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Diels–Alder reaction of anthracene and *N*-ethylmaleimide on the carbosilane dendrimer

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Abstract

Dendrimers with bicyclo-groups on the periphery were synthesized by the Diels–Alder (DA) reaction between anthracene derivatives, which have 24, 48 and 96 end-groups, and *N*-ethylmaleimide under the mild condition. The structural information of the DA product on dendritic periphery was obtained from hyperfine structural view of ^{1}H-NMR spectroscopy. The purity of the products was determined by size exclusion chromatography.

Keywords: Dendrimer; Carbosilane; Siloxane; Diels–Alder; Maleimide

1. Introduction

The dendrimer has been one of the most extensively studied materials during the last decade [1] which has been devoted to new macromolecules because of their prime usability in nano-science [2] that may serve as a chemical sensor [3], catalyst [4], molecular device [5], chemo-delivery in biology [6], etc. Therefore, dendrimers with characteristically designed models can be easily approached for such scientific purposes. Recently, carbosilane as well as carbosiloxane dendrimers have appeared as one of the important families of dendritic macromolecules [7]. The synthetic method of silicone-containing dendrimers was reported by a great number of researchers who used the simple repeating procedures such as hydrosilation, dehydrocoupling, alkenylation as well as alcoholysis [8,9]. The additive method of the anthracene group onto dendrimers was reported by our previous work [9c]. As an extension of our previous work, we now try to find the Diels–Alder (DA) reaction with *N*-ethylmaleimide on the dendritic periphery.

The DA reaction is a powerful tool employed frequently in the preparation of six-membered rings with the stereo- and regio-selective control system. The use of the DA reaction in the synthesis of dendrimers is a new method for functionalization on the periphery (Scheme 1). It is a widely used traditional concept in the preparation of new compounds [10]. The present paper describes the synthetic method and identification of the DA reaction on the dendritic periphery.

2. Results and discussion

Dendrimers with anthracenemethoxy groups on the peripheral layer (G*n*-*m*AM: $n=3$, $m=24$; $n=4$, $m=48$; $n=5$, $m=96$) were prepared from the reaction of Si–Cl bonded parent dendrimers (G*n*-*m*Cl; $n=3$, $m=24$; $n=4$, $m=48$; $n=5$, $m=96$) and anthracene-9-carbinol under the presence of tetramethylethylenediamine (TMEDA) [9c]. The DA reaction between the anthracene on the dendrimers G*n*-*m*AM and *N*-ethylmaleimide (EA) progressed well under the boiling THF condition. The reaction of anthracene-9-trimethylsiloxymethane and EA produced the DA adduct which for the interpretation of DA adduct by ^{1}H-NMR. The characterization of the reference DA products was carried out using NMR spectroscopy, which can be

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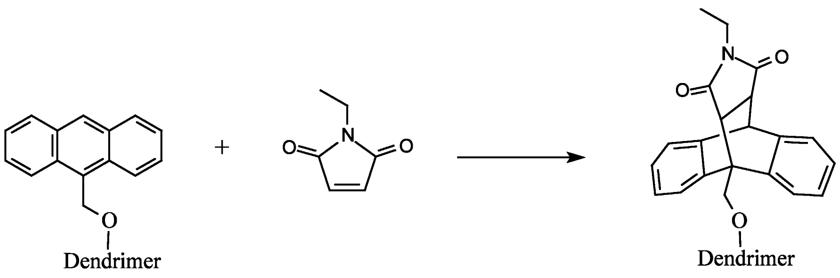

Gn-mAM

Gn-mAMI

Scheme 1.

easily detected by characteristic signals at the reaction position (Fig. 1). The selected data for the DA products are given in Table 1. The hyperfine ^{1}H-NMR spectrum of the reference DA product observed interesting structural information at 4.70 ppm for H_a, 3.30 ppm for H_b 3.47 ppm for H_c, and 4.88 and 5.02 ppm for H_x and H_y respectively, and the coupling constants J_{ab} J_{bc} and J_{xy} revealed at 3.18, 8.79 and 10.12 Hz respectively (Fig. 1). This result followed the Karplus curve that coupling occurs at the vicinal inter-proton between H_a and H_b as well as H_b and H_c and according to it, the dihedral angle between H_a and H_b is 53° and H_b and H_c is zero.

