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Polymerization of a biscalic[5]arene derivative†

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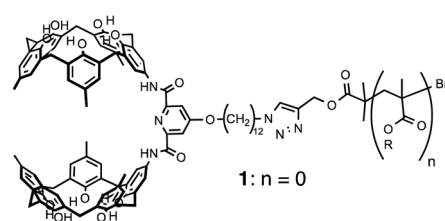
Recent decades have seen an increased interest in the preparation of polymers possessing host or guest moieties as the end group, which has enabled new polymeric materials such as self-healable, shape-memory, and stimuli-responsive materials. Such polymers are commonly synthesized by tethering the host or guest moieties to polymers. On the other hand, there are limited reports demonstrating the preparation of host- or guest-appended polymers by directly polymerizing the corresponding host- or guest-appended monomers, which is valuable for easy access to diverse polymers from single molecular species. However, reactive host and/or guest moieties of the monomer interfere with the polymerization reaction. Here, we report that a biscalic[5]arene host-appended molecule can be polymerized with various monomers to form the corresponding host-appended polymers. The host–guest complexation behavior of calix[5]arene-appended polymers with fullerene derivatives was studied by ¹H NMR and UV/Vis spectroscopic techniques, which revealed that the long polymer chains did not prevent host–guest complexation even when the fullerene derivative was equipped with a polymer chain. Thus, the present study shows the potential for developing polymers that have various combinations of polymer chains.

Introduction

Increased interest in the combination of supramolecular chemistry and polymer science has emerged in recent years. The introduction of host–guest moieties onto the polymer termini endows the polymers with a dynamic nature, leading to the development of functional soft materials.^{1,2} In addition, the host–guest approach has enabled easy access to distinctly shaped polymers such as block, star, and brush polymers.^{3–9} Macrocyclic hosts, *e.g.*, cyclodextrins,^{10–16} crown ethers,^{17–21} pillararenes,^{22–25} calixpyrroles,^{26–28} calixarenes^{29–33} and others,^{34–36} have been commonly adopted as host moieties due to their high binding affinity toward the corresponding guests. To date, many polymeric materials relying on host–guest complexation between macrocyclic hosts and the corresponding guests have been reported, which has corroborated that the host–guest approach is a powerful tool for the development of new polymeric materials, including self-healable, shape-memory, and stimuli-responsive materials.^{37–40}

To fully leverage the potential of host- or guest-appended polymers, challenges still remain in their synthetic pathway to be addressed. Polymers possessing a host or guest moiety as the

end group have been commonly prepared by tethering the host or guest moieties to polymers. On the other hand, there are limited reports describing the preparation of host- or guest-appended polymers by directly polymerizing the corresponding host- or guest-appended monomers.^{41,42} Although the latter synthetic pathway is valuable for easy access to diverse polymers from single molecular species, reactive host and/or guest moieties of the monomer prevent the polymerization reaction.



poly-1a: R = Me, n = 37
poly-1b: R = Me, n = 118
poly-1c: R = *t*Bu, n = 23
poly-1d: R = *t*Bu, n = 45
poly-1e: R = Bn, n = 51
poly-1f: R = Bn, n = 54
poly-1g: R = C₁₂H₂₅, n = 57
poly-1h: R = C₁₂H₂₅, n = 761

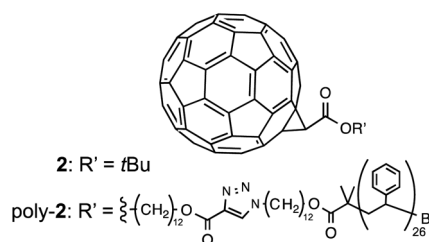


Fig. 1 Molecular structures of a calix[5]arene monomer, calix[5]arene polymers and fullerene derivatives.

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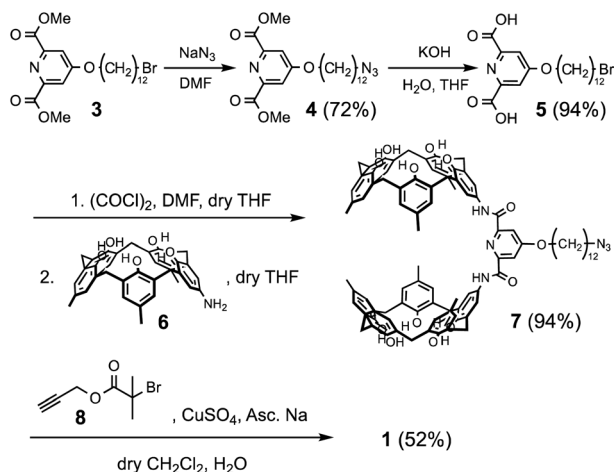


We thus sought to examine whether an appropriately designed host-appended monomer molecule can be polymerized to form the corresponding host-appended polymers.

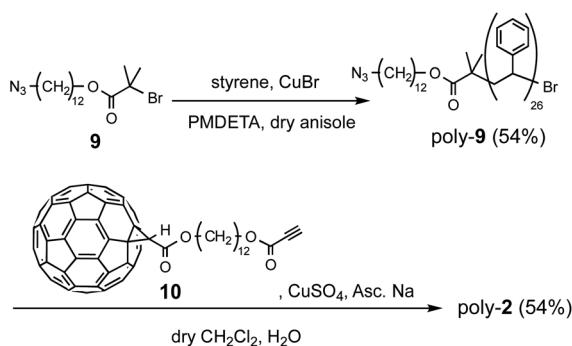
Our group has developed structurally well-defined supra-molecular architectures using host-guest interactions between calix[5]arene and fullerene,^{43–45} one of which corroborated that the strong calix[5]arene–fullerene association can be used for tethering long polymer chains.⁴⁶ In this work, we designed calix[5]arene-appended monomer **1** with a 2-bromoisobutylate moiety as an atom transfer radical polymerization (ATRP) initiator (Fig. 1). **1** was subjected to ATRP reaction with various methacrylate monomers to produce corresponding calix[5]arene-appended polymers.

