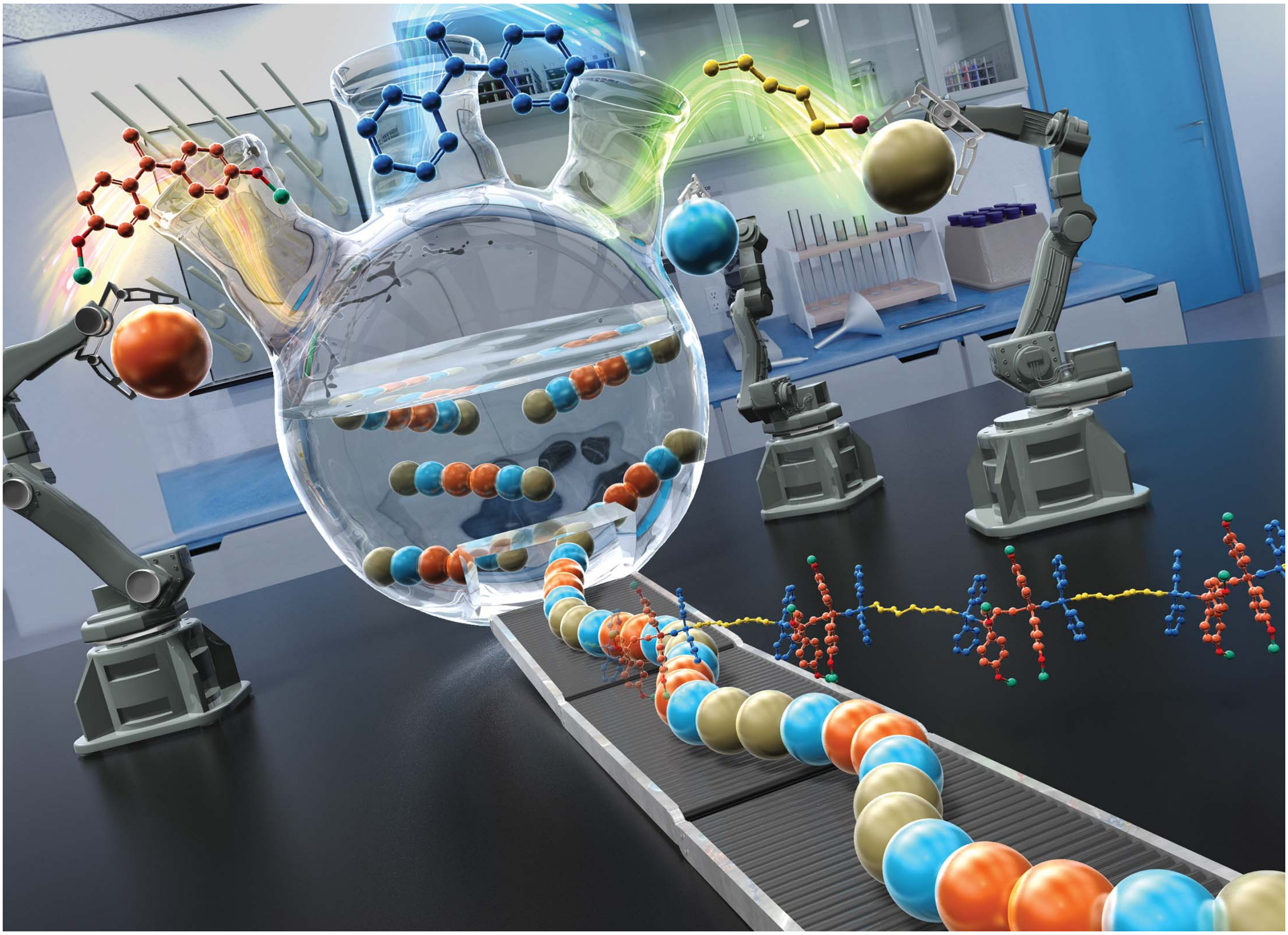

Showcasing research from Professor Ishizone's laboratory, School of Materials and Chemical Technology, Institute of Science Tokyo, Tokyo, Japan.