The preparation of bicyclo-adducts between the anthracene on the dendritic periphery and N-ethylmaleimide was performed by the use of Gn-mAM ($n=3$, $m=24$; $n=4$, $m=48$; $n=5$, $m=96$) with N-ethylmaleimide in the same method as the above-mentioned reference reaction (Scheme 1). The structural information obtained from the ^{1}H-NMR spectrum of the model reaction showed the same hyperfine structure in the reaction position between 3.25 and 5.16 ppm and the coupling constants revealed the same result (Table 1). For example, the ^{1}H-NMR spectrum of G3-24AMI viewed the hyperfine structure at 4.77 ppm for H_a, 3.27 for H_b, 3.30 for H_c, and 5.00 and 5.16 for H_x and H_y and the coupling constants J_{ab} J_{bc} and J_{xy} revealed at 3.33, 8.37 and 11.60, respectively (Table 1).

The ^{13}C-NMR spectrum showed 10 signals between 121.8 and 142.3 ppm and two carbonyl carbon signals between 175.7 and 176.7 ppm. The G4-48AMI and G5-96AMI showed the same evidence (Figs. 2–5). The dendrimers (G3-24AMI, G4-48AMI and G5-96AMI) observed the maximal absorbance (λ_{max}) at 231 nm but

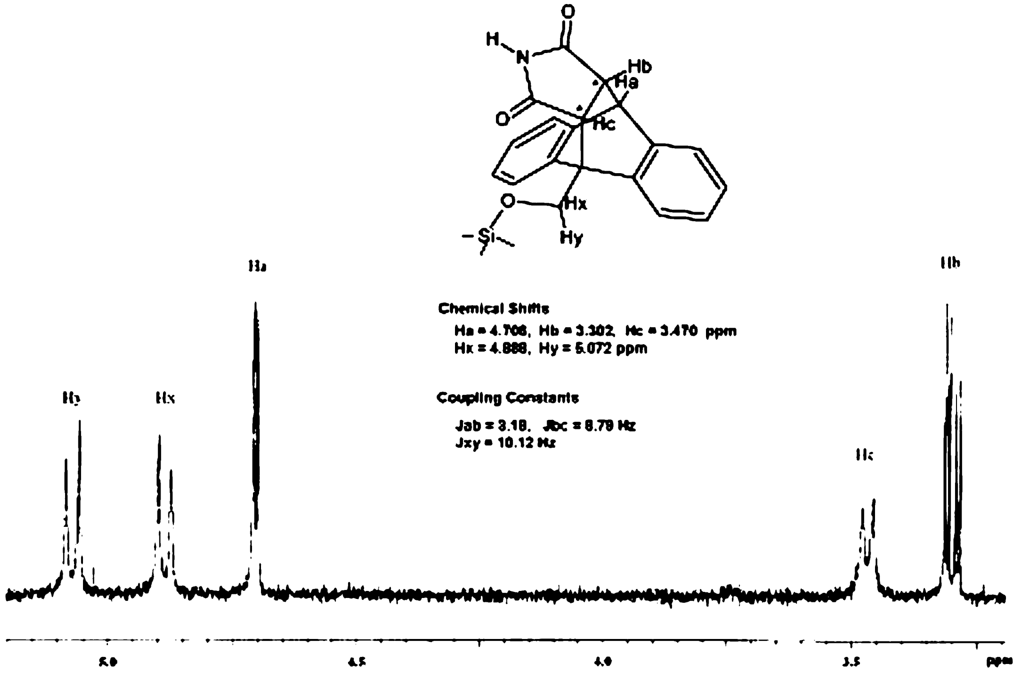

Fig. 1. ^{1}H-NMR spectrum of the standard DA product on reaction sites.

