

Synthesis and properties of polymer brush consisting of poly(phenylacetylene) main chain and poly(dimethylsiloxane) side chains

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Received 9 January 2007; received in revised form 28 February 2007; accepted 6 March 2007

Available online 12 March 2007

Abstract

A novel polymer brush consisting of poly(phenylacetylene) (PPA) main chain and poly(dimethylsiloxane) (PDMS) side chains was synthesized by the polymerization of phenylacetylene-terminated PDMS macromonomer (M-PDMS). The macromonomer was prepared by the esterification of monohydroxy-ended PDMS (PDMS-OH, degree of polymerization (DP) = 42) with *p*-ethynylbenzoic acid. The polymerization of M-PDMS using [(nbd)RhCl]₂/Et₃N catalyst led to polymer brush, poly(M-PDMS), with M_n up to 349 000 (DP of main chain 104). Poly(M-PDMS) with narrow molecular weight distribution ($M_n = 39 900$, $M_w/M_n = 1.11$) was obtained with a vinyl-Rh catalyst, [Rh{C(Ph)=CPh₂}(nbd){P(4-FC₆H₄)₃}] / (4-FC₆H₄)₃P. Poly(M-PDMS)s were brown to orange viscous liquids and soluble in organic solvents such as toluene and CHCl₃. The UV–vis absorptions of poly(M-PDMS) were observed in the range of 350–525 nm, which are attributable to the PPA main chain.

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Keywords: Poly(dimethylsiloxane); Poly(phenylacetylene); Polymer brush

1. Introduction

Cylindrical polymer brushes, which possess a long linear main chain and densely grafted side chains [1], have attracted considerable attention due to their unique properties in solution and bulk [2], as well as their potential applications in the preparation of nanowires [3], molecular actuators [4], and crystallization modifiers [5]. The homopolymerization of macromonomers [6] is a convenient and effective method to access polymer brushes by one-step polymerization compared to “grafting from” [7] and “grafting onto” [8] techniques. Tsukahara reported the homopolymerization of methacryloyl end-functionalized polystyrene (PS) macromonomers to give extremely high molecular weight poly(macromonomers) for the first time [9]. Then several poly(macromonomers) such as those based on a poly(methyl methacrylate) (PMMA)

main chain and poly(ethylene oxide) (PEO) [10], poly(2-vinylpyridine) [11] and PMMA [12] side chains were successfully synthesized with the macromonomer technique. Aiming at the synthesis of well-defined polymer brushes, ring-opening metathesis polymerization [13], living anionic polymerization [14], and atom transfer radical polymerization (ATRP) [15] of macromonomers have been examined.

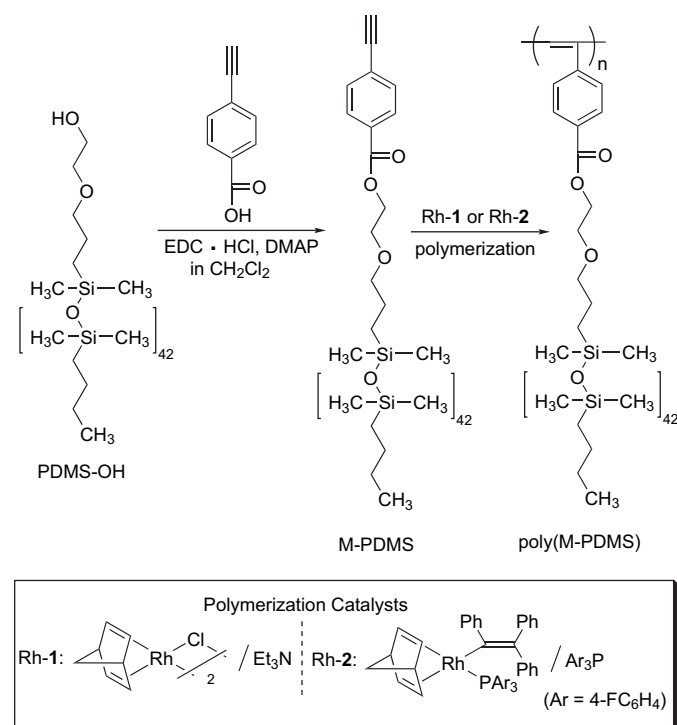
Substituted polyacetylenes have been extensively studied so far [16], and recently there is growing interest in synthesis and properties of poly(macromonomers) having polyene main-chain structure, obtained by the homo- and copolymerizations of acetylene-terminated macromonomers using Rh catalysts. The successful synthesis of polyacetylene brushes bearing polypeptide [17,18], polycarbohydrate ionophores [19], PS [20,21], PMMA [21] and PEO [22] as side chains has been well documented. A series of optically active, stereoregular poly(phenylacetylenes) (PPAs) bearing polypeptide grafts were also synthesized by the homopolymerization of poly-(γ -benzyl-L-glutamate)-based macromonomers [18]. We have recently reported the synthesis of polyacetylenes grafted

