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Preparation of a Daisy Chain via Threading-Followed-by-Polymerization

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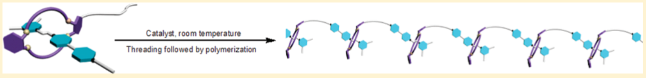
Supporting Information



ABSTRACT: A daisy chain, a linear array of self-complementary (plerotopic) molecules linked together by mechanical bonds, was prepared by polyesterification of two complementary host—guest units based on the dibenzo-24-crown-8/1,2-bis(pyridinium)ethane recognition motif conveniently via "threading-followed-by-polymerization", an approach different from the formerly reported method, in which mechanically interlocked monomers were first prepared and then polymerized, used in the construction of this kind of polymers. It was characterized by various techniques including ^{1}H NMR, COSY, NOESY, GPC, TGA, dynamic laser light scattering (DLS), UV—vis, and viscosity. Its molecular weight M_n was 64 kDa with polydispersity of 1.5 as determined by GPC, indicating that 45 repeating units existed in a single polymer chain. Its hydrodynamic diameter in a dilute acetonitrile solution was about 250 nm as determined by DLS. These studies not only proved the successful fabrication of the desired daisy chain polymeric structure but also provided a convenient method to construct linear mechanically interlocked polymers, avoiding the tedious syntheses of AB-type mechanically interlocked monomers.

1. INTRODUCTION

Mechanically interlocked molecules (MIMs) have attracted great attention not only due to their topological importance[1] but also because of their wide applications in the construction of molecular machines[2,3] and mechanically interlocked polymers.[4,5] Mechanically interlocked polymers, polymers whose repeating units are connected by mechanical bonds, have shown some unique and interesting physical and mechanical properties owing to the introduction of mechanical bonds, suggesting their potential applications in material science and nanotechnology. Therefore, a series of mechanically interlocked polymers have been widely synthesized and studied. Among them, daisy chains, in which self-complementary (plerotopic) molecules are linked together by mechanical bonds, are one of the most fundamental structures, and hence their preparation is of great importance.[6a] Stoddart et al. have tried to synthesize daisy chains using both the dibenzo-24-crown-8(DB24C8)/secondary ammonium salt[6] and crown ether/paraquat[7] recognition motifs, but only cyclic dimers ([*c*2]daisy chain) were obtained. They also used the "Wittig exchange" of stoppers with [2]rotaxane monomers to construct daisy chain polymers,[8] but still only [*c*2]daisy chains and other configurational [*c*2] and [*c*3] isomers were obtained. Later, Stoddart, Grubbs and co-workers incorporated the [*c*2]daisy chains into polymerization monomers with two functional groups and then polymerized these monomers to produce [*c*2]daisy chain dimer polymers,[9] which showed acid/base-promoted extension/contraction properties. However, the preparation of these monomers was tedious and time-consuming. Recently, Gibson et al. reinvestigated the self-assembly of daisy chain oligomers containing secondary ammonium ion and DB24C8,[10] in which they found the existence of hexamer with an intensity of only 0.27% in MALDI-TOF mass spectrum. Takata et al. also synthesized a daisy chain based on the DB24C8/secondary ammonium salt recognition motif.[11] A [2]rotaxane AB monomer with two functional groups was first synthesized, followed by Sonogashira polycondensation, a daisy chain was got with a molecular weight of 6.85 kDa as determined by GPC, indicating that only 6 to 7 repeating units existed in a single polymer chain. This method contains four steps: threading, blocking, acylative neutralization and polymerization. Later, Harada et al. synthesized a daisy chain using α-CD as the ring component.[12] A cinnamamide-α-CD, which would form polypseudo[2]rotaxane in solution, was first synthesized. After it was blocked by adamantane, a daisy chain was isolated. The MALDI-TOF mass spectrum showed the existence of high-molecular-weight polymers, but most of the products were still low-molecular-weight oligomers. Hadziioannou et al. developed a stepwise approach to synthesize daisy chains,[13] but it included two deprotection reactions and one coupling reaction in each step, which was time-consuming and inconvenient.

