APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 108–112

Diels–Alder reaction of anthracene on grafted polysiloxane and cylindrical carbosilane dendrimer

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Received 13 May 2004; Revised 10 June 2004; Accepted 5 July 2004

Anthracene-grafted polysiloxane was prepared by the dehydrocoupling between linear siloxane polymers and anthracenecarbinol. The cylindrical type of dendritic polysiloxane was prepared up to the second generation by the hydrosilation between polysiloxane and vinyltrichlorosilane, and the continual addition of allyl alcohol. The anthracene groups on cylindrical dendrimers were prepared by the reaction of Si–Cl bonds on the polymer and anthracenecarbinol. The Diels–Alder reaction of anthracene moieties on polysiloxane and maleimide derivatives, maleic acid anhydride, and 1,4-quinone derivatives was carried out under mild conditions. The polymers prepared were characterized by NMR and gel-permeation chromatography. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: dendrimer; Diels–Alder reaction; silane; anthracene; maleimide; quinone.

INTRODUCTION

The chemistry of linear polysiloxane with specific functions is a rapidly growing area due to the wide variety of the applications of this system and the easy preparation methods by catalytic reactions, such as hydrosilation, dehydrocoupling, etc.[1–3] The dehydrocoupling between Si–H bonds of polymethylhydrosiloxane (PMHS: $Me_3SiO(MeSiHO)_nSiMe_3$) and E–H bonds (E = C, N, O, S, etc.) by the elimination of hydrogen molecules is a well-known catalytic procedure.[4,5] By the use of this procedure, the polymer could contain regular and characteristic properties on each backbone unit.[6–9] For example, the dehydrocoupling reaction between hydrosilane and 9-anthracenecarbinol (AM) can easily lead to the anthracene group attaching to the silane with high conversion yield.[8]

The polysiloxane with dendritic architecture, which is termed a cylindrical dendrimer, was prepared by a divergent method.[8,9] Ball-type dendrimers have the same structural characteristics, but time-consuming methods had to be used for their preparation.[10–14] On the contrary, the lengths of cylindrical dendrimers are not all the same, but their substituents are extended like a dendrimer. The preparation of the cylindrical dendrimers frequently used the same repeating procedure as the preparation of the ball-type dendrimer. The preparation of the Si–E bond (E = O, N, etc.) on the siloxane skeleton was used as the dehydrocoupling method.

The Diels–Alder reaction on the dendritic periphery is a very useful synthetic method for the addition of organic functionalities on polymers.[15,16] We now demonstrate the dehydrocoupling reaction of siloxane polymer, the preparation of a linear-constructed cylindrical dendrimer and the Diels–Alder reaction on the polymer backbone of end-grafted polysiloxane (Scheme 1).

EXPERIMENTAL

All reactions and solvents were carried out under a dried nitrogen atmosphere. NMR spectra were recorded on a Bruker AC-200 spectrometer. For gel-permeation chromatography (GPC), the combination of three columns (Ultrastyragel, 7.8 cm × 30 cm; 10^3, 10^4, 10^5) was employed and tetrahydrofuran (THF) was used as eluent. Polysiloxane $Me_3SiO{-}(MeSiH{-}O)_n{-}SiMe_3$ was purchased from Aldrich Chemical Co. The synthesis of **7**–**9** has been reported previously.[9]

Polymer 1: synthesis of anthracene-grafted polysiloxane

0.23 g (3.83 mmol, calculated from the fundamental unit of the polymer backbone MeSiHO) of PMHS and 1.10 g (4.86 mmol)

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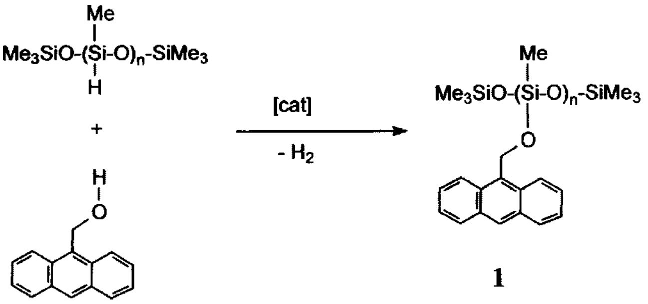