Table 1
Chemical shifts and coupling constants of DA products

Dendrimer	Chemical shift (ppm)					Coupling constant (Hz)		
	H_a	H_b	H_c	H_x	H_y	J_{ab}	J_{bc}	J_{xy}
Std*	4.706	3.302	3.470	4.888	5.072	3.180	8.790	10.120
G3-24AMI	4.771	3.275	3.330	5.001	5.162	3.336	8.370	11.600
G4-48AMI	4.765	3.269	3.330	4.994	5.155	3.336	8.370	11.600
G5-96AMI	4.757	3.259	3.326	4.984	5.146	3.336	8.370	11.600

Std*, standard DA product with $-CH_2OSiMe_3$ group on 9-position of anthracene.

the molar absorbance intensity (ε_{max}) for each dendrimer was approximately in proportion to the increasing tendency of number of end-functional groups. The pure dendrimers were established by the flash chromatography of the reaction products with a silica gel and THF as an eluent for the removal of excess *N*-ethylmaleimide. However, all such suitable bicyclo-compounds have to be introduced in reasonable yields (77–84%). Unfortu-

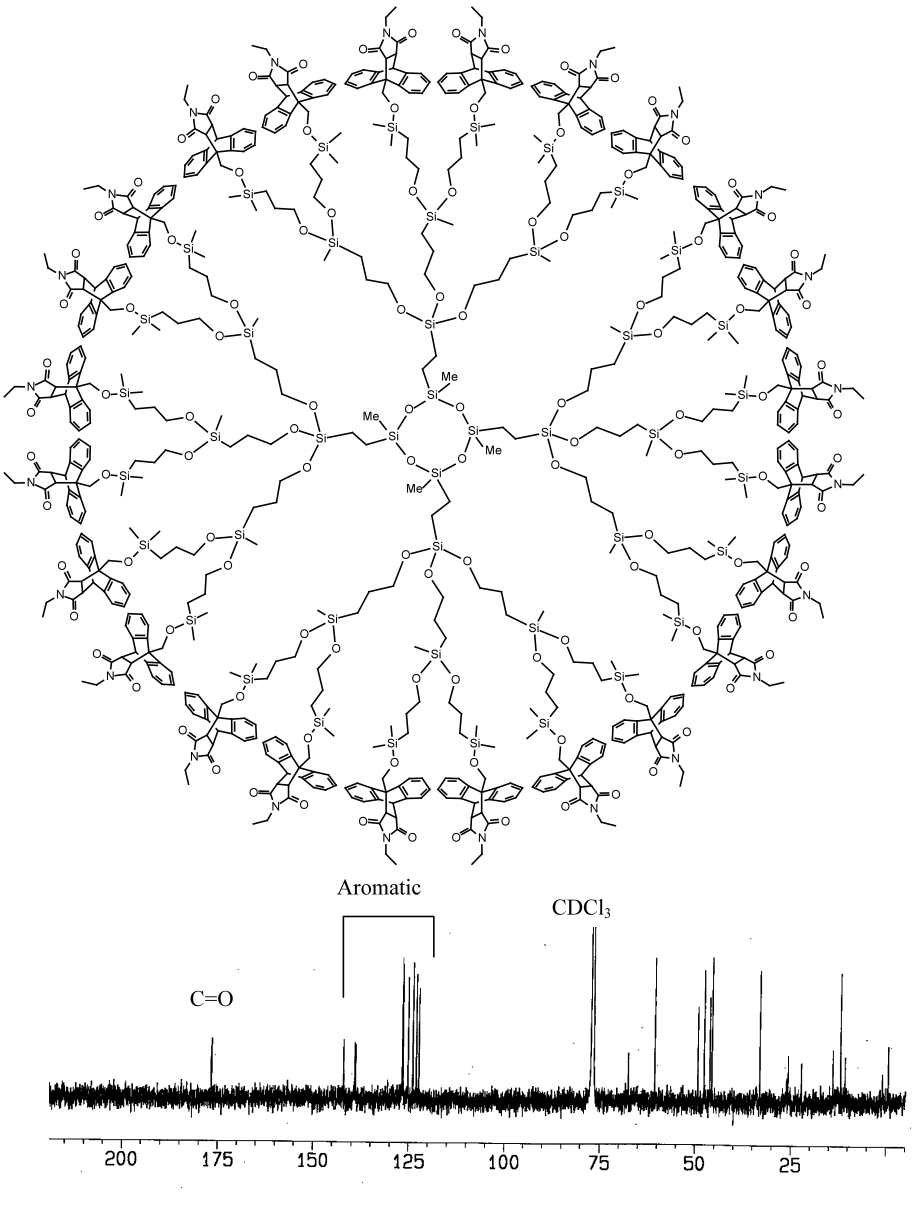

Fig. 2. Planar view of G3-24AMI and ^{13}C-NMR spectrum.