Results and discussion

The syntheses of **1** and poly-2 are outlined in Schemes 1 and 2. **3** (ref. 47) was prepared according to a reported method. Azidation of **3** and subsequent hydrolysis afforded **5** in good yield. **5** converted into corresponding acid chloride, which was subjected to condensation reaction with separately prepared **6** (ref. 44) to afford biscalix[5]arene monoazide **7** in 94% yield. The



Scheme 1 Synthesis of **1**. DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran, Asc.Na = sodium ascorbate.

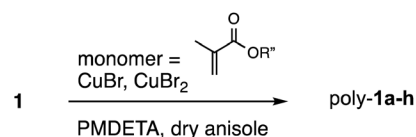


Scheme 2 Synthesis of poly-2. PMDETA = *N,N,N',N'',N''*-pentamethyl-diethylenetriamine.

copper mediated cyclization reaction between **7** and **8** (ref. 48) yielded the target monomer molecule **1** in 52% yield. The synthesis of poly-2 commenced with the polymerization reaction of a known compound **9**.⁴⁶ The ATRP reaction of **9** with styrene monomer successfully proceeded to give poly-9. The copper mediated cyclization reaction between poly-9 and **10** (ref. 49) furnished desired poly-2.

The polymerizations of **1** with the methacrylate monomers were conducted at two different mixing ratios, as summarized in Scheme 3 and Table 1. The ATRP reaction proceeded for methyl methacrylate to afford the corresponding polymers poly-**1a,b**. When **1** was mixed with 100 equiv. of methyl methacrylate monomer, poly-**1a** ($M_n = 5250$, PDI = 1.28) was given by the polymerization reaction (entry 1). A higher molecular weight was achieved (poly-**1b**; $M_n = 13\,400$, PDI = 1.24) when the reaction was performed in the presence of 1000 equiv. of methyl methacrylate monomer (entry 2). **1** was polymerized with *tert*-butyl and benzyl methacrylate monomers to yield the corresponding polymers poly-**1c–f** (entries 3–6). Fair increases in the molecular weight were observed for the polymerizations with *tert*-butyl and benzyl methacrylate monomers when the mixing ratio of [**1**] : [monomer] was increased from 1 : 100 to 1 : 1000. Polymers with large molecular weights were produced by the polymerization reaction with *n*-dodecyl methacrylate monomer (entries 7 and 8). The conversion yield of the methacrylate monomers to the polymers surpasses that of the previously reported polymerization reactions of host or guest appended monomer molecules.^{41,42} These results indicate that the calix[5]arene moiety does not interfere with the ATRP reaction, which allows access to polymers with various molecular structures in their side chains from single monomeric species.

The difference in the resulting molecular weight is most likely due to the solubility of polymers toward the anisole solvent. For example, the solubility of the benzyl methacrylate polymer gradually decreased upon increasing the degree of polymerization. When approximately 55 monomers were incorporated into the polymer chain through the ATRP reaction, the benzyl methacrylate polymer may have precipitated out, which results in the termination of the polymerization process to yield poly-**1e,f**. Thus, despite the initial concentration of methyl methacrylate, approximately 55 equiv. of benzyl methacrylate was consumed by the polymerization reaction. The termination of the polymerization reaction in anisole by an increase in methacrylate content within the polymer chain was seen in the methyl and *tert*-butyl methacrylate polymers (poly-**1a–d**). On the other hand, independent of the initial concentration of *n*-dodecyl methacrylate, ≈ 60 –75% methacrylate was incorporated into the resulting polymer poly-**1g,h**. The *n*-dodecyl methacrylate polymer had good solubility owing to the



Scheme 3 Polymerization of **1** with methacrylate monomers. The results were summarized in Table 1.



Table 1 Summary of the results of polymerization of **1** under various conditions. Me = methyl. tBu = *tert*-butyl. Bn = benzyl

Entry ^a	Monomer	Equiv. ^b	Resulting polymer	M_n^c (g mol ⁻¹)	PDI ^c	K_a^d (L mol ⁻¹)
1	R'' = Me	100	Poly-1a	5250	1.28	26 000 ± 1000
2	R'' = Me	1000	Poly-1b	13 400	1.24	15 000 ± 1000
3	R'' = tBu	100	Poly-1c	4820	1.20	17 000 ± 300
4	R'' = tBu	1000	Poly-1d	7960	1.23	15 300 ± 600
5	R'' = Bn	100	Poly-1e	10 600	1.47	15 000 ± 500
6	R'' = Bn	1000	Poly-1f	11 000	1.47	13 000 ± 1000
7	R'' = <i>n</i> -C ₁₂ H ₂₅	100	Poly-1g	16 000	1.49	20 500 ± 400
8	R'' = <i>n</i> -C ₁₂ H ₂₅	1000	Poly-1h	195 000	1.21	19 700 ± 700

^a Detailed synthetic procedures are shown in the ESI. ^b Equivalent methacrylate monomers used for polymerization. ^c Determined by size-exclusion chromatography (SEC) based on polystyrene standards in chloroform. ^d Binding constant between the resulting polymer and **2**.

long dodecyl side chain, which supports the efficient proceeding of the ATRP reaction; thus, a larger degree of polymerization was observed in the *n*-dodecyl methacrylate polymer (poly-1g,h) than in the other methacrylate polymers (poly-1a–f).