As described above, although many groups have devoted efforts to the syntheses of daisy chains, the preparation of high-molecular-weight daisy chains is still a challenge. Herein, we used a formerly reported method,[14] which can be called "threading followed by polymerization", to synthesize a daisy chain conveniently. We synthesized a ring host component (DB24C8)

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with a carbonyl chloride group and a linear guest component, 1,2-bis(pyridinium)ethane, with a hydroxyl group, separately. These two components were put together at very low temperature to minimize the esterification and maximize complexation between them. Then the temperature was gradually raised up to make the two functional groups react fully. Finally, the daisy chain was isolated by simple precipitation.

2. EXPERIMENTAL SECTION

Materials and Methods. Thionyl chloride, 3,5-lutidine, 4,4′-bipyridine, 2-iodoethanol, triethylamine, 1,2-dibromoethane, and ammonium hexafluorophosphate (NH_4PF_6) were reagent grade and used as received. DB24C8 acid **1** was synthesized according to a literature procedure.[15] DMF and acetone were dried according to the typical procedures described in the literature. The other solvents were employed as purchased.

NMR spectra were collected on a Bruker AVANCE DMX-500 spectrometer or a Varian Unity INOVA-400 spectrometer with TMS as the internal standard. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-T FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

Viscosity measurements were carried out with Ubbelohde micro dilutionviscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 30 °C in acetonitrile.

Molecular weight distributions were measured on a conventional gel permeation chromatography (GPC) system equipped with a Waters 1525 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR1, HR2 and HR4, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using a DMF solution as the eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards.

Thermogravimetric analysis (TGA) of the polymer was recorded on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 20 °C/min from 20 to 600 °C.

Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature.

Compound 2. 3,5-Lutidine (6.72 g, 62.7 mmol) was dissolved in 1,2-dibromoethane (150 mL) and heated at reflux overnight. After cooling, the solution was filtered and washed by 1,2-dibromoethane (50 mL × 3). The precipitate was dissolved in hot water, and then saturated NH_4PF_6 aqueous solution was added until no further precipitation was observed. The precipitate was collected, washed by water (100 mL × 3) and then dried under vacuum to give compound **2** (19.4 g, 86%) as a while solid; mp 141.3−144.0 °C. ^1H NMR (400 MHz, CD_3COCD_3, room temperature) δ (ppm): 8.90 (s, 2H), 8.47 (s, 1H), 5.17 (t, J = 4.6 Hz, 2H), 4.18 (t, J = 4.6 Hz, 2H), 2.61 (s, 6H). ^{13}C NMR (100 MHz, CD_3COCD_3, room temperature) δ (ppm): 147.6, 141.9, 138.9, 61.8, 30.1, 17.3. LRESIMS: m/z 214.1 $[M - PF_6]^+$ (100%). HRESIMS: m/z calcd for $[M - PF_6]^+$ $C_9H_{13}BrN^+$, 214.0226; found, 214.0235; error, 4.2 ppm.

Compound 3. An ethanol solution (100 mL) of **2** (3.60 g, 10.0 mmol) and 4,4′-bipyridine (4.69 g, 30.0 mmol) was heated at reflux for 3 days. After cooling, the solution was filtered and washed with ether (100 mL × 3), yielding a gray solid which was purified by flash column chromatography (SiO_2: CH_3OH: 2 M NH_4Cl: CH_3NO_2 = 40:2:1) to give a crude product. The crude product was dissolved in water and ion exchanged with saturated aqueous NH_4PF_6 solution to give compound **3** as a white solid (2.43 g, 42%); mp >200 °C (dec.). ^1H NMR (400 MHz, CD_3CN, room temperature) δ (ppm): 8.87 (d, J = 4.0 Hz, 2H), 8.69 (d, J = 6.0 Hz, 2H), 8.38 (d, J = 6.0 Hz, 2H), 8.35 (d, J = 4.4 Hz, 2H), 8.27 (t, J = 4.0 Hz, 1H), 7.83 (d, J = 4.4 Hz, 2H), 5.11 (t, J = 6.4 Hz, 2H), 5.01 (t, J = 6.4 Hz, 2H), 2.47 (s, 6H). ^{13}C NMR (100 MHz, CD_3COCD_3, room temperature) δ (ppm): 155.3, 151.1, 148.4, 146.0, 142.2, 141.1, 139.9, 126.6, 60.2, 17.4. LRESIMS: m/z 145.6 $[M - 2PF_6]^{2+}$ (100%), 436.2 $[M - PF_6]^+$ (20.8%). HRESIMS: m/z calcd for $[M - PF_6]^+$ $C_{19}H_{21}F_6N_3P^+$, 436.1372; found, 436.1371; error, −0.2 ppm.