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with polystyrene chains by the copolymerization of a propargyl-terminated PS macromonomer with low molecular weight comonomers (PA or propargyl 2-bromopropionate) [20]. Our research group has also accomplished the synthesis of polymer brushes (absolute M_w up to 2 740 000) with PPA main chain and either PS or PMMA side chains by the Rh-catalyzed polymerization of the corresponding PA-terminated macromonomers [21].

Poly(dimethylsiloxane) (PDMS) is known to have characteristic properties such as high mechanical elasticity, high stability toward oxidation, excellent thermal stability, low surface energy, and nontoxicity [23]. Thus, they are viable candidates for applications to thermoplastic elastomers, surfactants, lubricants, water repellents, and antifoaming agents. Although block and graft copolymers containing PDMS segments have been investigated considerably [24], there are few reports on the synthesis of polymer brushes with PDMS side chains [25,26]. For example, it has been reported that a polymer brush composed of PMMA main chain and PDMS side chains is synthesized by ATRP of monomethacryloxypropyl PDMS macromonomer [25].

We herein report successful synthesis of a new polymer brush with PPA main chain and PDMS side chains by the polymerization of PDMS macromonomer having an acetylene end group [16a,27] (Scheme 1). The PA-terminated PDMS macromonomer (M-PDMS) was polymerized with a typical binary Rh catalyst to give a polymer brush with long main chain (DP of main chain up to 104). The polymerization of M-PDMS by a vinyl-Rh catalyst yielded a well-defined poly(macromonomer) with narrow molecular weight distribution (MWD) (e.g., $M_w/M_n = 1.11$).



Scheme 1. Synthesis of M-PDMS and poly(M-PDMS).

2. Experimental section

2.1. Materials

The monohydroxy-terminated poly(dimethylsiloxane) [PDMS-OH; M_n ($^1\text{H NMR}$) = 3340, degree of polymerization (DP) = 42] was donated by Shin-Etsu Chemical Co., Ltd. (Japan). 1-(3-(Dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) was purchased from Eiweiss Chemical Corporation (Japan) and used as received. 4-(Dimethylamino)pyridine (DMAP) (Wako, Japan; 98%), triethylamine (Et_3N) (Wako, Japan; 98%), and (4- FC_6H_4) $_3\text{P}$ (Aldrich, 99%) were used without further purification. *p*-Ethynylbenzoic acid [28], [(nbd)RhCl] $_2$ (nbd = 2,5-norbornadiene) [29] and [Rh{C(Ph)=CPh $_2$ }(nbd){P(4- FC_6H_4) $_3$ }] [30] were synthesized according to the literature. All the polymerization solvents were purified by the standard methods.