Scheme 1. Synthesis of anthracene-grafted polysiloxane.

of AM were dissolved in 25 ml of toluene. The mixture was degassed in vacuum under liquid nitrogen conditions and 0.01 g of chlorotris(triphenylphospine)rhodium(I) was added. The mixture was refluxed for 3 days. The volatile components were removed in vacuum. The remaining AM was removed by flash chromatography with silica gel and toluene as eluent. Yield: 1.02 g (3.19 mmol, 83%). ^{1}H NMR (ppm, CDCl$_3$): $\delta = -0.80$–0.41 (m, 3H, MeSi), 5.68 (s, 2H, OCH$_2$), 6.96–8.44 (m, 9H, anthracene). ^{13}C NMR (ppm, CDCl$_3$): $\delta = 0.28$ (MeSi), 57.37 (OCH$_2$), 123.84, 125.07, 126.43, 128.36, 129.11, 130.19, 131.49 (anthracene). GPC: polydispersity index (PDI) (M_w/M_n), 1.07 (5095/4762); R_t 19.88 min.

Polymer 2: Diels–Alder reaction of 1 and maleic anhydride

0.48 g (1.82 mmol, calculated from the fundamental unit C$_{16}$H$_{14}$O$_2$Si; 266.37) of **1** and 0.19 g (2.03 mmol) of maleic anhydride (MA) were dissolved in 25 ml of THF and the mixture was refluxed for 3 days. The volatile components were removed in vacuum, leaving a yellow precipitate. The excessive MA was removed by washing with pentane. The product was obtained from flash chromatography with a silica gel column with THF as eluent. Yield: 0.67 g (1.83 mmol, 90%), yellow precipitate. ^{1}H NMR (ppm, CDCl$_3$): $\delta = 0.08$–0.76 (SiMe), 2.81–4.00, 4.42–4.79 (MA), 4.85–5.21 (m, 2H, OCH$_2$), 6.63–7.40, 7.43–7.88 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, CDCl$_3$): $\delta = -4.14$ (SiMe), 45.56, 45.48, 46.23 (MA), 59.27 (OCH$_2$), 121.76, 123.93, 125.29, 126.63, 127.46, 138.28, 140.98, 141.64 (aromatic rest in anthracene), 169.55, 170.47 (MA). GPC: PDI (M_w/M_n), 1.30 (5744/4835); R_t, 16.71 min.

Polymer 3: Diels–Alder reaction of 1 and maleimide

The same method as for the preparation of **2** was used in the reaction of **1** (0.48 g, 1.82 mmol), using 0.18 g (1.87 mmol) maleimide (MI) and THF (25 ml). The MI-free product was obtained by washing with ethanol. Yield: 0.38 g (1.05 mmol, 56%), yellow precipitate. ^{1}H NMR (ppm, CDCl$_3$): $\delta = 0.09$–0.67 (m, 3H, SiMe), 2.60–3.41, 4.41–4.43 (m, MI), 4.83–5.42 (m, 2H, OCH$_2$), 6.59–7.38, 7.42–7.78 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, CDCl$_3$): $\delta = -3.84$ (SiMe), 45.51, 46.31, 49.01, 49.03 (MI), 59.83 (OCH$_2$), 121.88, 123.65, 124.20, 125.15, 126.34, 127.76, 138.90, 141.91, 124.20, 125.15, 126.34, 126.76, 138.90, 141.91, 142.32 (aromatic rest in anthracene), 176.17, 178.20 (MI). GPC: PDI (M_w/M_n), 1.31 (5501/4191); R_t, 17.08 min.