The binding ability of the end groups within poly-1a–h was studied using UV/Vis spectroscopy. **2** exhibited a discernible absorption band up to 700 nm with characteristic peaks at 329 and 427 nm and a broad band at 501 nm in chloroform (Fig. 2a and S24†). An increase in the absorption band at approximately 450 nm was observed upon the addition of poly-1a. No discernible absorption band was observed at 430 nm in the solution of poly-1a; thus, the increase in the UV/Vis spectra of **2** suggests that the calix[5]arene–fullerene host–guest complex is formed in solution. The binding constant of $(2.6 \pm 0.1) \times 10^4$ L mol⁻¹ was estimated by a 1 : 1 fitting model⁵⁰ based on the changes in the absorption intensity at 430 nm. Increases in the intensity of absorption were also seen in the solutions of **2** upon the addition of poly-1b–h (Fig. S25–S31†), indicating the formation of calix[5]arene–fullerene host–guest complexes in solution. The binding constant between poly-1b–h and **2** was

estimated to be on the order of 10^4 L mol⁻¹ (Table 1). The binding constants are close to those observed in the host–guest complexes between biscalic[5]arenes and C₆₀ derivatives;^{43,46,51} thus, these results indicate that the long polymer chains do not impact the binding affinity between calix[5]arene and fullerene.

The ¹H NMR study supported the formation of calix[5]arene–fullerene host–guest complexes in solution. Calix[5]arene stably exists in a cone conformation due to the intramolecular cyclic hydrogen bonding of five phenolic hydroxyl groups.^{44,52} The calix[5]arene ring undergoes ring inversion at room temperature, which is slow on the NMR timescale. Therefore, the methylene protons give a broad ¹H NMR resonance at room temperature. A characteristic broad resonance appeared at approximately 4 ppm in the chloroform-*d* solution of poly-1c,⁵³ which is assignable to bridge methylene protons of calix[5]arene moieties (Fig. 3a). When 1.0 equiv. of **2** was added to the chloroform solution, the broad resonance split into two resonances (Fig. 3b). The change in the resonance reflects that the ring inversion of calix[5]arene moieties became slower, which comes from an increase in the energetic barrier of the ring inversion by the encapsulation of fullerene molecules in the calix[5]arene cavity.

To gain detailed insight into calix[5]arene–fullerene complexation, time-dependent changes in UV/Vis absorption were monitored. A chloroform solution of a 1 : 1 mixture of **1** and **2** was placed in a quartz cuvette, and the absorbance value at 427 nm was recorded every 80 s. A gradual increase in the absorption value was observed in the solution (Fig. S32†). When the measurement time reached approximately 10 min, the

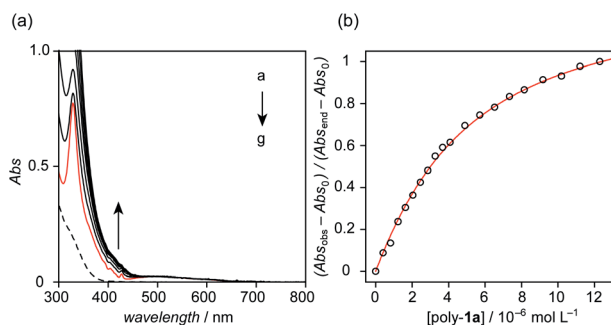


Fig. 2 (a) Changes in the UV/Vis absorption spectrum of **2** (2.0×10^{-5} mol L⁻¹) upon the addition of poly-1a. The concentrations of poly-1a are (a–g) 0.0, 2.0, 4.0, 6.4, 8.0, 10, and 12×10^{-5} mol L⁻¹, estimated from its M_n . The red line and broken line indicate the absorption spectra of poly-1a (2.0×10^{-5} mol L⁻¹) and **2** (2.0×10^{-5} mol L⁻¹), respectively. The spectra were recorded in chloroform at 25 °C. (b) Plot of normalized Δ Abs (400 nm) against [poly-1a] and the fitting curve obtained by a 1 : 1 fitting model, where Abs_{obs}, Abs₀, and Abs_{end} denote the observed Abs at each concentration, the Abs of poly-1a, and the Abs of poly-1a in the presence of **2** (12×10^{-5} mol L⁻¹), respectively.

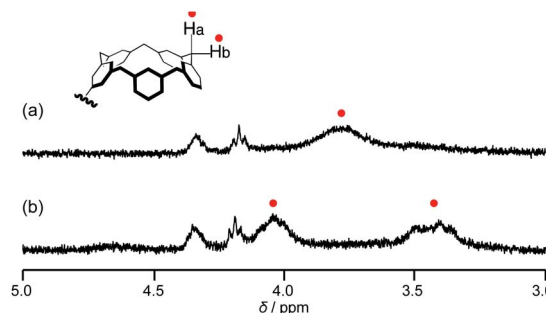


Fig. 3 Expanded ¹H NMR spectra of poly-1c (a) in the absence and (b) in the presence of **2** in chloroform-*d*.