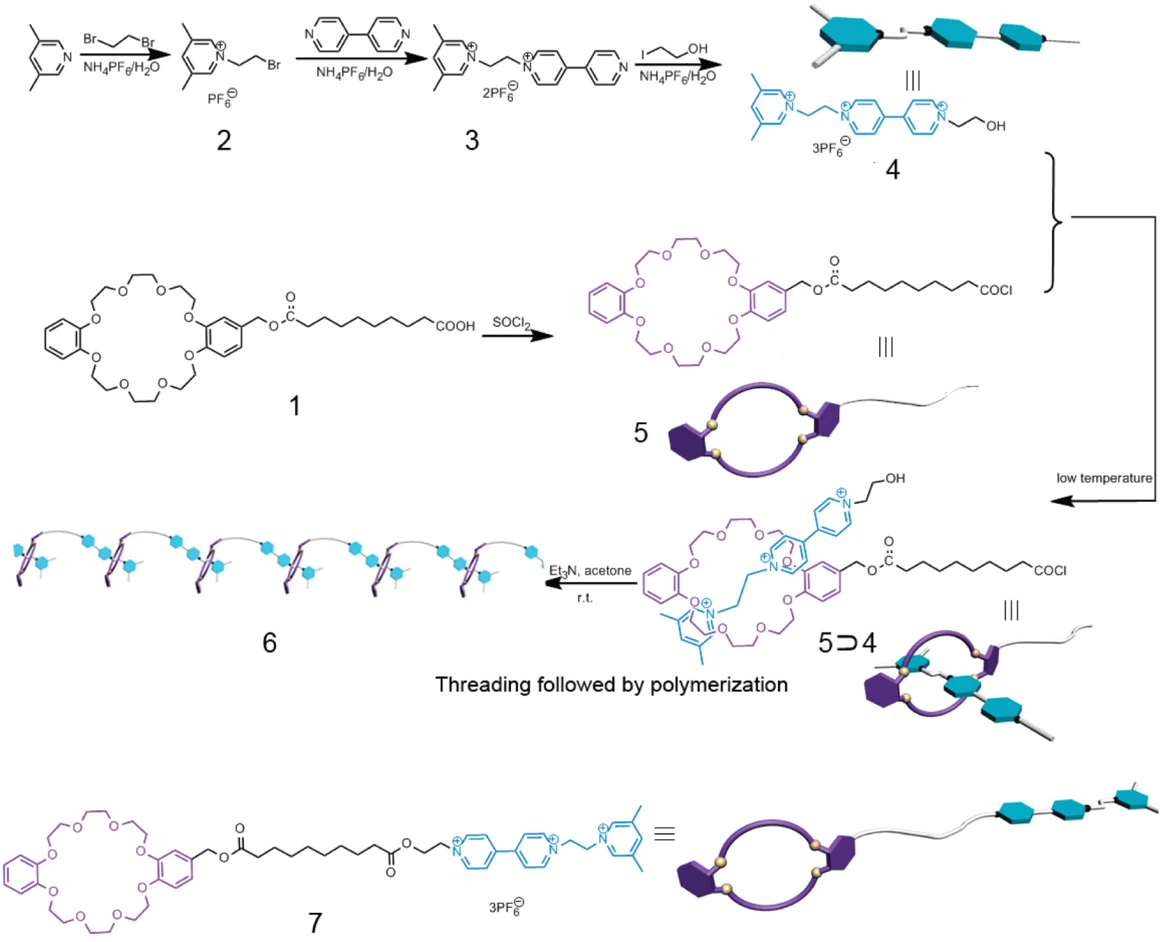
Compound 4. An acetonitrile solution (100 mL) of **3** (1.16 g, 2.0 mmol) and 2-iodoethanol (0.68 g, 4.0 mmol) was heated at reflux for 3 days. After cooling, the solution was filtered and washed with ether (100 mL × 3) to yield a yellow solid, which was purified by flash column chromatography (SiO_2: CH_3OH: 2 M NH_4Cl: CH_3NO_2 = 25:2:1) to give a crude product. The crude product was dissolved in water and ion exchanged with saturated aqueous NH_4PF_6 solution to give compound **4** as a white solid (0.86 g, 56%); mp 219.5−222.0 °C. ^1H NMR (400 MHz, CD_3COCD_3, room temperature) δ (ppm): 9.39 (t, J = 5.2 Hz, 4H), 8.89 (d, J = 5.2 Hz, 4H), 8.80 (d, J = 6.0 Hz, 2H), 8.49 (t, J = 6.0 Hz, 1H), 5.75 (t, J = 6.4 Hz, 2H), 5.56 (t, J = 6.4 Hz, 2H), 5.06 (t, J = 4.4 Hz, 2H), 4.21(t, J = 4.4 Hz, 2H), 2.56 (s, 6H). ^{13}C NMR (100 MHz, CD_3COCD_3, room temperature) δ (ppm): 151.1, 148.4, 146.0, 142.2, 139.9, 126.6, 60.2, 17.4. LRESIMS: 240.6 $[M - 2PF_6]^{2+}$ (100%), 626.1 $[M - PF_6]^+$ (65.3%). HRESIMS: m/z calcd for $[M - PF_6]^+$ $C_{21}H_{26}F_{12}N_3OP_2^+$, 626.1354; found, 626.1352; error, −0.3 ppm.