One-pot synthesis of sequence-controlled macromonomers *via* living anionic addition reaction and subsequent acyclic diene metathesis polymerization

In this study, we achieved the one-pot synthesis of divinyl-functionalized sequence-controlled BAAB-type macromonomers by the sequential reaction of 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (**A**), 1,1-diphenylethylene (**B**), and 5-bromo-1-pentene with potassium naphthalenide in tetrahydrofuran. During the successive reactions, five covalent bonds were quantitatively formed in the macromonomer framework. The defect-free macromonomer functionalized with 5-bromo-1-pentene was easily isolated, and underwent the acyclic diene metathesis polymerization with transition metal catalyst to yield the sequence-controlled polymer with well-defined BAABR-type repeating units composed of the DPE derivative tetramer.

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One-pot synthesis of sequence-controlled macromonomers *via* living anionic addition reaction and subsequent acyclic diene metathesis polymerization

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We developed a new synthetic approach for sequence-controlled polymers through a 1 : 1 addition reaction, living anionic addition reaction (LAAR) of 1,1-diphenylethylene (DPE) derivatives and acyclic diene metathesis (ADMET) polymerization. Divinyl-functionalized sequence-controlled BAAB-type oligomers were synthesized in high yield by sequentially reacting potassium naphthalenide (K-Naph) with 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (OSi, **A**), DPE (H, **B**), and an alkyl halide possessing a vinyl group in one pot. Five covalent bonds were quantitatively formed during the reactions, so the desired symmetrical oligomers were easily isolated without tedious purification such as column chromatography. The following ADMET polymerization of the resulting divinyl-functionalized oligomer gave the sequence-controlled polymer with a well-defined BAABR-type repeating unit composed of the DPE tetramer. Our proposed synthetic approach based on the combination of LAAR and ADMET polymerization realized the facile and precise control of the monomer sequence.

Introduction

The primary structures of a polymer are the most essential factor that determines its properties. Among them, the monomer sequence has a significant influence on copolymer properties and functions, obvious in the natural polymers such as DNA and enzymes. Recently, various strategies have been developed to artificially synthesize sequence-controlled polymers.[1–4]

The approach using sequence-controlled macromonomers is most reliable since polymers with strictly regulated monomer sequences can be obtained. In order to synthesize high-molecular-weight polymers, the effective polymerization mechanism must be carefully selected. Click reactions are well-known for their high efficiency in designing and modifying complex molecular architectures without byproducts.[5] Bowman *et al.* reported the thiol-ene polymerization of the ABC-type macromonomer, which was prepared by iterative thiol-Michael reactions and deprotection reactions, to obtain DNA-like polymers.[6] Guan *et al.* utilized Cu-catalyzed azide–alkyne cycloaddition to polymerize telechelic sequence-controlled macromonomers with a pre-encoded pentapeptide sequence, and successfully obtained protein-like polymers.[7]

Besides these approaches, metathesis reactions are established tools for connecting olefin molecules by forming carbon–carbon double bonds, and commercially available Grubbs catalysts exhibit high functional group tolerance. As an example of applying them to monomer sequence control, acyclic diene metathesis (ADMET) polymerization, a step-growth polymerization of α,ω-diene monomers, has been used to synthesize polyethylene-like polymers periodically possessing functional groups.[8] The rational design of symmetrical α,ω-diene (macro) monomers can place functional groups at regular intervals along the polymer chain. In addition, entropically driven ring-opening metathesis polymerization (ED-ROMP) of macrocyclic olefins has drawn attention because it allows for control of molecular weight as well as monomer sequences.[9]

As stated above, the macromonomer approaches have been employed using various reactions to precisely synthesize sequence-controlled polymers. However, the preparation of those macromonomers usually requires multi-step reactions and tedious purification at each synthetic step, because both the construction of the complex monomer sequence and the introduction of the polymerizable groups are necessary. These procedures are time-consuming, and often result in a low yield of macromonomers.