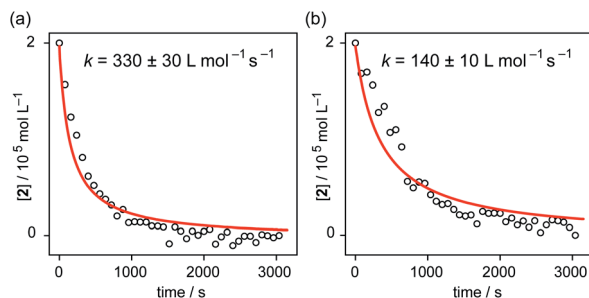


Fig. 4 Time-dependent concentration changes of **2** seen in (a) an equimolar mixture of **1** and **2** and (b) an equimolar mixture of poly-**1b** and **2** in chloroform. The concentrations of **2** were estimated by the absorbance value at 427 nm.

increase in the absorption value was saturated. On the other hand, the absorbance value of 427 nm of a 1 : 1 mixture of poly-**1b** and **2** slowly increased and saturated after approximately 20 min. Assuming that all **2** molecules were consumed by the association at 3000 s, the association rate constants of **1** and **2** and poly-**1b** and **2** were estimated to be $(330 \pm 30) \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ and $(140 \pm 10) \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$, respectively (Fig. 4).⁵⁴ The slower association between poly-**1b** and **2** most likely comes from the long methyl methacrylate chains of poly-**1b**. The long methacrylate chain of poly-**1b** fairly prevented **2** from approaching its calix[5]arene cavity.

Finally, the formation of a styrene-methacrylate diblock polymer was studied using poly-**1c** and poly-**2** (Fig. 5a and S33†). Analogous to **2**, poly-**2** exhibited a discernible absorption band up to 700 nm with characteristic peaks at 329 and 429 nm. Upon the addition of poly-**1c**, the absorption band at approximately 420 nm gradually became intense, which indicates the formation of a calix[5]arene–fullerene host–guest complex in solution. The 1 : 1 fitting model gave rise to a binding constant of $(2.4 \pm 0.2) \times 10^4 \text{ L mol}^{-1}$ (Fig. 5b). The binding constant is in the same order of magnitude as that of a biscalix[5]arene–C₆₀ complex

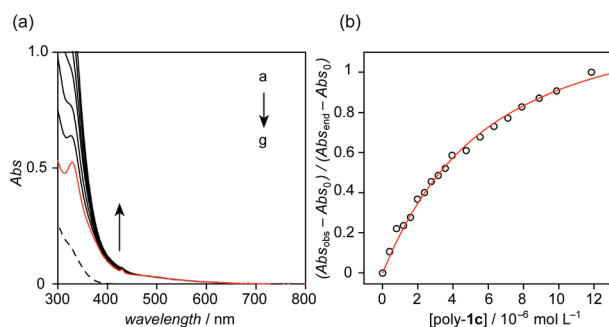


Fig. 5 (a) Changes in the UV/Vis absorption spectrum of poly-**2** ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) upon the addition of poly-**1c**. The concentrations of poly-**1c** are (a–g) 0.0, 2.0, 4.0, 6.3, 8.0, 10, and $12 \times 10^{-5} \text{ mol L}^{-1}$ estimated from its M_n . The red line and broken line indicate the absorption spectra of poly-**1c** ($2.0 \times 10^{-5} \text{ mol L}^{-1}$) and poly-**2** ($2.0 \times 10^{-5} \text{ mol L}^{-1}$), respectively. The spectra were recorded in toluene at 25 °C. (b) Plot of normalized ΔAbs (400 nm) against [poly-**1c**] and the fitting curve obtained by a 1 : 1 fitting model, where Abs_{obs} , Abs_0 , and Abs_{end} denote the observed Abs at each concentration, the Abs of poly-**1c**, and the Abs of poly-**1c** in the presence of poly-**2** ($12 \times 10^{-5} \text{ mol L}^{-1}$), respectively.

reported.²⁹ This result indicates that the end groups of calix[5]arene and fullerene within the polymer chains can recognize each other to form host–guest complexes, which is not prevented by the polymer chain.

Conclusions

In summary, methacrylate polymers were successfully prepared via an ATRP reaction using a calix[5]arene-appended monomer. The complexation capability between the calix[5]arene moiety and fullerene molecule was determined by UV/Vis absorption spectroscopy and NMR spectroscopy. Time-dependent UV analysis revealed that a long methacrylate chain fairly prevented fullerene from approaching the calix[5]arene cavity, although the polymer chains did not influence the binding affinity between calix[5]arene and fullerene. In addition, host–guest complexation was observed in a mixture of calix[5]arene-appended polymethacrylate and fullerene-appended polystyrene, which indicates that the high binding affinity between calix[5]arene and fullerene is effective in developing styrene-methacrylate diblock polymers. The present work shows the potential for developing various diblock polymers.

Experimental section

General

All reagents and solvents were commercial reagent grade and were used without further purification unless otherwise noted. Dry anisole and dry *N,N*-dimethylformamide (DMF) were obtained by distillation over CaH₂. Methacrylate monomers were passed through aluminum oxide before being used for the polymerization reactions. The styrene monomer was washed with saturated aqueous NaOH, and the resulting oil was distilled over CaH₂ under the reduced pressure before being used for the polymerization reaction. ¹H and ¹³C NMR spectra were recorded on a Varian mercury-300 spectrometer, and chemical shifts were reported on the delta scale in ppm relative to residual chloroform ($\delta = 7.26$ and 77.0 for ¹H and ¹³C, respectively). UV/Vis absorption spectra were recorded on a JASCO V-760 spectrometer. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL hybrid FTMS by electron spray ionization (ESI) methods. Melting points (Mp) were measured with a Yanagimoto micro melting point apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZeSe ATR accessory. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60 N (spherical, neutral)). Recycling preparative GPC-HPLC separations were carried out on JAI LC-5060 using preparative JAIGEL-2.5HH, 2HH, columns in series. Size exclusion chromatogram was recorded on Shimadzu LC-20AC with CTO-20AC accessory and TOSOH UV-8011 detector using preparative Shodex GPC-K-804, K-803, K-802.5 columns in series. The number-average molecular weights (M_n) of the poly methyl methacrylates (PMMA)s were determined by the size exclusion chromatography (SEC) based on polystyrene standards in chloroform. **3**,⁴⁷ **6**,⁴⁴ **8**,⁴⁸ **9** (ref. 46) and **10** (ref. 49) were synthesized according to reported methods.