2.2. Measurements

$^1\text{H NMR}$ spectra were recorded in chloroform-*d* (CDCl_3) on a JEOL EX-400 spectrometer (400 MHz). Infrared spectra (IR) were recorded on a JASCO FTIR-4100 spectrophotometer. Number- and weight-average molecular weights (M_n and M_w , respectively) and MWDs (M_w/M_n) were determined by gel permeation chromatography (GPC) on a Jasco Gulliver System (PU-980, CO-965, RI-930, and UV-1570) equipped with a series of PS gel columns (Shodex KF805L \times 3, bead size: 10 μm , molecular weight range up to 4×10^6 , flow rate 1 mL/min), using THF as an eluent at 40 $^\circ\text{C}$ with a PS calibration. UV-vis spectra were recorded on a Shimadzu UV-2200 spectrophotometer.

2.3. Synthesis of macromonomer, M-PDMS

p-Ethynylbenzoic acid (0.45 g, 3.1 mmol) and DMAP (0.12 g, 0.98 mmol) were successively added to a solution of PDMS-OH (5.8 g, 1.7 mmol) and EDC·HCl (0.88 g, 4.6 mmol) in CH_2Cl_2 (40 mL) under argon at 0 $^\circ\text{C}$, and stirred at room temperature for 24 h. Then the mixture was filtered and the filtrate was washed with saturated Na_2CO_3 solution and brine. The solution was dried over MgSO_4 and concentrated by rotary evaporation. The obtained product was vacuum dried until it reached a constant weight. It afforded 5.0 g of M-PDMS as a colorless liquid in 80% yield. M_n (GPC) = 3350, $M_w/M_n = 1.23$; M_n ($^1\text{H NMR}$) = 3470. $^1\text{H NMR}$ (CDCl_3 , ppm): $\delta = 7.9$ (d, 2H, aromatic H), 7.5 (d, 2H, aromatic H), 4.4 (t, 2H, $\text{CH}_2\text{CH}_2\text{OCO}$), 3.7 (t, 2H, $\text{CH}_2\text{CH}_2\text{OCO}$), 3.4 (t, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 3.1 (s, 1H, $\equiv\text{C-H}$), 1.6 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.2 (m, 4H, CH_2 in butyl), 0.8 (t, 3H, CH_3 in butyl), 0.5 (m, 4H, CH_2Si), 0.1 (s, 258H, SiCH_3). IR (KBr, cm^{-1}): $\nu = 3315$ ($\equiv\text{C-H}$), 1729 (C=O), 1259 (Si-CH_3), 1103 (Si-O), 798 (Si-CH_2).

2.4. Polymerization of M-PDMS

The polymerization using [(nbd)RhCl] $_2$ / Et_3N was carried out under the following conditions: [M-PDMS] = 0.075 M

(calculated by M_n of M-PDMS = 3350 determined by GPC), $[Rh] = 5.0$ mM, $[Et_3N] = 50$ mM. A typical procedure is as follows: a solution of $[(nbd)RhCl]_2$ and Et_3N in a distilled solvent was added to a solution of M-PDMS in the same solvent under argon. After stirring vigorously for a given time at a given temperature, the solution was poured into a large amount of acetone to precipitate the polymer, which was collected and vacuum dried until it reached a constant weight. The polymerization catalyzed by a living polymerization catalyst, $[Rh\{C(Ph)=CPh_2\}(nbd)\{P(4-FC_6H_4)_3\}]/(4-FC_6H_4)_3P$, was carried out under the following conditions: $[M-PDMS] = 0.075$ M, $[Rh] = 5.0$ mM, $[(4-FC_6H_4)_3P] = 25$ mM. The polymerization procedure was similar to that of $[(nbd)RhCl]_2/Et_3N$ catalyst.

3. Results and discussion

M-PDMS bearing a polymerizable PA end group was prepared by condensation reaction of monohydroxy-terminated PDMS (PDMS-OH, DP of dimethylsiloxane ~ 42) with *p*-ethynylbenzoic acid in the presence of 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) and 4-(dimethylamino)pyridine (DMAP) (Scheme 1). As shown in Fig. 1, the hydroxy resonance at $\delta 1.9$ ppm in the spectrum of PDMS-OH (signal k) was not observed in the