Polymer 4: Diels–Alder reaction of 1 and *N*-ethylmaleimide

The same method as for the preparation of **2** was used in the reaction of 0.46 g (1.75 mmol) of **1**, using 0.22 g (1.76 mmol) of *N*-ethylmaleimide (EMI) and THF (25 ml). The EMI-free product was obtained by washing with pentane. Yield: 0.56 g (1.43 mmol, 82%), yellow precipitate. ^{1}H NMR (ppm, CDCl$_3$): $\delta = 0.02$–0.76 (m, 3H, SiMe), 1.26–1.31 (m, CH$_3$, EMI), 3.71–3.77 (m, CH$_2$, EMI), 2.81–3.20, 4.41–4.63 (m, EMI), 4.89–5.45 (M, 2H, OCH$_2$), 6.60–7.28 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, CDCl$_3$): $\delta = -4.02$ (SiMe), 11.86 (CH$_3$ (EMI)), 32.81 (CH$_2$ (EMI)), 59.83 (OCH$_2$), 44.89, 45.87, 47.30, 49.15 (EMI), 121.76, 123.57, 124.30, 125.07, 126.48, 139.00, 142.27 (aromatic rest in anthracene), 175.36, 176.61 (EMI). GPC: PDI (M_w/M_n), 1.35 (4687/3451); R_t, 17.56 min.

Polymer 5: Diels–Alder reaction of 1 and benzoquinone

The same method as for the preparation of **2** was used in the reaction of 0.30 g (1.12 mmol) of **1**, using 0.21 g (1.94 mmol) of benzoquinone (BQ) and toluene (25 ml). The BQ-free product was obtained by washing with ethanol and pentane in succession. Yield: 0.32 g (0.85 mmol, 76%), yellow precipitate. ^{1}H NMR (ppm, CDCl$_3$): $\delta = 0.18$–0.79 (SiMe), 2.78–3.28, 4.42–4.79 (BQ), 4.65–5.19 (m, 2H, OCH$_2$), 6.81–7.51, (m, aromatic rest in anthracene). ^{13}C NMR (ppm, CDCl$_3$): $\delta = -4.14$ (SiMe), 45.56, 45.48, 46.23 (BQ), 59.27 (OCH$_2$), 121.76, 123.93, 125.29, 126.63, 127.46, 138.28, 140.98, 141.64 (aromatic rest in anthracene), 169.55, 170.47 (BQ). GPC: PDI (M_w/M_n), 1.47 (1370/929); R_t, 18.05 min.

Polymer 6: Diels–Alder reaction of 1 and naphthoquinone

The same method as for the preparation of **2** was used in the reaction of 0.34 g (1.30 mmol) of **1**, using 0.22 g (1.39 mmol) of 1,4-naphthoquinone (NQ) and toluene (25 ml) for 2 days in refluxing conditions. The NQ-free product was obtained by washing with ethanol and pentane in succession. Yield: 0.32 g (0.85 mmol, 76%), yellow precipitate. ^{1}H NMR (ppm, CDCl$_3$): $\delta = -0.28$–0.77 (SiMe), 2.63–3.29, 4.26–5.20 (NQ), 5.21–5.81 (m, 2H, OCH$_2$), 6.18–8.40, (m, aromatic rest in anthracene). ^{13}C NMR (ppm, CDCl$_3$): $\delta = -3.89$ (SiMe), 50.10, 51.65, 56.83, 60.89 (NQ), 60.89 (OCH$_2$), 122.97, 124.33, 124.56, 125.83, 127.80, 128.56, 130.17, 131.21, 132.88, 133.50, 134.71, 136.48, 139.29, 139.66, 141.70, 142.40 (aromatic rest in anthracene), 196.80, 197.93 (NQ). GPC: PDI (M_w/M_n), 1.51 (1596/1056); R_t, 17.75 min.