Dimethyl 4-((12-azidododecyl)oxy)pyridine-2,6-dicarboxylate (4)

To a solution of **3** (1.56 g, 3.38 mmol) in dry DMF (33.8 mL) was added NaN_3 (440 mg, 6.77 mmol). After being stirred overnight at 100 °C under an argon atmosphere, the reaction mixture was diluted with ethyl acetate, and passed through celite. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (0–60% ethyl acetate in *n*-hexane, eluent) gave desired product **4** as a white solid (1.02 g, 72%). Mp 124–126 °C; ^1H NMR (300 MHz, CDCl_3): 7.79 (s, 2H), 4.13 (t, $J = 7.2$ Hz, 2H), 4.00 (s, 6H), 3.25 (t, $J = 7.7$ Hz, 2H), 1.79–1.88 (m, 2H), 1.53–1.64 (m, 2H), 1.21–1.48 (m, 16H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 167.2, 165.2, 149.7, 114.6, 69.1, 53.2, 51.5, 29.5, 29.4, 29.2, 29.1, 28.8, 28.7, 26.7, 25.8 ppm; FTIR-ATR (KBr): ν 2920, 2854, 2103, 1735, 1723, 1595, 1463, 1435, 1345, 1370, 1313, 1246, 1099, 1056, 1011, 757 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{33}\text{N}_4\text{O}_5$ m/z 421.24455 $[\text{M} + \text{H}]^+$, found m/z 421.24432.

4-((12-Azidododecyl)oxy)pyridine-2,6-dicarboxylic acid (5)

To a solution of **4** (1.00 g, 2.38 mmol) in THF (23.8 mL) was added KOH (668 mg, 11.9 mmol) diluted with water (23.8 mL). After being stirred for 2 h at 40 °C under an argon atmosphere, the reaction mixture was added ethyl acetate and water. The water layer was washed with ethyl acetate, and acidified with 1 M hydrochloric acid to pH 1. The precipitate was filtered off, washed with water, and dried over *in vacuo* to give desired product **5** as a white solid (874 mg, 94%). Mp 144–146 °C; ^1H NMR (300 MHz, CD_3OD): 7.82 (s, 2H), 4.22 (t, $J = 7.1$ Hz, 2H), 3.26 (t, $J = 7.6$ Hz, 2H), 1.80–1.89 (m, 2H), 1.48–1.62 (m, 4H), 1.32–1.42 (m, 14H) ppm; ^{13}C NMR (75 MHz, CD_3OD): δ 168.2, 165.5, 148.8, 113.7, 69.2, 51.0, 29.2, 28.9, 28.8, 28.5, 28.4, 26.4, 25.5 ppm; FTIR-ATR (KBr): ν 3503, 3096, 2928, 2851, 2096, 1923, 1728, 1597, 1464, 1329, 1185, 1035, 683 cm^{-1} ; HRMS (ESI^-) calcd for $\text{C}_{19}\text{H}_{27}\text{N}_4\text{O}_5$ m/z 391.19869 $[\text{M} - \text{H}]^-$, found m/z 391.19836.

((12-Azidododecyl)oxy)biscalix[5]arene 7

To a solution of **5** (480 mg, 1.20 mmol) and dry DMF (60 μL , 0.060 mmol) in dry THF (60 mL) was added oxalyl chloride (1.03 mL, 12.0 mmol) at 0 °C. After being stirred for 2 h at room temperature under an argon atmosphere, the reaction mixture was concentrated *in vacuo*. The crude product in dry THF (60 mL) was added **6** (1.80 g, 2.99 mmol). After being stirred for 24 h at room temperature under an argon atmosphere, the reaction mixture was concentrated *in vacuo*. The crude product was diluted with ethyl acetate. The precipitate was filtered off, washed with ethyl acetate, and dried over *in vacuo* to give desired product **7** as a yellow solid (1.76 g, 94%). Mp >300 °C; ^1H NMR (300 MHz, CDCl_3): 9.37 (s, 2H), 8.81 (s, 10H), 7.90 (s, 2H), 7.61 (s, 4H), 6.90–7.02 (m, 16H), 4.16 (t, $J = 7.3$ Hz, 2H), 3.40–4.00 (m, 20H), 3.25 (t, $J = 7.7$ Hz, 2H), 2.23 (s, 12H), 2.11 (s, 12H), 1.91 (s, 6H), 1.77–1.90 (m, 2H), 1.52–1.65 (m, 2H), 1.41–1.52 (m, 2H), 1.20–1.41 (m, 14H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 168.1, 161.5, 151.21, 147.8, 147.7, 130.8, 130.6, 129.8, 129.7,

127.5, 126.5, 126.4, 125.8, 121.8, 111.5, 69.2, 51.5, 31.5, 31.3, 29.5, 29.2, 29.2, 28.8, 28.7, 20.5, 20.4 ppm; FTIR-ATR (KBr): ν 3279, 3012, 2924, 2856, 2095, 1684, 1599, 1540, 1483, 1457, 1344, 1288, 1226, 1035, 859, 780 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{97}\text{H}_{103}\text{N}_6\text{O}_{13}$ m/z 1559.75776 $[\text{M} + \text{H}]^+$, found m/z 1559.75970.