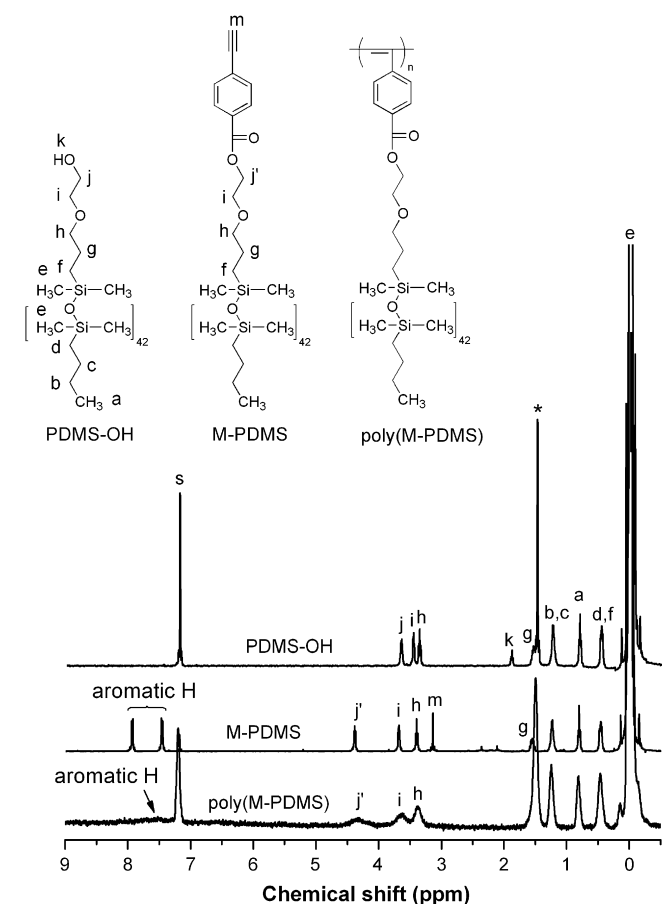


Fig. 1. 1H NMR spectra of PDMS-OH, M-PDMS and poly(M-PDMS) (run 5, Table 2) (s: solvent, *: H_2O).

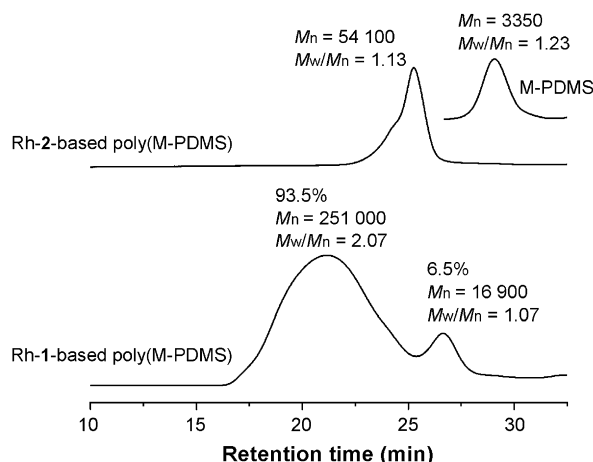


Fig. 2. GPC curves of M-PDMS and poly(M-PDMS)s obtained with Rh-1 (run 5, Table 2) and Rh-2 (run 3, Table 3). Measured with THF as an eluent and linear PS standards.

product, while an acetylenic proton signal at $\delta 3.1$ ppm (signal m) and the resonances for aromatic protons at $\delta 7.5$ and 7.9 ppm appeared newly in the spectrum of the product. The methylene protons (signal j) of PDMS-OH at $\delta 3.7$ ppm shifted downfield to $\delta 4.4$ ppm (signal j') after esterification. All the assignments clearly show the formation of M-PDMS, which are also supported by the NMR data reported for analogous compounds [31]. The M_n of the product, M-PDMS, was determined as 3470 based on peak areas in the 1H NMR spectrum. This value was very close to that determined by gel permeation chromatography (GPC), in which M_n was estimated as 3350 with $M_w/M_n = 1.23$ (Fig. 2).