Polymer 10: Addition of anthracene on cylindrical-type polysiloxane dendrimer

The same method as for the preparation of **1** was used. ^{1}H NMR (ppm, $CDCl_3$); $\delta = -0.12-0.52$ (m, 21H, MeSi), 2.21–2.41 (CH_2), 5.92 (s, 6H, OCH_2), 7.26–8.79 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, $CDCl_3$): $\delta = 0.28$ (MeSi), 57.37 (OCH_2), 5.04, 8.59 (CH_2), 123.84, 125.07, 126.43, 128.36, 129.11, 130.19, 131.49 (aromatic rest in anthracene). GPC: PDI (M_w/M_n), 1.21 (17 341/14 260); R_t, 14.21 min.

Polymer 11: Diels–Alder reaction of 10 and MA

The same method as for the preparation of **3** was used in the reaction of 0.51 g (0.48 mmol) of **10**, using 1.10 g (1.20 mmol) of MA and THF (25 ml) for 2 days in refluxing THF. The MA-free product was obtained by washing with pentane. Yield: 0.60 g (0.43 mmol, 91%), yellow precipitate. ^{1}H NMR (ppm, $CDCl_3$): $\delta = 0.07-0.65$ (m, 21H, SiMe (G0–G2)), 2.81–4.00, 4.42–4.79 (MA), 3.41–3.88 (m, 6H, OCH_2), 6.63–7.40, 7.43–7.88 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, $CDCl_3$): $\delta = -3.72$ (SiMe), 5.03, 8.80 (CH_2 (G1)), 14.26, 25.82 (CH_2 (G2)), 45.56, 45.48, 46.23 (MA), 65.82 (OCH_2), 121.76, 123.93, 125.29, 126.63, 127.46, 138.28, 140.98, 141.64 (aromatic rest in anthracene), 169.55, 170.47 (MA). GPC: PDI (M_w/M_n), 1.19 (16 540/13 822); R_t, 14.61 min.

Polymer 12: Diels–Alder reaction of 10 and MI

The same method as for the preparation of **3** was used in the reaction of 0.51 g (0.48 mmol) of **10**, using 0.14 g (1.50 mmol) of MI and THF (25 ml) for 2 days in refluxing conditions. The MI-free product was obtained by washing with ethanol. Yield: 0.57 g (0.41 mmol, 87%), yellow–brown precipitate. ^{1}H NMR (ppm, $CDCl_3$): $\delta = 0.08-0.56$ (m, 21H, SiMe (G0–G2)), 2.60–3.41, 4.41–4.43 (m, MI), 4.83–5.42 (m, 2H, OCH_2), 6.59–7.38, 7.42–7.78 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, $CDCl_3$): $\delta = -3.84$ (SiMe), 5.24, 9.02 (CH_2 (G1)), 14.88, 26.03 (CH_2 (G2)), 4.59, 8.95 (CH2 (G1)), 12.76, 26.22 (CH_2 (G1)), 45.51, 46.31, 49.01, 49.03 (MI), 65.34 (OCH_2), 121.88, 123.65, 124.20, 125.15, 126.34, 127.76, 138.90, 141.91, 124.20, 125.15, 126.34, 126.76, 138.90, 141.91, 142.32 (aromatic rest in anthracene), 176.17, 178.20 (MI). GPC: PDI (M_w/M_n), 1.22 (16 461/13 487); R_t, 14.30 min.