Polymer 6. DB24C8 acid **1** (330 mg, 0.50 mmol) and thionyl chloride (5.0 mL, 0.070 mol) were stirred at reflux for 24 h and the superfluous thionyl chloride was removed under reduced pressure.[14] Acid chloride **5** was not purified, but directly used in the next step. Acetone (2.0 mL) was added to dissolve the acid chloride and the solution was cooled to −70 °C. Then **4** (368 mg, 0.50 mmol) was added to form a pseudorotaxane-type heteroditopic monomer $\mathbf{5}\supset\mathbf{4}$ *in situ*. The orange solution was stirred for 30 min at −70 °C and gradually warmed to −50 °C. Then triethylamine (0.30 mL, 2.2 mmol) was added dropwise at −50 °C. The orange solution was allowed to warm by the removal of the cooling bath and stirred at room temperature for 2 days. Then the mixture was concentrated under reduced pressure and the residue was dissolved in DMSO (6.0 mL). The solution was then poured into a saturated aqueous solution of NH_4PF_6 to give a brown solid. The product was reprecipitated three times in this way. The final product was washed with water and ether. After drying under vacuum at 65 °C for 24 h, daisy chain **6** (460 mg, 65%) was afforded as a brown solid.

3. RESULTS AND DISCUSION

Design and Synthesis. Our strategy to prepare daisy chain is shown in Scheme 1. It is based on the well-studied DB24C8/1,2-bis(pyridinium)ethane recognition motif established by Loeb et al.[16] The monofunctional DB24C8 acid **1** was converted by reacting with thionyl chloride into acid chloride **5**, which was mixed with 1,2-bis(pyridinium)ethane derivative **4** in acetone (0.25 M for each compound) at −70 °C to minimize esterification and maximize complexation, forming a pseudorotaxane-type AB monomer $\mathbf{5}\supset\mathbf{4}$; then the temperature was allowed to rise slowly. At −50 °C, triethylamine was added to catalyze esterification and later the reaction system was warmed to room temperature. A daisy chain was produced from the *in situ* generated AB pseudorotaxane $\mathbf{5}\supset\mathbf{4}$. After the initial chloride counterions were exchanged to PF_6 counterions with aqueous NH_4PF_6, any unreacted monomers and side products were removed by the precipitation from DMSO, a dissociating solvent, into water, yielding daisy chain **6** as a brown solid; the color of the polymer was due to the charge transfer interactions between the electron-rich benzene rings of the DB24C8 moiety and

Scheme 1. Schematic Illustration of the Preparation of Daisy Chain 6 from Polycondensation of a Dynamic Difunctional AB Pseudorotaxane Monomer 5⊃4



the electron-poor pyridinium rings of the 1,2-bis(pyridinium)-ethane unit.