In contrast, single unit monomer insertion (SUMI), utilizing dormant species seen in the living radical polymerization

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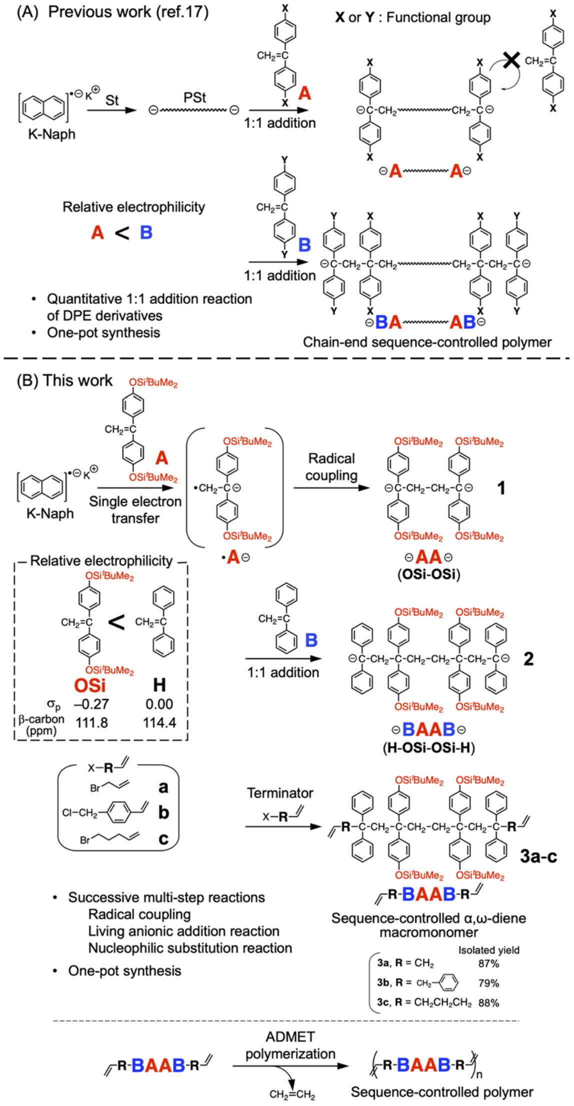
systems such as atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) polymerization, has been frequently employed to prepare sequence-controlled units.[10–12] The insertions of a single vinyl monomer into initiator and/or RAFT agents are repeated to afford AB, ABC, and ABCD-type oligomers. However, undesirable monomer insertions occur due to the inherent homopolymerizability of monomers, leading to the necessity of isolation in each step. It becomes more difficult as the molecular weight of the product is higher, so the iterative synthesis of sequence-controlled 'polymers' by only SUMI is not realistic. Accordingly, a new synthetic method with an innovative mechanism is required to overcome the challenges associated with sequence regulation.

In this paper, we have proposed a novel strategy to synthesize sequence-controlled polymers by utilizing the unique reactivity of 1,1-diphenylethylene (DPE) derivatives as candidate monomers. DPE derivatives show negligible homopolymerizability, but a quantitative 1 : 1 addition reaction between them and the nucleophilic carbanions occurs to afford the corresponding DPE anions which are stabilized by two aromatic rings.[13] Even if an excess amount of DPE derivative is present, no further reaction between the DPE anion and the residual DPE, homopropagation, occurs and the monoadduct is exclusively generated. It is noted that the DPE derivative anions can be used as bulky and relatively low nucleophilic initiators.[14] These stoichiometric reactions of DPE derivatives made it possible to synthesize not only chain-end and in-chain functionalized polymers[14,15] but also alternating and gradient copolymers.[16] The reactivity (electrophilicity) of DPE derivatives highly depends on its substituents. The DPE derivatives with electron-withdrawing groups such as cyano and acyl groups are highly electrophilic, and the generated DPE anions are less nucleophilic than the non-substituted DPE anion. Electron-donating groups also have opposite effects on the reactivity. We previously reported a quantitative 1 : 1 addition reaction between the DPE anion and other DPE derivatives with electron-withdrawing groups (bromo, trimethylsilylethynyl, acyl, or cyano groups) to form an AB-type terminal unit (Scheme 1A).[17] Furthermore, the one-pot syntheses of the AB, ABC and ABCD-type chain-end sequence-controlled polystyrenes were achieved by the sequential additions of DPE derivatives in increasing order of their electrophilicity, which can be roughly evaluated from the Hammett substituent parameter (σ_p) and their β-carbon chemical shifts.[17–19] We named this nucleophilic 1 : 1 addition reaction "living anionic addition reaction (LAAR)". LAAR enables the one-pot construction of DPE–DPE′ sequences, inaccessible by other techniques until now, in ~100% yield.



