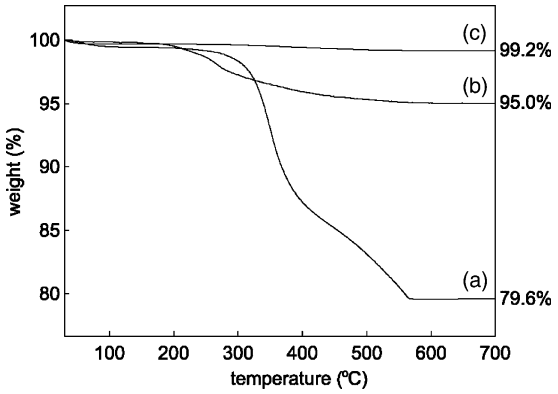


Fig. 6. TGA curves of PIPAAm–HBPS–silica (a), HBPS–silica (b), and original silica (c).

The polymer contents of PIPAAm–HBPS–silica and HBPS–silica were estimated by weight loss of TGA and elemental analysis (Fig. 6, Table 1). The TGA of PIPAAm–HBPS–silica (Fig. 6(a)) showed on-set decomposition temperatures (T_d) at 318 °C and the weight loss of 20.4% at 700 °C. The T_d is in agreement with that of the block copolymer HBPS–PIPAAm, indicating that the weight loss was originated from grafted HBPS–PIPAAm on the silica surface. The TGA of HBPS–silica (Fig. 6(b)) exhibited T_d at 221 °C originated from HBPS and the weight loss of 5.0% at 700 °C. In comparison with the weight loss of 0.8% of original silica (Fig. 6(c)), the polymer contents of PIPAAm–HBPS–silica and HBPS–silica are 19.6 and 4.2% of total amount, respectively. The values are in good agreement with the result of elemental analysis.

The surface morphology change was observed by SEM. Fig. 7 shows SEM images of original silica and PIPAAm–HBPS–silica. Compared with the porous surface of original silica, the image of PIPAAm–HBPS–silica showed flat surface, and the diameter of the silica bead slightly increased.

Table 1
Comparision of the weight losses (elemental analysis and TGA)

Sample	Elemental analysis			Weight loss (TGA[a]) (%)
	%H	%C	%N	
Original silica	0.8	0.00	0.00	0.08
HBPS–silica	0.65	3.44	0.00	5.0
PIPAAm–HBPS–silica	2.26	13.29	2.41	20.4

[a] Determined by char yield at 700 °C.

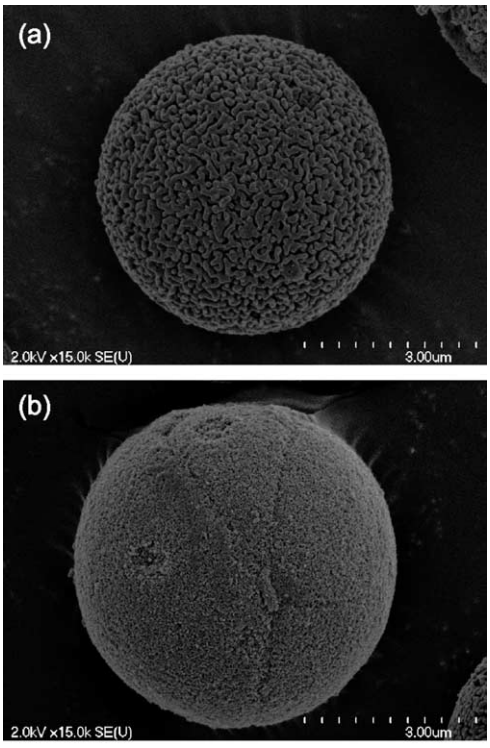


Fig. 7. SEM images of original silica (a) and PIPAAm–HBPS–silica (b).

Energy-filtering TEM (EFTEM) was employed to investigate HBPS–PIPAAm immobilized on the silica surface. EFTEM has emerged as a useful tool for the characterization of the polymer materials [38,39]. EFTEM enables us to acquire images showing a two-dimensional intensity distribution of inelastically scattered electrons in a given energy-loss interval [40]. The electron spectroscopic images allow the maps of the chemical elements. Fig. 8(a) and (b) shows the EFTEM image and nitrogen map of the HBPS–PIPAAm–silica bead, respectively, in which the upper side is curable epoxy resin and the lower side is the silica bead. In Fig. 8(b), the nitrogen distribution was visualized using green dots. Although the epoxy resin contains the nitrogen due to 2,4,6-tridimethylaminomethyl phenol as epoxy accelerator, the concentration of the nitrogen distribution on the silica bead was obviously higher than that of epoxy resin. It is emphasized that HBPS–PIPAAm is immobilized on the silica surface.