Proton NMR Characterization. The complexation between crown ether derivative **1** and 1,2-bis(pyridinium)ethane derivative **4** was first investigated as a model system. The association constant K_a of **1**⊃**4** was determined by a UV−vis titration method to be 870 (±70) M^{-1} in acetone (Figure S12, Supporting Information). As shown in Figure 1, the proton NMR spectrum of a 1:1 mixture of **1** and **4** shows only one set of peaks for the complex between **1** and **4**, indicating fast-exchange complexation on the proton NMR time scale.[16e] Obvious chemical shift changes were observed after mixing, indicating good interactions between host **1** and guest **4**. α-Pyridinium protons H_1 and H_5 moved downfield while β-pyridinium protons H_3 and H_4 and γ-pyridinium protons H_6 shifted upfield. Methylene protons H_7 and H_8 moved downfield while no obvious chemical shift changes were observed for methylene protons H_9 and H_{10}. Ethyleneoxy protons H_b, H_c, and H_d of DB24C8 acid **1** shifted downfield. All of these chemical shift changes indicated that the DB24C8 ring of **1** bound **4** at the 1,2-bis(pyridinium)ethane part. The synthesis of daisy chain **6** was carried out at a relatively low temperature and high concentration to improve the complexation between **5** and **4**.

Proton NMR spectra of crown ether acid **1**, daisy chain **6** and 1,2-bis(pyridinium)ethane derivative **4** in acetone-d_6 and DMSO-d_6 are given in Figures 2 and 3, respectively. The broad peaks of daisy chain **6** are typical characteristics of polymers. Chemical shift changes of daisy chain **6** in acetone-d_6 (Figure 2) are similar to the chemical shift changes after mixing equimolar **1** and **4** (Figure 1). α-Pyridinium protons H_1 and H_5 moved downfield while β-pyridinium H_3 and H_4 and γ-pyridinium protons H_6 shifted upfield. Methylene protons H_7 and H_8 moved downfield. It was worth mentioning that downshift changes were also observed for methylene protons H_9 and H_{10} due to the esterification reaction. These evidence indicated the formation of daisy chain and the DB24C8 ring located at the 1,2-bis(pyridinium)ethane in acetone-d_6.

In DMSO-d_6 (Figure 3), almost no chemical shift changes were observed for the protons of the guest **4** except for methylene protons H_9 and H_{10}, whose shifts were due to the esterification of hydroxyls on **1**, indicating that the interactions between DB24C8 ring and 1,2-bis(pyridinium)ethane units were greatly weakened in DMSO. However, obvious chemical shift changes could also be noticed for the host **1**. The aromatic protons H_{Ar} moved downfield and the methylene protons H_a of **1** moved upfield greatly. What is more, signals for the ether and long alkyl chain units showed some obvious shifts: ethyleneoxy protons H_b moved upfield while alkyl protons H_e and H_f changed into one set of peaks. The chemical shift changes in DMSO indicated the formation of mechanically interlocked polymers (daisy chain)