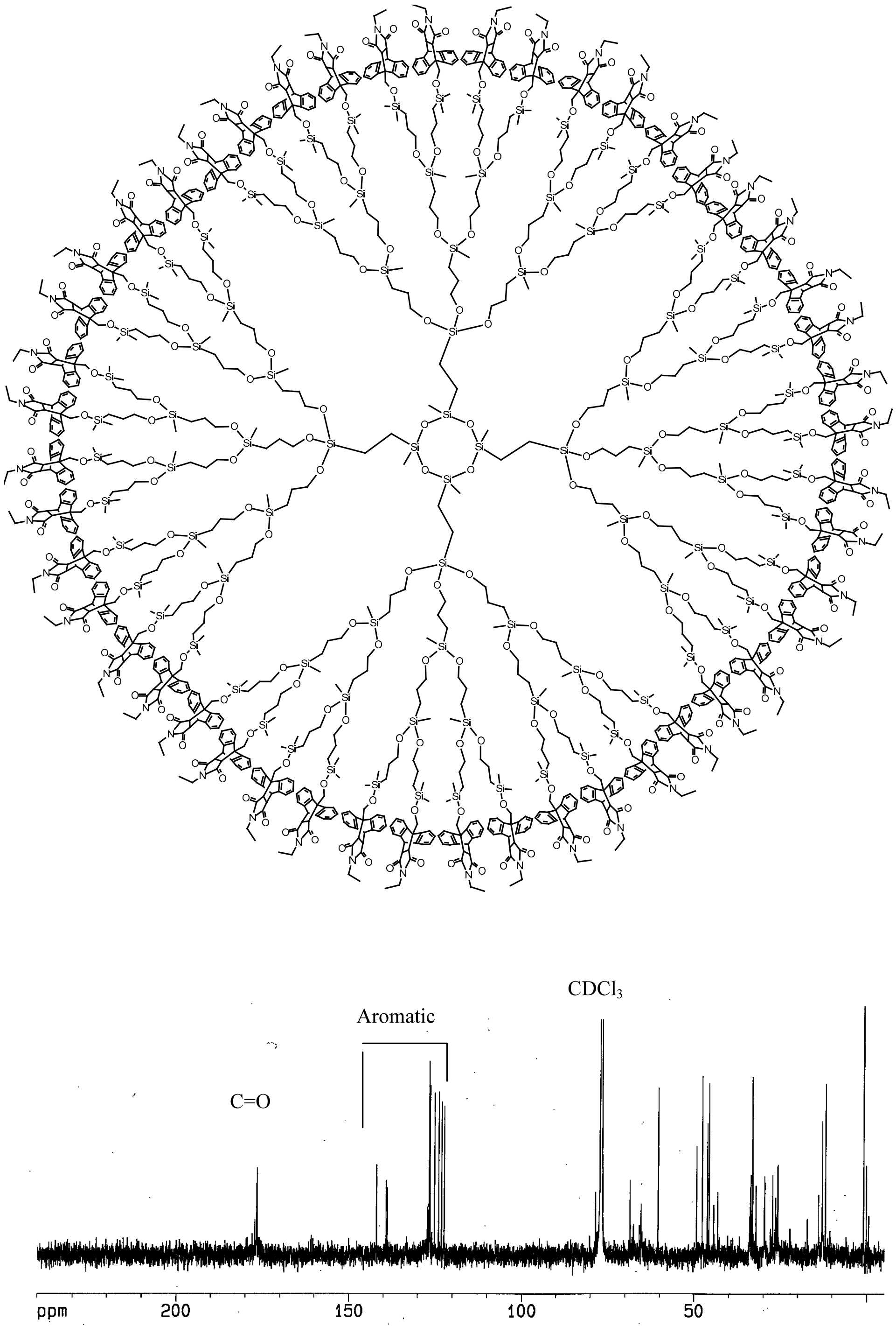

Fig. 3. Planar view of G4-48AMI and ^{13}C-NMR spectrum.

nately, the MALDI-mass spectra of the prepared dendrimers were not informed of molecular weight. The GPC attachment of the dendrimers showed the pure dendritic products that have very low polydispersity values (PDI) and regular retention time (Table 2). That is, the prepared dendrimers are pure products. In addition, the element analysis also showed values very near to the calculated one.