Polymer 13: Diels–Alder reaction of 10 and EMI

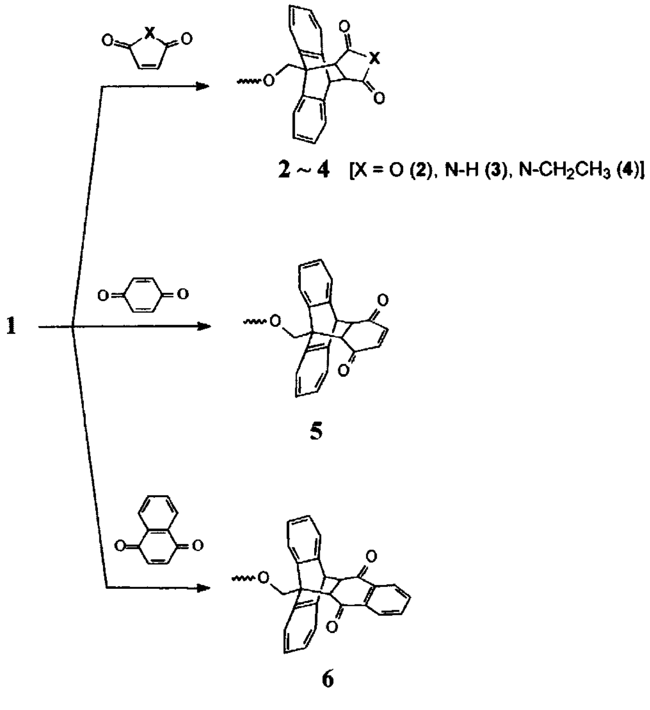
The same method as for the preparation of **3** was used in the reaction of 0.60 g (0.65 mmol) of **10**, using 0.30 g (2.30 mmol) of EMI and THF (25 ml) for 2 days in refluxing conditions. The EMI-free product was obtained by washing with pentane. Yield: 0.78 g (0.53 mmol, 97%), yellow–brown precipitate. ^{1}H NMR (ppm, $CDCl_3$): $\delta = 0.07-0.46$ (m, 21H, SiMe (G0–G2)), 1.25–1.34 (m, 9H, CH_3, EMI), 3.71–3.77 (m, 6H, CH_2, EMI), 2.81–3.20, 4.41–4.63 (m, EMI), 3.42–3.90 (M, 6H, OCH_2), 6.60–7.28 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, $CDCl_3$); $\delta = -3.4$ (SiMe), 5.01, 9.00 (CH_2 (G1)), 11.86 (CH_3 (EMI)), 13.26, 26.36 (CH_2 (G1)), 32.81 (CH_2 (EMI)), 65.35 (OCH_2), 44.89, 45.87, 47.30, 49.15 (EMI), 121.76, 123.57, 124.30, 125.07, 126.48, 139.00, 142.27 (aromatic rest in anthracene), 175.36, 176.61 (EMI). GPC: PDI (M_w/M_n), 1.19 (18 045/15 354); R_t, 14.21 min.