Biscalix[5]arene-appended monomer 1

To a solution of **7** (400 mg, 0.26 mmol) in CH_2Cl_2 (13 mL) and water (3.3 mL) were added **8** (110 mg, 0.51 mmol), sodium ascorbate (Asc.Na) (100 mg, 0.51 mmol), and CuSO_4 (82 mg, 0.51 mmol). After being stirred for 48 h at room temperature under an argon atmosphere, the reaction mixture was diluted with CH_2Cl_2 . The organic layer was washed with water, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (0–20% ethyl acetate in toluene, eluent) and was passed through HPLC (10–12.5% ethyl acetate in toluene, eluent) gave desired product **1** as a yellow solid (240 mg, 52%). Mp >300 °C; ^1H NMR (300 MHz, CDCl_3): 9.36 (s, 2H), 9.08 (s, 2H), 8.80 (s, 4H), 8.78 (s, 4H), 7.91 (s, 2H), 7.60 (s, 4H), 7.60 (s, 1H), 6.92–7.02 (m, 16H), 5.31 (s, 2H), 4.32 (t, $J = 8.0$ Hz, 2H), 4.16 (t, $J = 7.0$ Hz, 2H), 3.40–4.00 (m, 20H), 2.22 (s, 12H), 2.11 (s, 12H), 1.91 (s, 6H), 1.78–1.90 (m, 4H), 1.40–1.53 (m, 2H), 1.20–1.40 (m, 14H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 171.5, 168.2, 161.5, 151.21, 147.8, 147.7, 142.2, 130.8, 130.6, 130.6, 129.9, 129.7, 127.5, 126.5, 126.5, 126.4, 125.8, 123.6, 121.9, 111.6, 69.1, 59.2, 55.7, 50.4, 31.6, 31.3, 30.6, 30.2, 29.5, 29.4, 29.4, 29.2, 29.0, 26.4, 25.8, 20.4, 20.4 ppm; FTIR-ATR (KBr): ν 3231, 3009, 2922, 2855, 1734, 1684, 1600, 1549, 1481, 1456, 1378, 1347, 1283, 1224, 1156, 1102, 1035, 856, 790, 691 cm^{-1} ; HRMS (ESI^+) calcd for $\text{C}_{104}\text{H}_{112}\text{BrN}_6\text{O}_{15}$ m/z 1763.73636 $[\text{M} + \text{H}]^+$, found m/z 1763.73911.

Poly-1a

1 (20.0 mg, 11.3 μmol), dry anisole (240 μL), and methyl methacrylate (MMA) (130 μL , 1.22 mmol, Nacalai Tesque, Inc., Japan, $\geq 99\%$) were placed in a Schlenk-flask. After three cycles of freeze-pump-thaw, CuBr (1.8 mg, 13 μmol), CuBr_2 (1.4 mg, 6.3 μmol), and N,N,N',N',N'' -pentamethyl-diethylenetriamine (PMDETA) (5.1 μL , 25 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH_2Cl_2 , passed through aluminum oxide 90 (CH_2Cl_2 , eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH_2Cl_2 solution with *n*-hexane to afford desired product poly-**1a** as a white solid (16.5 mg, 28%). ^1H NMR (300 MHz, CDCl_3): δ 9.31 (s, 2H), 9.08 (s, 2H), 8.79 (s, 8H), 7.92 (s, 2H), 7.58 (s, 4H), 7.57 (s, 1H), 6.93–6.99 (m, 16H), 5.18 (s, 2H), 4.33 (m, 2H), 4.16 (m, 2H), 3.40–4.00 (m, 20H), 3.59 (m, 3H \times n), 2.22 (s, 12H), 2.13 (s, 12H), 1.72–2.04 (m, 4H + 2H \times n), 1.16–1.49 (m, 22H), 0.70–1.14 (m, 3H \times n) ppm; $M_{n,\text{SEC}} = 5252 \text{ g mol}^{-1}$, PDI = 1.28.

Poly-1b

1 (20.0 mg, 11.3 μmol), dry anisole (240 μL), and methyl methacrylate (MMA) (1.30 mL, 12.2 mmol, Nacalai Tesque, Inc., Japan,



≥99%) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (1.8 mg, 13 μmol), CuBr₂ (1.4 mg, 6.3 μmol), and *N,N,N',N',N''*-pentamethyl-diethylenetriamine (PMDETA) (5.1 μL, 25 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH₂Cl₂, passed through aluminum oxide 90 (CH₂Cl₂, eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH₂Cl₂ solution with *n*-hexane to afford desired product poly-1b as a white solid (85 mg, 56%). ¹H NMR (300 MHz, CDCl₃): δ 9.29 (s, 2H), 9.09 (s, 2H), 8.79 (s, 8H), 7.93 (s, 2H), 7.58 (s, 4H), 7.58 (s, 1H), 6.94–7.01 (m, 16H), 5.18 (s, 2H), 4.33 (m, 2H), 4.14 (m, 2H), 3.40–4.00 (m, 20H), 3.59 (m, 3H × n), 2.22 (s, 12H), 2.14 (s, 12H), 1.70–2.04 (m, 4H + 2H × n), 1.16–1.52 (m, 22H), 0.71–1.12 (m, 3H × n) ppm; *M*_{n,SEC} = 13 353 g mol^{−1}, PDI = 1.24.

