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Synthesis of Main-Chain-Type Polyrotaxanes by New Click Polymerization Using Homoditopic Nitrile *N*-Oxides via Rotaxanation−Polymerization Protocol

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ABSTRACT: Main-chain-type poly[2]rotaxanes (**9** and **12**) and poly[3]rotaxanes (**10** and **13**) were synthesized by a new click polymerization using unstable and stable homoditopic nitrile *N*-oxides according to rotaxanation and polymerization protocol. Rotaxane monomers were prepared from ethynyl-functionalized crown ether and *sec*-ammonium salt via the typical urethane end-capping protocol. The homoditopic nitrile *N*-oxide **8′** was generated *in situ* through the reaction of the corresponding hydroxamoyl chloride **8** with molecular sieves 4 Å. The click polymerization of diethynyl-functionalized [2]rotaxane **5** and [3]rotaxane monomer **7** with **8′** efficiently proceeded in the absence of a catalyst to afford well-defined polyrotaxanes **9** and **10** containing a polyisoxazole backbone in high yields. The polymerization of a newly developed kinetically stabilized homoditopic nitrile *N*-oxide **11** with rotaxane monomers yielded well-defined polyrotaxanes **12** and **13** in high yields under similar conditions. The structures of poly[2]rotaxanes (**9** and **12**) and poly[3]rotaxanes (**10** and **13**) were confirmed by ^{1}H NMR, SEC, and IR analyses. The properties of polyrotaxanes such as solubility and thermal stability were evaluated. These polyrotaxanes showed relatively high thermal stability and good film-forming property based on their good solubility toward ordinary organic solvents.

Introduction

Polyrotaxane, a new class of polymer characterized by the mechanical linkage of its components, shows unique physical, chemical, mechanical, and rheological properties.[1−17] Most polyrotaxanes prepared so far are comprised of cyclodextrines[12,18−20] and crown ethers as the wheel components in addition to linear polymers.[21,22] A feature of crown ether-based polyrotaxanes is that they are structure-definite; however, the polyrotaxanes need *sec*-ammonium station in their construction. We have extensively studied the synthesis of main-chain-type[23,24] and side-chain-type polyrotaxanes[25,26] using structure-definite rotaxane monomers consisting of crown ether and ammonium salt. Among crown-ether-based main-chain-type polyrotaxanes, those made by the connection of the wheel components of [2]rotaxanes (Scheme 1) are a fascinating class of polyrotaxanes due to their unique structure, e.g., capable of leading to "graft polyrotaxane",[19c] possessing a polymer axle component. There are two approaches to synthesize the main-chain-type polyrotaxane: one undergoes through initial rotaxanation followed by its polymerization (route A), and the other involves initial polymerization of the wheel followed by rotaxanation of the resulting polymer (route B), as shown in Scheme 1. Especially, the rotaxanation−polymerization protocol (route A) seems a very useful approach to the preparation of structure-definite polyrotaxanes using ditopic [2]rotaxane monomer. Using this protocol, we have synthesized main-chain-type poly[2]rotaxanes[27] and poly[3]rotaxanes[28] by polycondensations via the Mizoroki−Heck coupling[29] of divinyl-functionalized rotaxanes with dihaloarenes. Although these syntheses proceeded very efficiently, they required somewhat skilled technique and several catalysts. Construction of highly sophisticated supramolecular systems like these polyrotaxanes strongly requires viable means of powerful, highly reliable, and selective reactions.[30−34] One of the best solutions is click chemistry[35] based on the Huisgen dipolar cycloaddition of azides and alkynes that has recently generated particular interest as a powerful synthetic tool for molecular integration.[36] However, the explosiveness of the multitopic azides in addition to the requirement of Cu(I) catalyst lead to some limitations to their use.[37] Recognizing these issues, we noted the potential usefulness of nitrile *N*-oxide as the substitute for azide,[28−41] which allows the efficient [2 + 3] cycloaddition with not only alkynes but also alkenes and nitriles to selectively give the corresponding heterocycles.[42] We have recently reported a new click polymerization exploiting in situ generated homoditopic nitrile *N*-oxide with olefinic and acetylenic monomers, which features mild conditions, simple procedure, easy work-up, and applicability to further transformations.[43−45] Recently, we have prepared a stable nitrile *N*-oxide undergoing easy polymerization with ditopic acetylenes. Thus, the polycycloaddition using ditopic nitrile *N*-oxide is expected to render the powerful and highly reliable entry to the construction of sophisticated supramolecular architectures. Herein, we describe the synthesis of well-defined main-chain-type polyrotaxanes by the click polymerization of diethynyl-functionalized [2]- and [3]rotaxanes with unstable and stable homoditopic nitrile *N*-oxides (Scheme 2).