Homopolymerization of M-PDMS was carried out in the presence of a conventional binary Rh catalyst $[(nbd)RhCl]_2/Et_3N$ (Rh-1, nbd = 2,5-norbornadiene), which is well known as an active catalyst for the polymerization of PA and its ring-substituted derivatives [32]. The polymerization in toluene at $30^\circ C$ for 1 h gave poly(M-PDMS) with a high molecular weight ($M_n = 206\,800$, DP = 62) in a moderate yield (run 1, Table 1). Increasing the polymerization time to 6 h

Table 1
Polymerization of M-PDMS ($M_n = 3350$) with Rh-1^a

Run	Temp. ($^\circ C$)	Time (h)	Poly(M-PDMS)			
			Yield (%) ^b	M_n^c	M_w/M_n^c	DP ^d
1	30	1	64	206 800	1.71	62
2	30	6	81	240 000	2.22	72
3	30	24	92	349 000	3.19	104
4	0	6	76	Gel	Gel	—
5	60	6	90	75 400 (33%)	1.11	23
				14 900 (67%)	1.10	4

^a Conditions: Rh-1 = $[(nbd)RhCl]_2/Et_3N$, $[M-PDMS] = 0.075$ M, $[Rh] = 5.0$ mM, $[Et_3N] = 50$ mM.

^b Acetone-insoluble product.

^c Main peak (area ratio > 93%) of bimodal GPC traces (measured by GPC with a PS calibration). The other peak corresponds to a low molecular weight oligomer ($M_n \sim 10\,000$ – $20\,000$, area ratio < 7%).

^d Degree of polymerization (calculated by $M_n/3350$).

Table 2
Solvent effects on the polymerization of M-PDMS ($M_n = 3350$) with Rh-1^a

Run	Solvent	Poly(M-PDMS)			
		Yield (%) ^b	M_n^c	M_w/M_n^c	DP ^d
1	Toluene	81	240 000	2.22	72
2	Benzene	64	225 800	2.12	67
3	CHCl ₃	82	225 100	2.27	67
4	CH ₂ Cl ₂	82	230 000	1.95	69
5	THF	73	251 000	2.07	75

^a Conditions: Rh-1 = [(nbd)RhCl]₂/Et₃N, [M-PDMS] = 0.075 M, [Rh] = 5.0 mM, [Et₃N] = 50 mM, 30 °C, 6 h.

^b Acetone-insoluble product.

^c Main peak (area ratio > 93%) of bimodal GPC traces (measured by GPC on the basis of PS standards). The other peak corresponds to a low molecular weight oligomer ($M_n \sim 10\,000$ – $20\,000$, area ratio < 7%).

^d Degree of polymerization (calculated by $M_n/3350$).

improved both polymer yield (81%) and molecular weight ($M_n = 240\,000$, DP = 72), although the MWD became a little broader ($M_w/M_n = 2.22$) (run 2). The highest molecular weight ($M_n = 349\,000$, DP = 104) of M-PDMS was achieved by polymerization for 24 h, although the MWD further broadened ($M_w/M_n = 3.19$) (run 3). At 0 °C, the polymerization gave an insoluble gel (run 4). Although the polymerization at 60 °C afforded soluble polymer, the product possessed two major polymer fractions in the GPC curve: high molecular weight products ($M_n = 75\,400$, DP = 23, 33% GPC area) and low molecular weight products ($M_n = 14\,900$, DP = 4, 67% GPC area) (run 5). This is probably due to partial deactivation of the active species at high temperature.

The polymerization was carried out in several solvents, the results of which are summarized in Table 2. The polymerizations in benzene, CHCl₃, CH₂Cl₂, and tetrahydrofuran (THF) also afforded poly(M-PDMS) in good yields (64–82%) and the molecular weights were similar to any of these solvents ($M_n = 225\,100$ – $251\,100$, DP = 67–75).