3.4. Temperature-responsive chromatography for steroids

Okano et al. have developed a new system of temperature-responsive HPLC for steroids using thermo-responsive poly(*N*-isopropylacrylamide) (PIPAAm)-modified silica as a column packing material and water as an eluent [2–8]. The elution time of steroids can be controlled by changing the external temperature, because PIPAAm grafted on the silica surface exhibits a thermally reversible hydrophilic–hydrophobic change in response to temperature changes across a lower critical solution temperature (LCST). At the temperature over LCST, the hydrophobic interaction between steroids and PIPAAm grafted on the silica surface becomes stronger and as the result, the retention time increases. The change of the retention time for hydrophobic steroid is larger than that of hydrophilic steroid because of the stronger hydrophobic interaction.

Using the column packed with PIPAAm–HBPS–silica, the separation of two steroids, hydrocortisone as hydrophilic steroid and testosterone as hydrophobic steroid, was carried out by changing the temperature of the column. As shown in Fig. 9, the retention time for testosterone increased with raising the temperature, while that of hydrocortisone hardly changed. The relatively sudden change in the retention time between 30 and 40 °C seems to be cause by the wettability change of PIPAAm on the silica surface, since HBPS–PIPAAm has a LCST at 34 °C. The elution behavior was almost the same as reported in the reference paper [8]. However, the retention time for testosterone more increased and the signal became broader than that of the reference paper. It is considered that HBPS moiety in the silica bead draws the testosterone into the branching structure of HBPS by the hydrophobic interaction between siloxane bond and steroids.

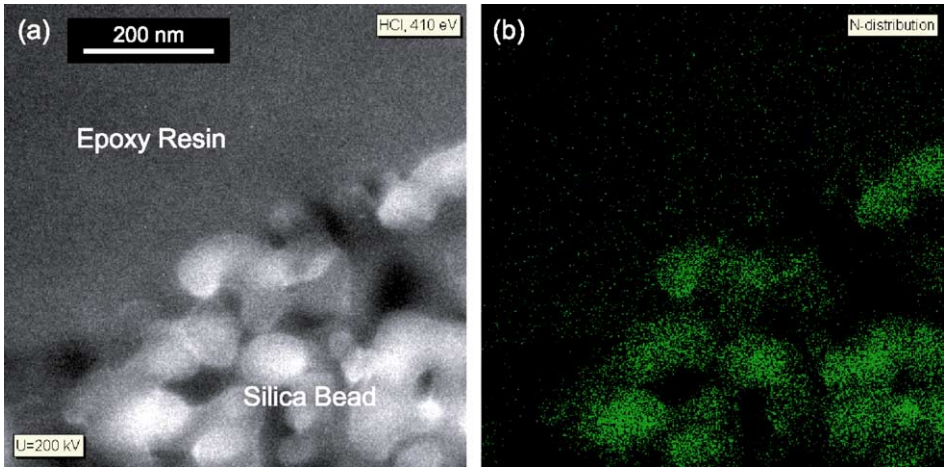


Fig. 8. EFTEM image (a) and nitrogen map (b) of PIPAAm–HBPS–silica.

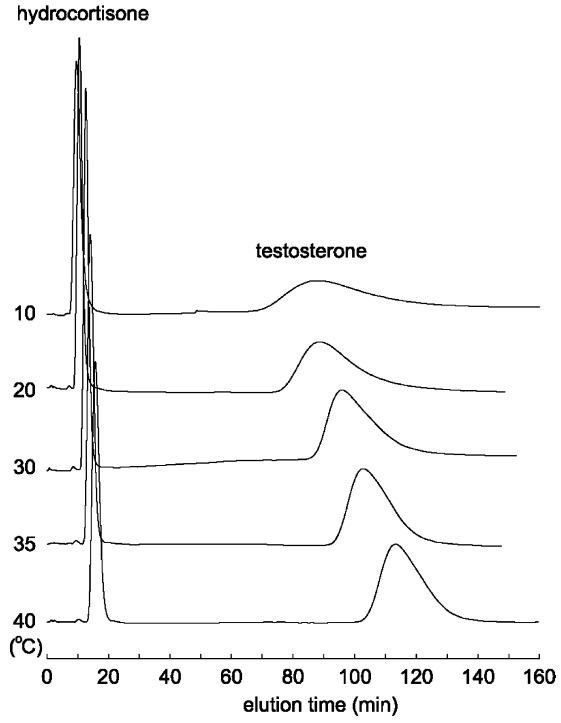


Fig. 9. Chromatograms of a mixture of hydrocortisone and testosterone.

4. Conclusion

PIPAAm could be successfully grafted by the ATRP method on the silica surface where 2-bromoisobutyryl terminated HBPS were immobilized. The silica bead obtained was applied as a column packing material for temperature-responsive HPLC. The result that hydrophobic and hydrophilic steroids were separated by this HPLC system supported immobilization of PIPAAm on the silica surface. In the present work, HBPS act as a polymer brush to modify the silica surface into 2-bromoisobutyryl functional group that is the initiation point of ATRP.

Acknowledgements

The authors thank Prof Takashi Ishizone of Tokyo Institute of Technology for helpful discussion and Mr Manabu Ueno for his help in carrying out the light transmittance measurement.

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