Polymer 14: Diels–Alder reaction of 10 and BQ

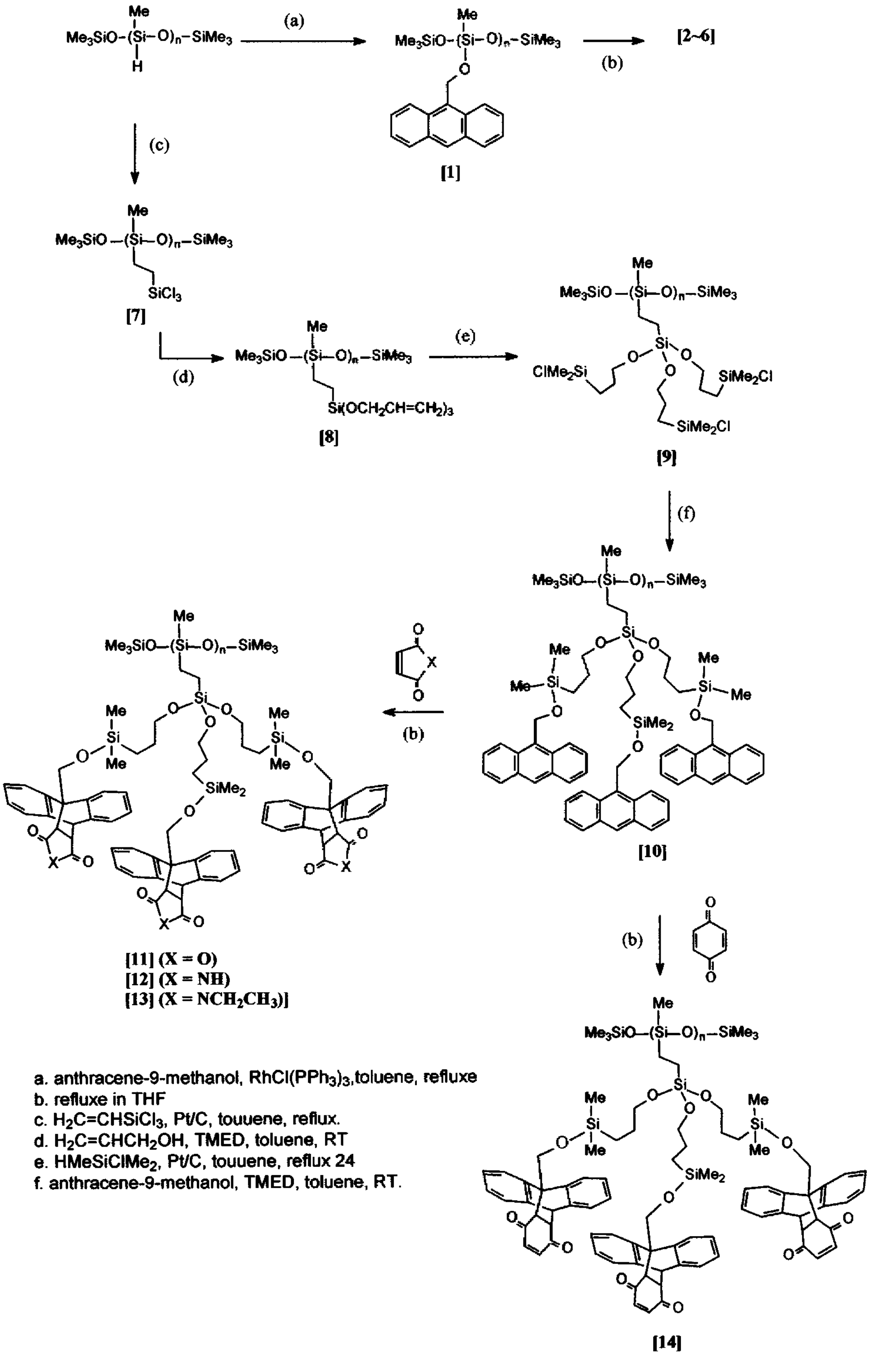
The same method as the preparation of **3** was used in the reaction of 0.33 g (0.31 mmol) of **10**, using 0.20 g (1.35 mmol) of BQ and THF (25 ml) for 2 days in refluxing conditions. The EMI-free product was obtained by washing with pentane and ethanol in succession. Yield: 0.34 g (0.24 mmol, 79%), yellow–brown precipitate. ^{1}H NMR (ppm, $CDCl_3$): $\delta = 0.10-0.47$ (m, 21H, SiMe (G0–G2)), 0.63–1.21 (m, 4H, CH_2 (G1)), 1.57–1.88 (m, 12H, CH_2 (G2)), 2.67–3.20 (m, BQ), 3.61–4.18 (m, 6H, OCH_2), 4.41–4.83 (m, BQ), 6.61–7.78 (m, aromatic rest in anthracene). ^{13}C NMR (ppm, $CDCl_3$): $\delta = -1.13$ (SiMe), 5.24, 8.20 (CH_2 (G1)), 12.85, 27.19 (CH_2 (G2)), 46.51, 47.06, 48.98, 49.02 (BQ), 123.33, 123.94, 124.29, 124.83, 125.91, 137.26, 140.02, 141.16 (aromatic rest in anthracene), 169.76, 170.69 (BQ). GPC: PDI (M_w/M_n), 1.20 (17 922/14 926); R_t, 14.20 min.