3. Experimental

All reactions were carried out under a dried N_2 atmosphere. NMR spectra were recorded on a Bruker AC-200 and hyperfine structural ^{1}H-NMR spectra were obtained by a Bruker DMX 600 spectrometer from KBSI in Daejeon. UV spectra were measured by an HP 8452A diode array UV–vis spectrophotometer. For

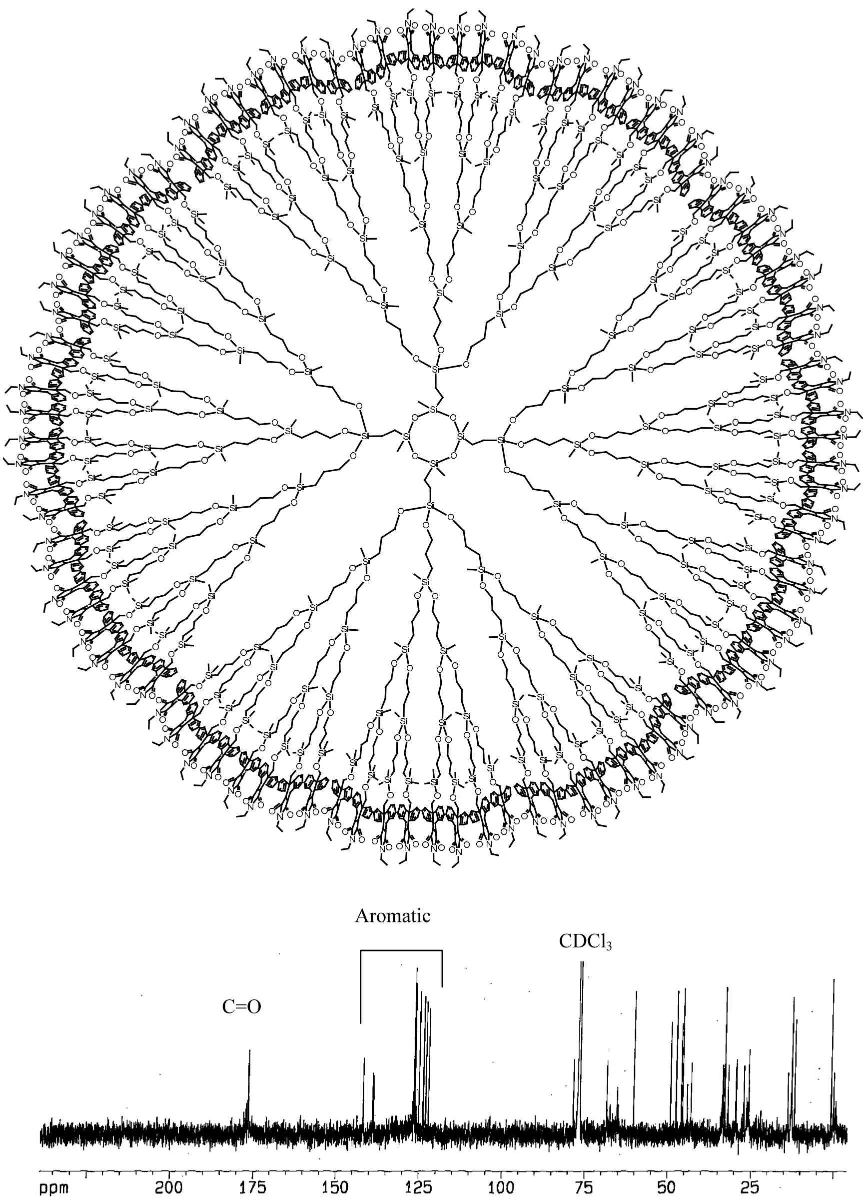

Fig. 4. Planar view of G5-96AMI and ^{13}C-NMR spectrum.