Scheme 1 (A) One-pot synthesis of chain-end sequence-controlled polymers by LAAR. (B) Synthesis of sequence-controlled macromonomers and polymers by LAAR and ADMET polymerization.

We herein apply LAAR for the synthesis of "sequence-controlled polymers" (Scheme 1B). To achieve this goal, we focused on the reaction between DPE and potassium naphthalenide (K-Naph).[20] Single-electron transfer from K-Naph to DPE rapidly occurs and a DPE radical anion is produced, followed by its instantaneous radical coupling to form a symmetrical DPE dimer (AA-type oligomer) dianion, in which two DPE units are linked in a tail-to-tail fashion. Then, we performed LAAR with another DPE derivative showing higher electrophilicity to link the DPE derivative in a head-to-tail fashion and prepare a symmetrical BAAB-type tetramer dianion. No further reaction of the residual DPE derivatives occurred with the produced DPE anions. Since the resulting dianion after LAAR was still alive, we conducted the nucleophilic substitution reactions with electrophilic alkyl halides (**a**–**c**)[21] to introduce vinyl groups at both chain-ends of oligomers. In other words, defect-free divinyl-functionalized macromonomers were prepared through multi-step but one-pot reactions. This synthetic approach did not require the isolation of intermediates, unlike the conventional iterative synthesis such as SUMI approaches. In addition, we attempted to synthesize a sequence-controlled polymer with a BAABR-type repeating unit *via* ADMET polymerization of the obtained divinyl-functionalized macromonomer. The obtained polymer periodically possessed structurally rigid DPE tetrads along the main chain. This unique structure has never been prepared due to the non-homopolymerizability of DPE derivatives.

Results and discussion

One-pot synthesis of divinyl-functionalized BAAB-type oligomers

We reacted K-Naph with 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (OSi, **A**),[22] DPE (H, **B**) and a terminator (**a**–**c**) to synthesize divinyl-functionalized BAAB-type oligomers by one-pot reactions (Scheme 1B). The relative electrophilicity of H ($\sigma_p = 0.00$) is higher than that of OSi ($\sigma_p = -0.27$) from the Hammett substituent parameter. In fact, the quantitative reaction of the OSi anion with H has been reported in our recent publication.[17c]

At first, the OSi–OSi dimer dianion (**1**) was prepared by reacting K-Naph with OSi in THF. After the addition of 1.7-fold OSi to a dark green solution of K-Naph in THF at −78 °C, the colour immediately changed to dark red, indicating that the single electron transfer and the following radical coupling occurred rapidly. We confirmed this dimerization of OSi by quenching with acetic acid and characterizing the obtained product by ^{1}H and ^{13}C NMR, and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements (Fig. S1–S3, SI). As expected, the reaction between K-Naph and OSi occurred without side reactions to exclusively form a symmetrical tail-to-tail linked OSi–OSi dimer, which was isolated in 85% yield. After 15 min reaction of K-Naph with OSi, 1.7-fold H in THF was added to prepare the H–OSi–OSi–H tetramer dianion (**2**) by LAAR. The red colour of **1** changed to red orange, and its coloration was maintained for 24 h. Finally, allyl bromide (**a**) was reacted with **2** at −78 °C, and the colour of **2** immediately disappeared. After 1 h, the crude product was obtained by evaporating the solvent. For purification, the resulting powder was simply triturated with methanol and hexane several times. The residual DPE derivatives (OSi and H), naphthalene and potassium salt could be easily removed, and the objective oligomer (**3a**) was isolated as a white powder in 87% yield. ^{1}H and ^{13}C NMR, size exclusion chromatography (SEC) and MALDI-TOF-MS measurements of the obtained product ensured the successful formation of **3a** (Fig. S15–S18, SI). These characterization studies also revealed that LAAR of **1** with H proceeded as desired, and **2** retained sufficient reactivity for a quantitative substitution reaction with **a**, at −78 °C even after 24 h. We next reacted **2** with 4-chloromethylstyrene (**b**) as the terminating reagent instead of **a**. Since the colour change occurred more slowly, the reaction mixture of **2** and **b** was kept at −78 °C for 20 h to complete the reaction. The oligomer **3b** could be isolated in 79% yield by similar trituration and following recrystallization, without column chromatography. The structure of **3b** was confirmed by ^{1}H and ^{13}C NMR, SEC and MALDI-TOF-MS measurements (Fig. S19–S22, SI).