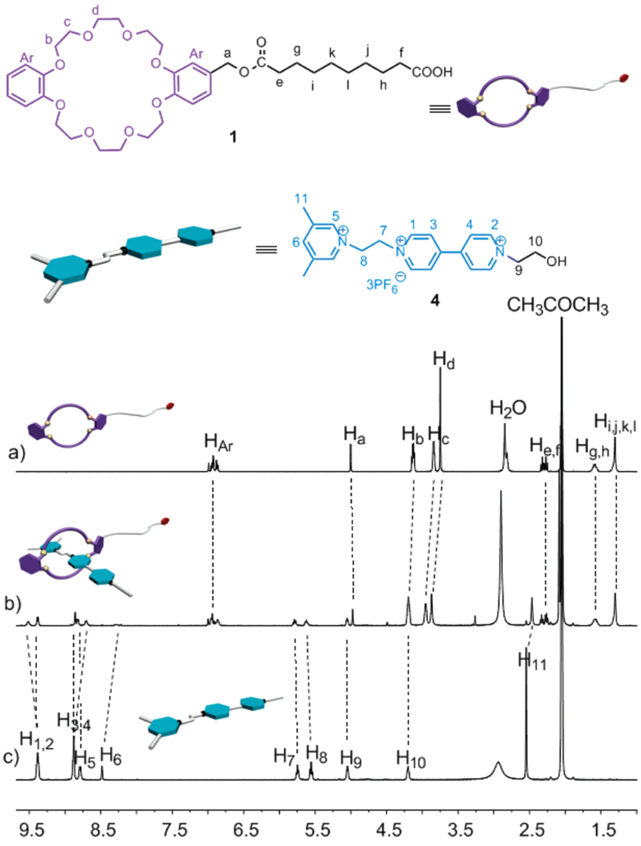


Figure 1. Proton NMR spectra (400 MHz, acetone-d_6, 25 °C) of **1** (a, top), a 1:1 equimolar mixture of 4.00 mM **1** and **4** (b, middle), and **4** (c, bottom).

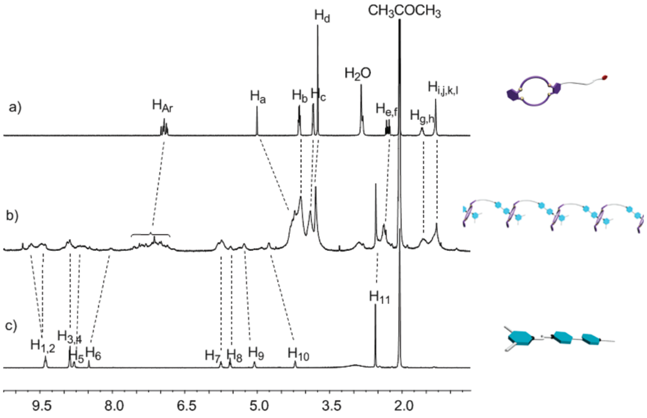


Figure 2. Proton NMR spectra (400 MHz, acetone-d_6, 25 °C) of **1** (a, top), daisy chain **6** (b, middle), and **4** (c, bottom).

because the axle 1,2-bis(pyridinium)ethane component was blocked by bulky 3,5-dimethylpyridine units, making it impossible for the dethreading process to take place.

H−H COSY NMR. Full H−H COSY spectra of daisy chain **6** in acetone-d_6 and DMSO-d_6 are shown in Figures 4 and 5, respectively. Correlated peaks were observed for α-pyridinium protons H_2 and β-pyridinium H_4, methylene protons H_9 and H_{10}, alkyl protons $H_{e,f}$ and $H_{g,h}$, $H_{g,h}$ and $H_{i,j}$, and ethyleneoxy protons H_b and H_c both in acetone-d_6 and DMSO-d_6. The similar correlated signals in the two different solvents were due to the mechanically interlocked nature of the daisy chain.

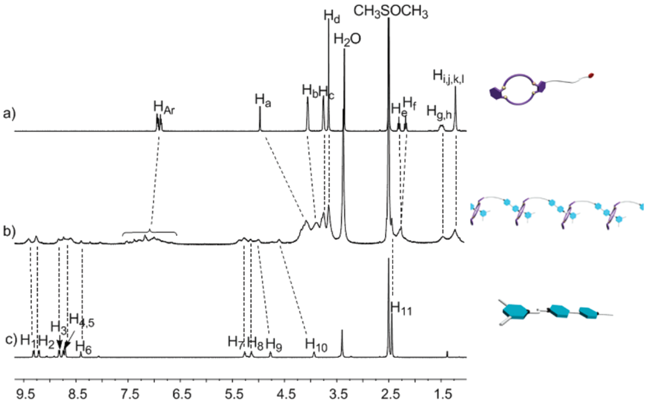


Figure 3. Proton NMR spectra (400 MHz, DMSO-d_6, 25 °C) of **1** (a, top), daisy chain **6** (b, middle), and **4** (c, bottom).