It has been reported that a vinyl-Rh catalyst, [Rh{C(Ph)=CPh₂}(nbd){P(4-FC₆H₄)₃}] with 5 equiv of (4-FC₆H₄)₃P (Rh-2) induces the living polymerization of PA [30]. The polymerization of M-PDMS by Rh-2 catalyst in toluene at 30 °C for 1 h afforded poly(M-PDMS) with a relatively low molecular weight ($M_n = 39\,900$) and a narrow MWD ($M_w/M_n = 1.11$) in a good yield of 71% (run 1, Table 3). When the

Table 3
Polymerization of M-PDMS ($M_n = 3350$) with Rh-2^a

Run	Temp. (°C)	Time (h)	Poly(M-PDMS)			
			Yield (%) ^b	M_n^c	M_w/M_n^c	DP ^d
1	30	1	71	39 900	1.11	12
2	30	6	87	46 500	1.15	14
3	30	24	90	54 100	1.13	16
4	0	6	29	32 800	1.11	10
5	60	6	88	71 800	1.18	21

^a Conditions: Rh-2 = [Rh{C(Ph)=CPh₂}(nbd){P(4-FC₆H₄)₃}] / (4-FC₆H₄)₃P, [M-PDMS] = 0.075 M, [Rh] = 5.0 mM, [(4-FC₆H₄)₃P] = 25 mM.

^b Acetone-insoluble product.

^c Measured by GPC on the basis of PS standards.

^d Degree of polymerization (calculated by $M_n/3350$).

Table 4
Solvent effects on the polymerization of M-PDMS ($M_n = 3350$) with Rh-2^a

Run	Solvent	Poly(M-PDMS)			
		Yield (%) ^b	M_n^c	M_w/M_n^c	DP ^d
1	Toluene	87	46 500	1.15	14
2	Benzene	88	63 000	1.17	19
3	CHCl ₃	88	83 700	1.36	25
4	CH ₂ Cl ₂	89	58 500	1.19	17
5	THF	88	54 000	1.18	16

^a Conditions: Rh-2 = [Rh{C(Ph)=CPh₂}(nbd){P(4-FC₆H₄)₃}] / (4-FC₆H₄)₃P, [M-PDMS] = 0.075 M, [Rh] = 5.0 mM, [(4-FC₆H₄)₃P] = 25 mM, 30 °C, 6 h.

^b Acetone-insoluble product.

^c Measured by GPC on the basis of PS standards.

^d Degree of polymerization (calculated by $M_n/3350$).

polymerization time was prolonged, both yield and M_n increased progressively, while the MWD remained around 1.13 (runs 2 and 3). In case of polymerization for 24 h, the initiator efficiency is calculated to be 97%. At 0 °C, the polymerization proceeded slowly to afford the polymer with lower M_n (32 800, DP = 10) in a low yield (run 4). The polymerization at 60 °C resulted in a slightly larger MWD ($M_w/M_n = 1.18$), although both molecular weight and polymer yield increased (run 5).

Solvent effects on the polymerization of M-PDMS with Rh-2 were studied, results are summarized in Table 4. Benzene, THF, and CH₂Cl₂ as solvents gave poly(M-PDMS) with slightly higher molecular weights ($M_n = 54\,000$ – $63\,000$, DP = 16–19) compared to that in toluene and similar MWDs ($M_w/M_n = 1.15$ – 1.19) in good yields (88–89%) (runs 2, 4 and 5). The MWD of the polymer obtained in CHCl₃ became broader compared to those in other solvents (run 3).

The structure of poly(M-PDMS) was examined by ¹H NMR spectroscopy (Fig. 1). Poly(M-PDMS) did not show the resonance of acetylenic proton at 3.1 ppm, which appeared in the spectrum of M-PDMS, indicating that no macromonomer remained in the obtained polymer. The signal of the aromatic protons in poly(M-PDMS) was broad, which is probably due to the direct attachment of the aromatic ring to the stiff polyacetylene backbone [33]. Highly stereoregular cis-transoidal PPAs are known to display a sharp signal at 5.7–6.0 ppm due to the olefinic proton in the main chain [34]. However, the cis olefinic proton signal was not observed in the present polymer brush, which should also be due to the low mobility of PPA main chain [18,21].