We finally used 5-bromo-1-pentene (**c**), a simple alkyl bromide showing lower electrophilicity than **a** and **b**. Nevertheless, the reaction between **2** and **c** proceeded at −78 °C within 20 h, which was obvious from a gradual fading of the characteristic colour of **2**. After concentration of the reaction mixture, the purification by trituration and recrystallization gave **3c** in 88% yield. Given that five covalent bonds were sequentially formed in one pot for the construction of **3c**, this high isolated yield means that the conversion of each reaction was quantitative. The slight decrease in the yield would be due to the purification procedure. The ^{1}H NMR spectrum of **3c** with all signal assignments is shown in Fig. 1A. The signals of the chain-end vinyl groups are observed at 5.4 and 4.7 ppm. The signals of five methylene groups in the backbone are also observed at 2.8, 1.4, 1.1, 0.8 and 0.5 ppm. On the other hand, the aromatic proton signals appear at 7.2–6.4 ppm. The signals of *tert*-butyldimethylsilyloxy groups in the OSi unit appear at 1.0 and 0.2 ppm. The intensity ratio of these signals matched the theoretical one calculated from the structure of **3c**. In the ^{13}C NMR spectrum, 19 sharp signals are observed and all are assigned as shown in Fig. 1B. Only two signals derived from the quaternary carbons in the OSi unit and H unit (2 and 4) overlapped at 49.7 ppm, but it was split into two, when the ^{13}C NMR spectrum was recorded at 45 °C (Fig. S23, SI). These NMR spectra clearly demonstrated the highly symmetrical structure of **3c** and its high purity. The MALDI-TOF-MS spectrum showed only one signal ($m/z = 1486.40$) matching the theoretical molar

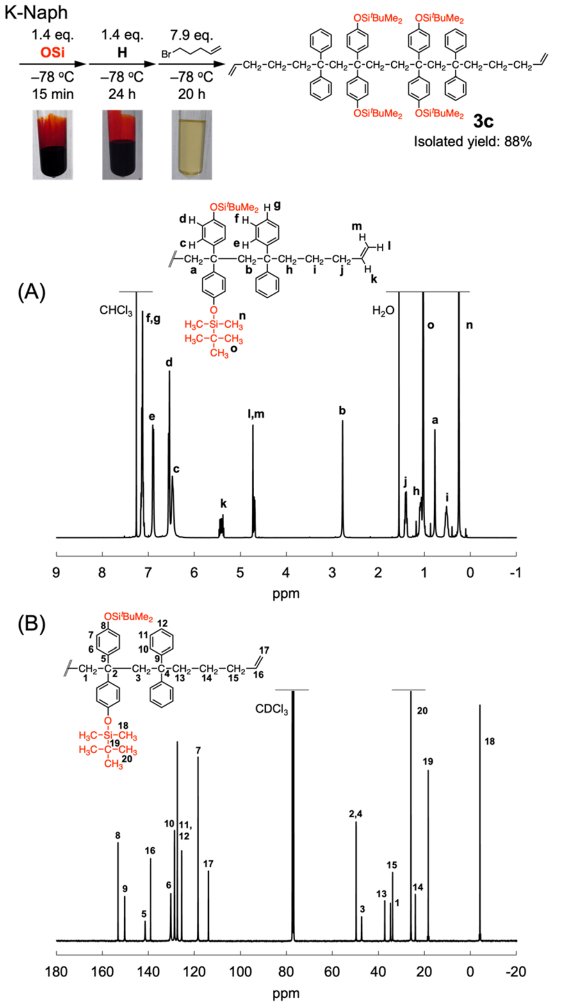


Fig. 1 (A) ^{1}H NMR and (B) ^{13}C NMR spectra of **3c** in $CDCl_3$ at 25 °C.