Poly-1c

1 (40.0 mg, 22.6 μmol), dry anisole (480 μL), and *tert*-butyl methacrylate (*t*BMA) (395 μL, 2.44 mmol, Tokyo Chemical Industry Co., Ltd., Japan, >98%) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (3.5 mg, 25 μmol), CuBr₂ (2.7 mg, 12 μmol), and *N,N,N',N',N''*-pentamethyl-diethylenetriamine (PMDETA) (10.2 μL, 48.9 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH₂Cl₂, passed through aluminum oxide 90 (CH₂Cl₂, eluent), and then concentrated *in vacuo*. The crude product was purified by GPC to give desired product poly-1c as a white solid (69.7 mg, 64%). ¹H NMR (300 MHz, CDCl₃): δ 9.29 (s, 2H), 9.09 (s, 2H), 8.79 (s, 8H), 7.93 (s, 2H), 7.58 (s, 4H), 7.58 (s, 1H), 6.94–7.01 (m, 16H), 5.18 (s, 2H), 4.34 (m, 2H), 4.17 (m, 2H), 3.40–4.00 (m, 20H), 2.22 (s, 12H), 2.14 (s, 12H), 1.70–2.14 (m, 4H + 2H × n), 0.84–1.51 (9H × n), 1.21–1.51 (m, 22H), 0.84–1.19 (m, 3H × n) ppm; *M*_{n,SEC} = 4821 g mol^{−1}, PDI = 1.20.

Poly-1d

1 (20.0 mg, 11.3 μmol), dry anisole (240 μL), and *tert*-butyl methacrylate (*t*BMA) (1.97 mL, 12.2 mmol, Tokyo Chemical Industry Co., Ltd., Japan, >98%) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (1.8 mg, 13 μmol), CuBr₂ (1.4 mg, 6.3 μmol), and *N,N,N',N',N''*-pentamethyl-diethylenetriamine (PMDETA) (5.1 μL, 25 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH₂Cl₂, passed through aluminum oxide 90 (CH₂Cl₂, eluent), and then concentrated *in vacuo*. The crude product was purified by GPC to give desired product poly-1d as a white solid (56.4 mg, 58%). ¹H NMR (300 MHz, CDCl₃): δ 9.29 (s, 2H), 8.81 (s, 10H), 8.62 (s, 4H), 7.93 (s, 2H), 7.58 (s, 4H), 7.58 (s, 1H), 6.94–7.00 (m, 16H), 5.18 (s, 2H), 4.33 (m, 2H), 4.18 (m,

2H), 3.40–4.00 (m, 20H), 2.22 (s, 12H), 2.14 (s, 12H), 1.70–2.14 (m, 4H + 2H × n), 0.80–1.50 (9H × n), 1.21–1.49 (m, 22H), 0.80–1.14 (m, 3H × n) ppm; *M*_{n,SEC} = 7957 g mol^{−1}, PDI = 1.23.

Poly-1e

1 (20.0 mg, 11.3 μmol), dry anisole (240 μL), and benzyl methacrylate (BnMA) (205 μL, 1.21 mmol, KYOEISHA CHEMICAL, Co., Inc., Japan, >97%) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (1.8 mg, 13 μmol), CuBr₂ (1.4 mg, 6.3 μmol), and *N,N,N',N',N''*-pentamethyl-diethylenetriamine (PMDETA) (5.1 μL, 25 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH₂Cl₂, passed through aluminum oxide 90 (CH₂Cl₂, eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH₂Cl₂ solution with methanol and by GPC to give desired product poly-1e as a white solid (67.1 mg, 52%). ¹H NMR (300 MHz, CDCl₃): δ 9.28 (s, 2H), 9.09 (s, 2H), 8.79 (s, 8H), 7.93 (s, 2H), 7.58 (s, 4H), 7.58 (s, 1H), 7.15–7.53 (m, 5H × n), 6.94–7.01 (m, 16H), 5.16 (s, 2H), 4.74–5.13 (m, 2H × n), 4.27 (m, 2H), 4.16 (m, 2H), 3.40–4.00 (m, 20H), 3.50 (m, 3H × n), 2.22 (s, 12H), 2.14 (s, 12H), 1.65–2.08 (m, 4H + 2H × n), 1.19–1.41 (m, 22H), 0.60–1.17 (m, 3H × n) ppm; *M*_{n,SEC} = 10 572 g mol^{−1}, PDI = 1.47.

Poly-1f

1 (20.0 mg, 11.3 μmol), dry anisole (240 μL), and benzyl methacrylate (BnMA) (2.05 mL, 12.1 mmol, KYOEISHA CHEMICAL, CO., Inc., Japan, >97%) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (1.8 mg, 13 μmol), CuBr₂ (1.4 mg, 6.3 μmol), and *N,N,N',N',N''*-pentamethyl-diethylenetriamine (PMDETA) (5.1 μL, 25 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH₂Cl₂, passed through aluminum oxide 90 (CH₂Cl₂, eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH₂Cl₂ solution with methanol and by GPC to give desired product poly-1f as a white solid (114 mg, 85%). ¹H NMR (300 MHz, CDCl₃): δ 9.28 (s, 2H), 9.10 (s, 2H), 8.79 (s, 8H), 7.93 (s, 2H), 7.58 (s, 4H), 7.58 (s, 1H), 7.11–7.54 (m, 5H × n), 6.93–7.04 (m, 16H), 5.20 (s, 2H), 4.73–5.16 (m, 2H × n), 4.28 (m, 2H), 4.17 (m, 2H), 3.40–4.00 (m, 20H), 2.22 (s, 12H), 2.14 (s, 12H), 1.65–2.08 (m, 4H + 2H × n), 1.20–1.41 (m, 22H), 0.50–1.18 (m, 3H × n) ppm; *M*_{n,SEC} = 10 953 g mol^{−1}, PDI = 1.42.