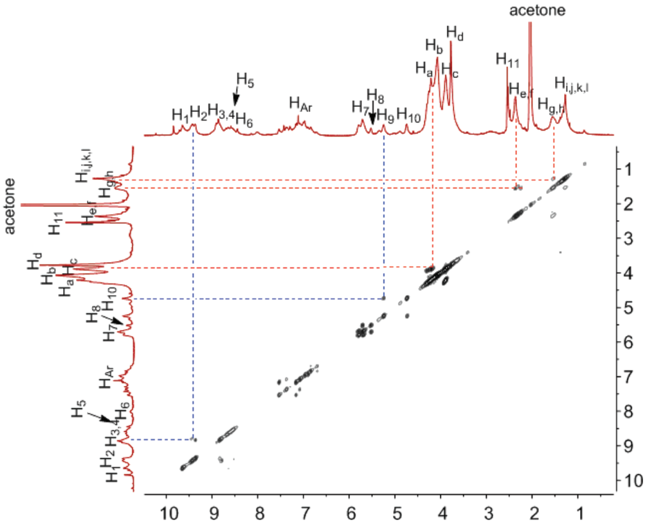


Figure 4. Full H−H COSY spectrum of daisy chain **6** in acetone-d_6.

2-D NOESY NMR. 2-D NOESY NMR spectra of daisy chain **6** in acetone-d_6 and DMSO-d_6 (Figures 6, 7, S10 and S11 (Supporting Information)) are also very similar due to the mechanically interlocked nature of the daisy chain. Ethyleneoxy protons H_b on DB24C8 units are correlated with the α-pyridinium protons H_1, β-pyridinium protons H_3, and the methylene protons H_7 on the 1,2-bis(pyridinium)ethane units, confirming the formation of the DB24C8/1,2-bis(pyridinium)ethane inclusion complex in the daisy chain backbone. NOE correlation signals were also found for β-pyridinium protons $H_{3,4}$ and alkyl protons $H_{e,f}$, indicating that the formation of threaded structures make the two sets of protons very close in space.

Polymer Characterization. Using conventional calculations with polystyrene as the standard and a DMF solution as the solvent, M_n and polydispersity of daisy chain **6** from GPC analysis (Supporting Information, Figure S13) were estimated to be 64 kDa and 1.5, respectively. This measured M_n value corresponds to about 45 repeating units **7** (Scheme 1) in a single polymer chain. The daisy chain **6** is clearly of high molecular weight.

Dynamic laser light scattering characterization of **6** was also carried out. The hydrodynamic diameter of **6** in dilute acetonitrile

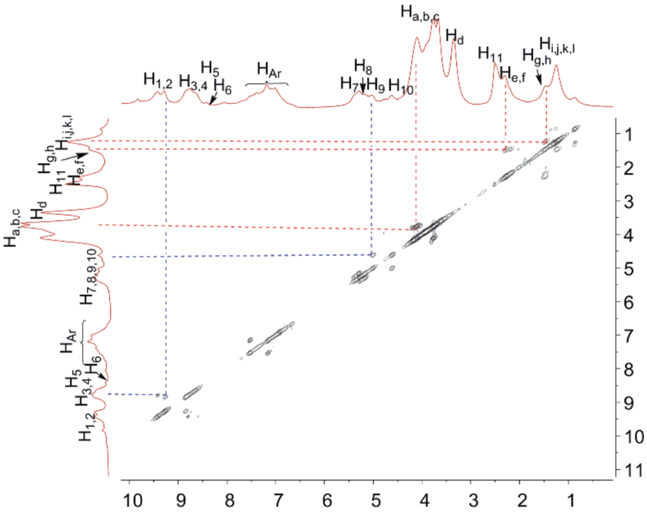


Figure 5. Full H−H COSY spectrum of daisy chain **6** in DMSO-d_6.

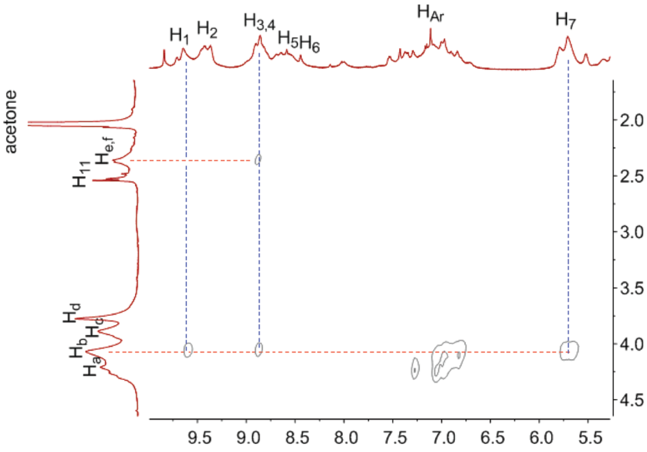


Figure 6. Partial NOESY spectrum of daisy chain **6** in acetone-d_6.

solution was determined to be about 250 nm, which further confirmed the considerable large size of daisy chain **6**.