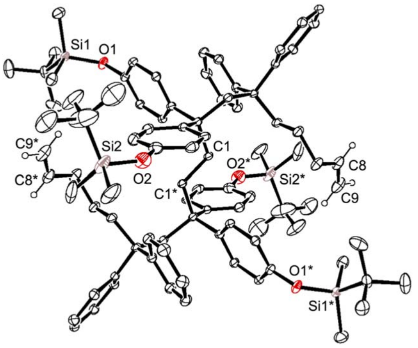


Fig. 2 Crystal structure of **3c**. Hydrogen atoms except for vinyl hydrogens are omitted for clarity.

mass of [**3c** + Ag]$^+$ = 1488.14 Da (Fig. S24, SI). There was no signal corresponding to byproducts such as oligomers lacking OSi units, H units or $CH_2CH_2CH_2CH{=}CH_2$ groups. In addition, the absence of the undesired homo-sequence and crossover sequence (for example, H–OSi–OSi–H–H and H–OSi–OSi–H–OSi) was confirmed, although excess amounts of OSi and H were present during the reaction. This result was attributed to the negligible homopolymerizability of DPE derivatives and the stability of the corresponding DPE anions.[17] Finally, single crystal X-ray analysis revealed the crystallographically imposed centrosymmetric structure of the divinyl-functionalized BAAB-type oligomer **3c** (Fig. 2). Thus, the successive one-pot reactions, constituted of dimerization of OSi, LAAR of H and the substitution (termination) reaction with electrophiles, proceeded stoichiometrically to form sequence-controlled α,ω-dienes. In this one-pot synthetic method, the sequential additions of reagents into the reaction mixture were only required and the oligomer could be isolated in high yield.

ADMET polymerization of the BAAB-type macromonomer

We next attempted the ADMET polymerization of three sequence-controlled α,ω-dienes using the second-generation Grubbs catalyst (G2) in toluene under nitrogen flow at 60 °C for 48 h to synthesize sequence-controlled polymers. However, the low solubility of **3a** and **3b** in common organic solvents hindered their ADMET polymerizations. The resulting products were almost initial macromonomers including trace amounts of oligomers (Fig. S18 and S22, SI). The spacer structure (CH_2 or CH_2–Ar) between the H units and vinyl groups should affect the flexibility of the chain-end vinyl groups. Together with the flexibility and the steric hindrance of two bulky aromatic rings on the H units adjacent to the reactive sites, the chemical structures of the vinyl groups including simple olefins (**3a** and **3c**) and a conjugated styryl moiety (**3b**) would also be important to result in the negligible polymerization of **3a** and **3b**.[23]