GPC, a combination of three columns (Ultrastyragel, 7.8 × 30 cm; 10^3, 10^4, 10^5) was employed and THF was used as an eluent. EA data were revised from Korean Basic Science Institute (KBSI) in Deagu. The parent dendrimers with allyloxy groups were prepared by the use of our owner products [9]. The anthracene group containing dendrimers were prepared by the reaction of Si–Cl containing parent dendrimers (G3-24Cl, G4-48Cl and G5-96Cl) and anthracene-9-carbinol in the presence of TMEDA [9]. The following abbreviations are used in this experiment: AM refers to anthracene-9-carbinol, EM refers to *N*-ethylmaleimide, and AMI refers to the bicyclo-adduct of maleimide on anthracene.

3.1. G3-24AMI

0.48 g (0.05 mmol) of G3-24AM and 0.20 g (1.60 mmol) of *N*-ethylmaleimide were dissolved in 25 ml of THF and refluxed for 2 h. The volatile components were removed under vacuum, leaving a yellow precipitate. By the ^{1}H-NMR spectrum of the reaction mixture, the anthracene groups in G3-24AM were converted to new signals. The solvent was removed under vacuum. The *N*-ethylmaleimide free product was obtained by washing the reaction mixture with pentane. The product was flash chromatographed by a silica gel and THF as an eluent. Yield: 0.62 g (0.084 mmol, 84%) of a light yellow

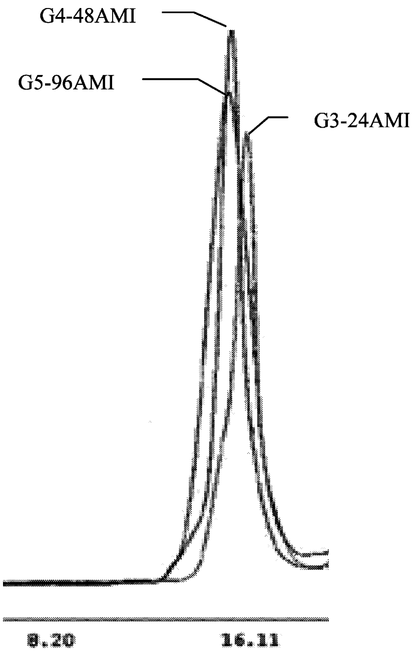

Fig. 5. GPC chromatogram of G*n*-*m*AMI.

powder. ^{1}H-NMR (200 MHz in ppm, $CDCl_3$): $\delta = 0.07$ (s, SiMe; G0–G2), 0.28 (s, SiMe; G3), 0.48–0.92, 1.50–2.19 (m, CH_2; G1–G3), 1.10–1.32 (CH_3; EM rest), 2.92–3.18, 3.18–3.40, 3.40–4.00 (m, OCH_2; G1–G3), 4.60–4.72, 4.72–4.95, 4.95–5.15 (EM rest), 6.90–7.35, 7.42–7.63 (AM rest). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -4.99$ (SiMe; G2), -2.22 (SiMe; G3), 9.46, 25.66 (CH_2; G1–G2), 12.87 (CH_3; EM rest), 12.07, 26.42 (CH_2; G3), 32.89 (CH_2; EM rest), 44.84, 45.93, 47.43, 49.43 (EM rest), 59.63 (OCH_2; G3), 65.29 (OCH_2; G1–G2), 121.80, 123.58, 124.22, 125.12, 126.19, 126.56, 139.08, 139.33, 142.16, 142.30 (AM rest), 175.75, 176.80 (EM rest). GPC: PDI (M_w/M_n), 1.06 (11 886/11 104); R_t, 15.78 min. Analysis for $C_{684}H_{856}O_{112}Si_{44}N_{24}$ ($M_w = 12424$): C, 66.06%; H, 6.89%; N, 2.70%. Found: C, 65.75%; H, 7.50%; N, 2.69%. FT-IR (KBr, cm^{-1}): $\upsilon_{(c=o)}$ 1697. UV–vis (THF): λ_{max}, 231 nm (ε_{max}, 1.07×10^5).