UV−vis absorbance data of 2.00 mmol/L **1**, 2.00 mmol/L **4**, 2.00 mmol/L **1⊃4** and 2.00 mmol/L **6** (concentration of repeating unit **7**) (Figure S14, Supporting Information) in acetone were also collected. The absorbance intensity of the daisy chain **6** was greatly increased compared with that of **1⊃4**, which could also confirm the formation of polymers because the formation of daisy chain would change the intermolecular interactions between **1** and **4** into intramolecular interactions in the daisy chain backbones, hence increasing the absorbance intensity of the polymer.[17]

We also measured the viscosity (Figure S15, Supporting Information) of daisy chain **6** to investigate its polymer properties. The intrinsic viscosity, $[\eta]$, of **6** in acetonitrile was measured to be 0.029 dL/g at 30 °C. This rather low intrinsic viscosity value can be at least partly ascribed to its polyelectrolyte nature.[18] The low intrinsic viscosity of daisy chain **6** does not imply a low molar mass but rather reflects its assembled structures in solution.

The thermal stability of daisy chain **6** was investigated by thermogravimetric analysis (Figure S16, Supporting Information). About 17% weight loss was observed up to 270 °C, which corresponds to the linked alkyl groups in daisy chain **6**. Upon further heating to 400 °C, the weight for crown ethers was lost, corresponding to about 32% weight. At last the bispyridinium units and the counterions were left after 400 °C, which account for about 51% weight of **6**.

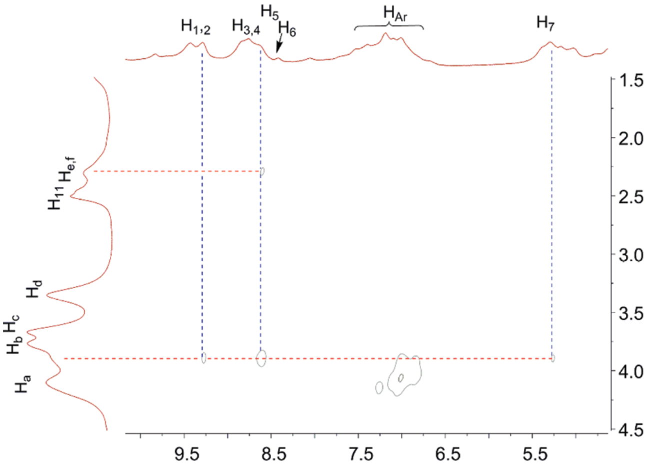


Figure 7. Partial NOESY spectrum of daisy chain **6** in DMSO-d_6.

4. CONCLUSIONS

In summary, we constructed a daisy chain using the "threading-followed-by-polymerization" approach based on the DB24C8/1,2-bis(pyridinium)ethane recognition motif. It has a molecular weight of M_n 64 kDa, indicating that 45 repeating units existed in a single polymer chain. It is another example to demonstrate that dynamic supramolecular monomers (monomers with different parts linked by noncovalent bonds) can be used to construct mechanically interlocked polymers conveniently.[14] The synthesis and study of daisy chain, the most fundamental structure in mechanically interlocked polymers or mechanical bonded macromolecules, will undoubtedly shed light on understanding and tuning the properties of mechanical bonds in complicated polymer environment. Furthermore, this daisy-chain-type structure also enables some potential applications in smart nanomaterials and drug delivery systems based on the relative movements between the ring and axle components.[9]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Characterizations, NOESY spectra, determination of the association constant, GPC analysis, UV/vis data, a viscosity study, and thermogravimetric analysis scans. This material is available free of charge via the Internet at http://pubs.acs.org.

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