On the other hand, **3c** with the longer and more flexible $CH_2CH_2CH_2$ spacer showed much higher solubility, suggesting that the chain-end structure had a huge impact on its properties. The polymerization of **3c** was conducted with G2 in a homogeneous solution of toluene (0.72 M) at 60 °C for 24 h (Table 1, run 1). The viscosity of the reaction mixture gradually increased, and a white powder was obtained in 94% yield after reprecipitation into methanol. The SEC curve of the product showed a multimodal shape in accordance with the formation of a series of oligomers (Fig. S4, SI). The number-average molecular weight ($M_{n,SEC}$) estimated from the SEC analysis using polystyrene calibration was 8.5 kg mol^{-1}, and the molecular weight of the peak top of the SEC curve (M_p) corresponded to 13.3 kg mol^{-1}. In order to further promote metathesis reactions, after **3c** was similarly polymerized in toluene for 24 h at 60 °C, a second feed of G2 in toluene was injected at room temperature. After the polymerization for an additional 24 h at 60 °C, a polymer was produced in 96% yield (run 2). The $M_{n,SEC}$ and M_p values of the resulting polymer reached 16.1 and 30.1 kg mol^{-1}, respectively (Fig. S5, SI). Thus, the step-growth polymerization, the cross-metathesis reaction, between the oligomers and/or **3c** further proceeded after the second addition of G2. Similar to the case of toluene solution, the homogeneous polymerization of **3c** with G2 in $CHCl_3$ at 50 °C afforded a polymer with a slightly lower $M_{n,SEC}$ (12.4 kg mol^{-1}) and M_p (21.9 kg mol^{-1}) in 83% yield (run 3, Fig. S6, SI). It is thus suggested that toluene is a preferrable solvent to synthesize high molecular weight polymers in high yield in this reaction system. However, the MALDI-TOF-MS and ^{1}H NMR measurements of the polymers obtained in both solvents indicated that the undesired olefin isomerization occurred, as previously reported in the metathesis reactions using G2.[24] As shown in Fig. S13, the MALDI-TOF-MS analysis revealed that such olefin isomerization during ADMET polymerization resulted in the lack of methylene groups in the main chain and the disorder of

Table 1 ADMET polymerization of **3c** [a]

					M_n (kg mol^{-1})					
Run	Time (h)	G2 (mol%)	BQ (mol%)	Yield[b] (%)	NMR[c]	SEC[d]	M_p[d] (kg mol^{-1})	M_w/M_n[d]	T_{10}[e] (°C)	T_g[f] (°C)
1	24	3	0	94	n.d[h]	8.5	13.3	1.55	338	154
2	24 + 24	3 + 3	0	96	n.d[h]	16.1	30.1	1.75	345	155
3 ($CHCl_3$)[g]	24 + 24	3 + 3	0	83	n.d[h]	12.4	21.9	1.63	349	161
4	24	3	6	88	5.8	5.4	4.3	1.30	352	143
5	24 + 24	3 + 3	6 + 6	92	10.9	8.2	11.5	1.47	345	152

[a] ADMET polymerizations were conducted in toluene under nitrogen flow at 60 °C unless otherwise stated. [b] Methanol insoluble part. [c] Determined from the intensity of terminal olefin signals in ^{1}H NMR. [d] Determined by SEC calibration using polystyrene standards in THF. [e] Determined by TGA. [f] Determined by DSC. [g] In $CHCl_3$ at 50 °C. [h] Difficult to determine because of the disappearance of terminal olefin signals in ^{1}H NMR.

the monomer sequence. In the ^{1}H NMR spectra of runs 1–3, the signals of the methine groups of the terminal olefin were not observed at all, implying that the terminal olefin was converted into the internal ones by olefin isomerization (Fig. S7–S9, SI).

Therefore, we conducted the polymerization of **3c** with G2 in the presence of 1,4-benzoquinone (BQ) in toluene at 60 °C for 24 h to suppress the olefin isomerization (run 4), since BQ has been reported to inhibit such isomerization effectively.[24] Similar to the polymerization without BQ, the second-feed of G2 was added after 24 h, and the second-stage polymerization was further continued by heating at 60 °C for 24 h (run 5). The yields of the methanol insoluble part were 88% after 24 h and 92% after 48 h. The estimated $M_{\mathrm{n,SEC}}$ value increased from 5.4 kg mol^{-1} (24 h) to 8.2 kg mol^{-1} after 48 h polymerization. As shown in Fig. 3, the SEC curve after 48 h (run 5) significantly shifts to a higher molecular weight side compared with that of run 4 after 24 h. The molecular weights of the product obtained in the presence of BQ were rather lower than those of the products without BQ (runs 1 and 2). Interestingly, the MALDI-TOF-MS spectrum of run 5 showed one series of peaks whose molar masses matched those of the ideal linear polymer obtained by ADMET polymerization of **3c** (Fig. S14, SI). Each peak was sharp, not complex, indicating negligible olefin isomerization and cyclization under the conditions in the presence of BQ. In the ^{1}H NMR spectrum of run 5 (Fig. S11, SI), the multiple signals of the methine proton on the terminal olefin carbon were observed at 5.4 ppm, located same as the starting macromonomer, **3c** (Fig. 1A). On the other hand, the signal of the internal olefin moiety was strongly observed at 4.7 ppm. The M_{n} values of run 4 and 5 calculated from the intensity ratios of those olefin signals were 5.8 and 10.9 kg mol^{-1}, close to those from the SEC calibrations (Table 1). The shapes of all other signals were similar but broader compared with **3c**, indicating the increased molecular weight and the maintained framework.