RESULTS AND DISCUSSION

The dehydrocoupling between alcohol and hydrosilane is a typical well-known method for the preparation of Si–E bonds (E=C, O, N, etc.) using transition-metal catalyst, such as Pt/C and $RhCl(PPh_3)_3$.[8] The dehydrocoupling reaction between PMHS ($Me_3SiO-(MeSiH-O)_n-SiMe_3$) and AM was carried



Scheme 2. Diels–Alder reaction on siloxane polymer and cylindrical dendrimer.



Scheme 3. Diels–Alder reaction and related reaction paths.

out in refluxing toluene for 3 days. The grafted siloxane polymer **1** was obtained in a very high condensing yield. The degree of dehydrocoupling of the polymer could be controlled and monitored by ^{1}H NMR spectroscopy. The chemical shift of products showed the complete disappearance of Si–H bonds at $\delta = 4.71$ ppm on siloxane polymer (PMHS) and the appearance of methyl groups on PMHS shift from 0.20 to 0.08 ppm. The integral in ^{1}H NMR spectrum of methyl groups on the polymer was in the ratio 3 to 1. The separation of anthracene-grafted siloxane polymer from the excess AM and the reaction mixture was carried out using flash chromatography utilizing a silica-gel column and chloroform as eluent. This produced light yellow gel-type solid, well soluble in organic solvents.

The conversion from PMHS to linear cylindrical dendrimer was carried out by the hydrosilation of polysiloxane and alcoholysis by allyl alcohol in succession. The hydrosilation between PMHS and vinyltrichlorosilane was carried out in the presence of platinum catalyst. Polymer **7** was obtained with high conversion yield and the product was monitored by NMR spectroscopy. The characteristic polymer **7** had three functional groups on each siloxane backbone unit. Polymer **8** was prepared by the reaction of **7** and allyl alcohol in tetramethylethylenediamine (TMEDA) containing toluene under room temperature by the elimination of TMEDA–HCl salt. The hydrosilation of **8** with chlorodimethylsilane with the platinum catalyst produced the same result as the preparation of **7**. The preparation of **10** was carried out by the reaction of **9** and AM under the same catalytic conditions as the preparation method of **8**. The conversion yield was observed to be very high by NMR spectroscopy. Siloxane polymer **1** and staff-type dendrimer **10** have one and three anthracene end groups respectively on each backbone unit. The Diels–Alder reaction of anthracene on siloxane polymer **1**, as well as cylindrical dendrimer **10** and MA, MI derivatives and NQ derivatives, gave stable bicyclo-adducts. The Diels–Alder adducts such as MA (**2**, **11**), MI derivatives (**3**, **4**, **12** and **13**) and NQ derivatives (**5**, **6** and **14**) were well characterized by NMR and GPC analyses. The preparation of Diels–Alder adducts **2**–**6** (Scheme 2) produced reasonable yields. The structural information of **2**–**6** was confirmed by the combination of ^{1}H and ^{13}C NMR spectroscopy, GPC and elemental analysis. The hyperfine structural information of Diels–Alder products was not observed in this case. By using GPC, the polydispersity (M_n/M_w) of Diels–Alder products for **1** to **6** were confirmed with no change. This means there is no further reaction except the Diels–Alder reaction itself. The other Diels–Alder products (**11**–**14**) on the cylindrical dendrimer (Scheme 3) were characterized using the same determination methods as above.

In conclusion, the dehydrogenative coupling reaction of Si–H in PMHS and ROH can be achieved via a simple rhodium complex, as well as by a platinum-catalyzed protocol. Large quantities did not pose any problem. The Diels–Alder reaction between anthracene on siloxane polymer and MI and quinone derivatives was carried out with reasonable conversion yields. The Diels–Alder reaction of **1**, as well as **10** and MI derivatives, was obtained in refluxing conditions with THF, and the reaction with BQ and NQ derivatives were developed in refluxing toluene.

Acknowledgements

This study was supported by the Dong-A University (2003).

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