Poly-1g

1 (20.0 mg, 11.3 μmol), dry anisole (240 μL), and dodecyl methacrylate (355 μL, 1.22 mmol, KYOEISHA CHEMICAL, CO., Inc., Japan, >98%) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (1.8 mg, 13 μmol), CuBr₂ (1.4 mg, 6.3 μmol), and *N,N,N',N',N''*-pentamethyl-



diethylenetriamine (PMDETA) (5.1 μL , 25 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 $^{\circ}\text{C}$, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH_2Cl_2 , passed through aluminum oxide 90 (CH_2Cl_2 , eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH_2Cl_2 solution with methanol and by GPC to give desired product poly-1g as a white solid (65.5 mg, 36%). ^1H NMR (300 MHz, CDCl_3): δ 9.29 (s, 2H), 9.09 (s, 2H), 8.79 (s, 8H), 7.92 (s, 2H), 7.58 (s, 4H), 7.56 (s, 1H), 6.94–7.01 (m, 16H), 5.16 (s, 2H), 4.32 (m, 2H), 4.16 (m, 2H), 3.40–4.00 (m, 20H), 3.91 (m, 2H \times n), 2.22 (s, 12H), 2.14 (s, 12H), 1.71–2.07 (m, 4H + 4H \times n), 1.13–1.51 (m, 22H + 18H \times n), 0.70–1.13 (m, 6H \times n) ppm; $M_{n,\text{SEC}} = 16\,006\text{ g mol}^{-1}$, PDI = 1.49.

Poly-1h

1 (20.0 mg, 11.3 μmol), dry anisole (240 μL), and dodecyl methacrylate (3.55 mL, 12.2 mmol, KYOEISHA CHEMICAL, CO., Inc., Japan, >98%) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (1.8 mg, 13 μmol), CuBr₂ (1.4 mg, 6.3 μmol), and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (5.1 μL , 25 μmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 3 h in the dark at 65 $^{\circ}\text{C}$, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH_2Cl_2 , passed through aluminum oxide 90 (CH_2Cl_2 , eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH_2Cl_2 solution with methanol and by GPC to give desired product poly-1h as a white solid (1.42 g, 60%). ^1H NMR (300 MHz, CDCl_3): δ 9.29 (s, 2H), 9.09 (s, 2H), 8.79 (s, 8H), 7.93 (s, 2H), 7.58 (s, 4H), 7.58 (s, 1H), 6.94–7.00 (m, 16H), 5.19 (s, 2H), 4.32 (m, 2H), 4.17 (m, 2H), 3.40–4.00 (m, 20H), 3.91 (m, 2H \times n), 2.21 (s, 12H), 2.13 (s, 12H), 1.69–2.04 (m, 4H + 4H \times n), 1.14–1.58 (m, 22H + 18H \times n), 0.60–1.13 (m, 6H \times n) ppm; $M_{n,\text{SEC}} = 195\,197\text{ g mol}^{-1}$, PDI = 1.21.

Poly-9

9 (110 mg, 0.30 mmol), dry anisole (3.0 mL), and styrene (17.2 mL, 1.22 mmol, Nacalai Tesque, Inc., Japan, $\geq 99\%$) were placed in a Schlenk-flask. After three cycles of freeze–pump–thaw, CuBr (43 mg, 0.30 mmol) and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (94 μL , 0.45 mol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 24 h in the dark at 80 $^{\circ}\text{C}$, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH_2Cl_2 , passed through aluminum oxide 90 (CH_2Cl_2 , eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH_2Cl_2 solution with methanol and by GPC to give desired product poly-9 as a white solid (500 mg, 54%). ^1H NMR (300 MHz, CDCl_3): δ 6.31–7.37 (m, 5H \times n), 4.34–4.57 (m, 2H), 3.47–3.61 (m, 3H), 3.26 (t, J = 7.8 Hz, 2H), 0.80–2.14 (m, 26H + 3H \times (n – 1)) ppm; $M_{n,\text{SEC}} = 3118\text{ g mol}^{-1}$, PDI = 1.08.

Poly-2

To a solution of poly-9 (60 mg) in CH_2Cl_2 (1.1 mL) and water (0.3 mL) were added 8 (23.5 mg, 23.0 μmol), sodium ascorbate (Asc.Na) (4.6 mg, 23 μmol), and CuSO_4 (3.7 mg, 23 μmol). After being stirred for 48 h at room temperature under an argon atmosphere, the reaction mixture was diluted with CH_2Cl_2 . The organic layer was washed with water, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The crude product was purified by GPC to give desired product poly-2 as brown solid (51 mg, 54%). ^1H NMR (300 MHz, CDCl_3): δ 8.04 (s, 1H), 6.31–7.75 (m, 5H \times n), 4.79 (s, 1H), 4.31–4.50 (m, 6H), 4.11–4.21 (m, 2H), 3.44–3.61 (m, 3H), 0.80–2.14 (m, 46H + 3H \times (n – 1)) ppm; $M_{n,\text{SEC}} = 4109\text{ g mol}^{-1}$, PDI = 1.02.

Conflicts of interest

There are no conflicts to declare.

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