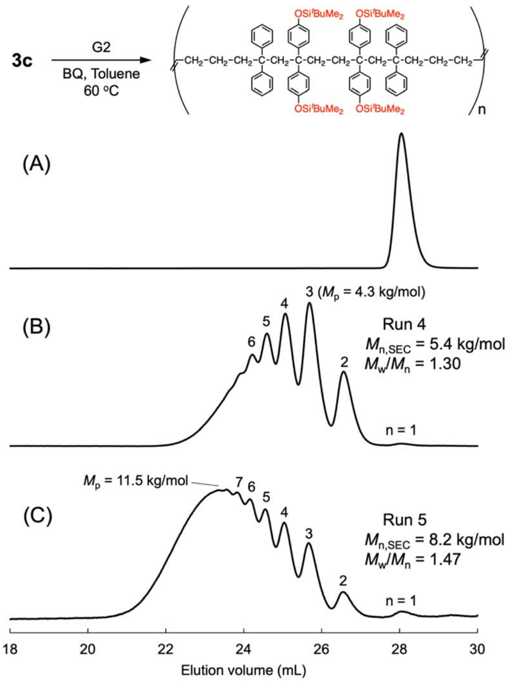


Fig. 3 SEC curves of **3c** (A), after ADMET polymerization of **3c** with BQ in toluene at 60 °C for 24 h (B) and for 48 h (C).

Thus, the polymer with a well-defined BAABR-type repeating unit composed of DPE derivatives could be obtained without sequence defects by ADMET polymerization of **3c**. We are currently exploring the suitable polymerization conditions in order to increase the molecular weight. The poly(**3c**) of run 5 started to decompose around 300 °C (10% decomposition temperature: 345 °C) and showed a glass transition temperature (T_g) at 152 °C, as shown in Table 1. All the resulting poly(**3c**) were soluble in hexane, benzene, chloroform and THF, but insoluble in methanol and water.

Conclusions

In conclusion, we successfully synthesized sequence-controlled α,ω-diene macromonomers in one pot by sequentially reacting K-Naph with OSi, H and a functional terminator. This series of reactions stoichiometrically proceeded, forming five covalent bonds to give the objective symmetrical BAAB-type oligomers without defects. The amount of DPE derivatives did not have to be adjusted, and the residual DPE derivatives could be easily removed from the objective macromonomer by simple trituration. The obtained α,ω-diene could be used as a macromonomer for ADMET polymerization to afford the sequence-controlled polymer possessing the DPE–DPE′ sequence. This approach using LAAR has the potential to easily produce a wide range of sequence-controlled oligomers because the applications of various DPE derivatives have been reported.[10–13] Further research is in progress by using not only OSi and H but also other various DPE derivatives having solubilizing groups and suitable electrophilicity tuned by the introduced functional groups. Furthermore, the hydrogenation of the carbon–carbon double bonds in the resulting ADMET polymer will afford an attractive sequence-regulated polymer having the exact oligoethylene units in the repeating unit in addition to the rigid BAAB-type unit. Thus, this novel strategy has achieved the precise and facile synthesis of sequence-controlled polymers and is expected to develop unprecedented polymer materials in the future.

Author contributions

T. I. and T. N. conceived the idea of project. T. N., K. T., and R. G. performed the experiments. S. K. conducted the X-ray analysis. T. N. and T. I. wrote the manuscripts. All the authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

CCDC 2446998 contains the supplementary crystallographic data for this paper.[25]

The data supporting this article have been included as part of the SI. Supplementary information is available. See DOI: https://doi.org/10.1039/d5sc05910k.

Acknowledgements

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