The GPC profiles of M-PDMS and poly(M-PDMS) are illustrated in Fig. 2. Poly(M-PDMS) catalyzed by Rh-1 (run 5, Table 2) exhibited a bimodal trace shifted to high molecular weight regions compared to that of M-PDMS, indicating that the resultant polymer consists of two fractions, namely, a high molecular weight polymer (~93%) and a low molecular weight polymer (~7%). In contrast, the GPC peak of poly(M-PDMS) obtained with Rh-2 (run 3, Table 3) was much narrower and practically unimodal.

The M-PDMS macromonomer was soluble in toluene, THF, CHCl₃ and acetone, but insoluble in more polar solvents such as methanol and *N,N*-dimethylformamide. The formed brush polymer, poly(M-PDMS), was also soluble in toluene,

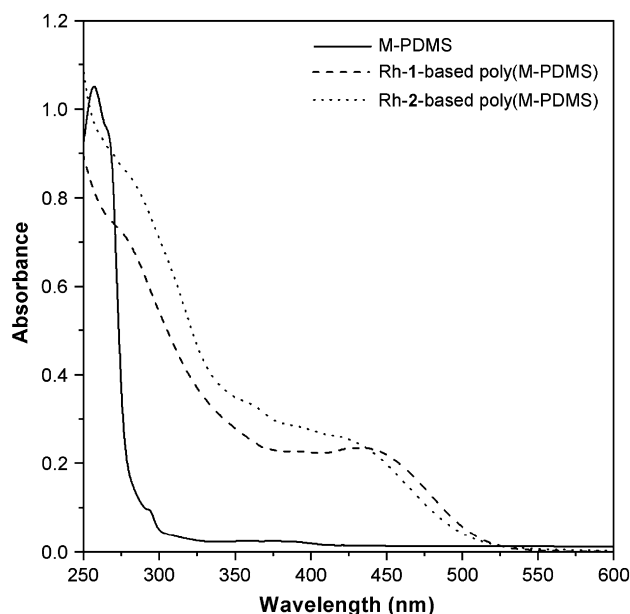


Fig. 3. UV-vis spectra of M-PDMS and poly(M-PDMS)s obtained with Rh-1 (run 5, Table 2) and Rh-2 (run 3, Table 3). Measured in THF (1.5×10^{-4} g/mL).

THF, and CHCl_3 , but insoluble in acetone and other polar solvents. Poly(M-PDMS)s obtained with Rh-1 and Rh-2 were brown and orange viscous liquids, respectively. Fig. 3 shows UV spectra of poly(M-PDMS)s obtained with Rh-1 and Rh-2 along with that of the macromonomer M-PDMS for comparison. While the UV spectrum of M-PDMS shows no peak above 300 nm, the poly(M-PDMS)s display absorptions in the range of 350–525 nm, which are attributed to the conjugated main chain.

4. Conclusions

In this study, we have successfully synthesized a novel polymer brush having conjugated polyacetylene main chain. A PDMS macromonomer with terminal PA unit ($M_n = 3350$, $DP = 42$) was polymerized by using a typical Rh catalyst $[(\text{nb})\text{RhCl}]_2/\text{Et}_3\text{N}$ to afford a polymer brush (M_n up to 349 000, DP up to 104) consisting of conjugated polyacetylene main chain and PDMS side chains. When a vinyl-Rh catalyst $[\text{Rh}\{\text{C}(\text{Ph})=\text{CPh}_2\}(\text{nb})\{\text{P}(\text{4-FC}_6\text{H}_4)_3\}]/(\text{4-FC}_6\text{H}_4)_3\text{P}$ was employed for the polymerization of the PDMS macromonomer, well-defined poly(macromonomer) with MWD as low as 1.11 was obtained.

Acknowledgements

W.Z. acknowledges Scholarship from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank Shin-Etsu Chemical Co., Ltd (Japan) for the donation of the monohydroxy-terminated PDMS.

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