3.2. *G4-48AMI*

The same method as that of G3-AMI was used in the reaction of 1.04 g of G4-AM (0.053 mmol) and 0.44 g of *N*-ethylmaleimide (3.50 mmol). The mixture was refluxed for 4 h. Yield: 1.04 g (0.04 mmol, 77%) of a yellow glass. ^{1}H-NMR (200 MHz in ppm, $CDCl_3$): $\delta = 0.07$ (s, SiMe; G0–G3), 0.30 (s, SiMe; G4), 0.48–0.82, 1.40–1.88 (m, CH_2; G1–G4), 0.98–1.42 (CH_3; EM rest), 2.92–3.22, 3.22–3.40, 3.40–3.82 (m, OCH_2; G1–G4), 4.60–4.78, 4.78–4.95, 4.95–5.20 (m, OCH_2), 6.90–7.42, 7.42–7.63 (AM rest). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -4.95$ (SiMe; G3), -2.18 (SiMe; G4), 9.53, 26.01 (CH_2; G1–G2), 12.12 (CH_3; EM rest), 12.12, 26.47 (CH_2; G3, G4), 32.89 (CH_2; EM rest), 44.87, 45.99, 47.48, 49.47 (EM rest), 59.66 (OCH_2; G4), 65.31 (OCH_2; G1–G3), 121.84, 123.61, 124.27, 125.16, 126.21, 126.56, 139.13, 139.38, 142.20, 142.35 (AM rest), 175.78, 175.74 (EM rest). GPC: PDI (M_w/M_n), 1.01 (22 030/21 811); R_t, 15.28 min. Analysis for C_{1404} $H_{1792}O_{232}Si_{92}N_{48}$ ($M_w = 25600$): C, 65.81%; H, 7.00%; N, 2.63%. Found: C, 65.21; H, 7.40%, N, 2.57%. FT-IR (KBr, cm^{-1}): $\upsilon_{(c=o)}$ 1690. UV–vis (THF): λ_{max}, 232 nm (ε_{max}, 2.0×10^5).

3.3. *G5-96AMI*

The same method as that of G3-24AMI was used in the reaction of G5-96AM (1.20 g, 0.03 mmol), *N*-ethylmaleimide (0.48 g, 3.83 mmol). The mixture was refluxed for 6 h. Yield: 1.20 g (0.023 mmol, 77%) of a yellow glass. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 0.06$ (s, SiMe; G0–G4), 0.30 (s, SiMe; G5), 0.48–0.92, 1.30–2.19 (m, CH_2; G1–G5), 0.95–1.35 (EM rest), 2.90–3.10, 3.10–3.40, 3.40–3.95 (m, OCH_2; G1–G5), 4.60–4.75, 4.75–4.95, 4.95–5.15 (EM rest), 6.95–7.42, 7.42–7.63 (AM rest). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -5.09$ (SiMe; G4), -2.29 (SiMe; G5), 9.38, 25.89 (CH_2; G1–G3), 11.82 (CH_3; EM rest), 11.98, 26.32 (CH_2; G4 and G5), 32.98 (CH_2; EM rest), 44.75, 45.56, 47.03, 49.34 (EM rest), 59.53 (OCH_2; G5), 65.17 (OCH_2; G1–G4), 121.71, 123.50, 124.13, 125.03, 126.09, 126.43, 139.00, 139.24, 142.07, 142.21 (AM rest), 175.70, 176.77 (EM rest). GPC: PDI (M_w/M_n), 1.03 (37 154/36 136); R_t, 15.06 min. Elemental analysis for C_{2844} $H_{3664}O_{472}Si_{188}N_{96}$ (51 952): C, 65.69%; H, 7.05%; N, 2.58%. Found: C, 65.29; H, 7.67%; N, 2.77%. FT-IR (KBr, cm^{-1}): $\upsilon_{(c=o)}$ 1699. UV–vis (THF): λ_{max}, 234 nm (ε_{max}, 2.89×10^5).

Table 2
PDI data of G*n*-*m*AMI

	Formula (calcd. M_w)	PDI (M_n/M_w)	Retention time (min)
G3-24AMI	$C_{684}H_{856}O_{112}Si_{44}N_{24}$ (12 424)	1.06 (11 886/11 104)	15.78
G4-48AMI	C_{1404} $H_{1792}O_{232}Si_{92}N_{48}$ (25 600)	1.01 (22 030/21 811)	15.28
G5-96AMI	C_{2844} $H_{3664}O_{472}Si_{188}N_{96}$ (51 952)	1.03 (37 154/36 136)	15.06

PDI, polydispersity index (M_w/M_n).

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