Experimental Section

Materials. CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves 4 Å (MS 4 Å). Anhydrous $CHCl_3$ (Aldrich Co., Ltd.) was used as received. Diformyl(crown ether) **A** was prepared from dibenzo-24-crown-8 ether (DB24C8) according to our previously reported method.[46,47] Monoformyl(crown ether)

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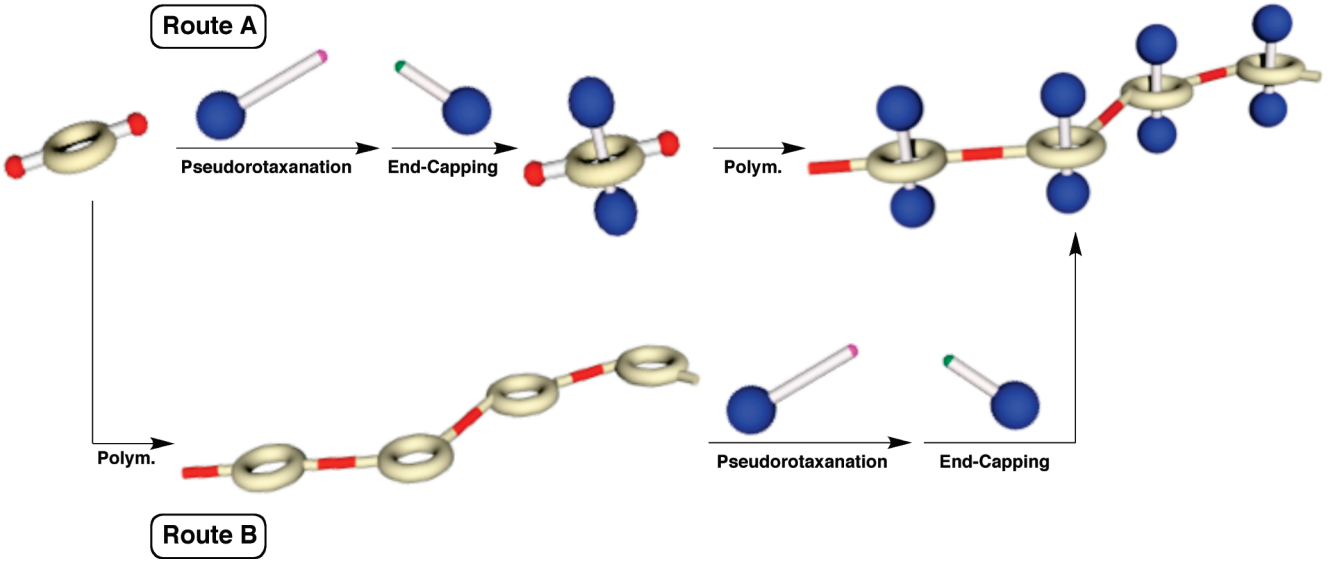
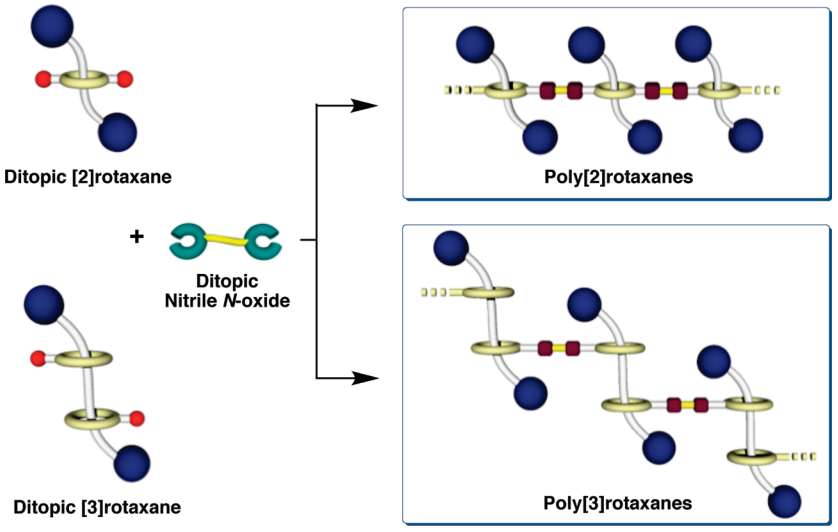
Scheme 1. Synthetic Strategy of Main-Chain-Type Polyrotaxane



Scheme 2. Schematic Representation of Click Polymerization of Ditopic [2]- and [3]Rotaxane Monomers Using Ditopic Nitrile *N*-Oxide



C was also prepared by a similar method.[47] Other commercially available solvents and reagents were used without further purifications except as noted below.

Measurement. ^{1}H NMR spectra were recorded on a JEOL AL-400 NMR spectrometer (400 MHz) in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL AL-400 NMR spectrometer operating at 100 MHz. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Preparative gel permeation chromatography (GPC) was carried out by a JAI HPLC LC-918 system equipped with two consecutive linear polystyrene gel columns (JASCO Megapack-Gel 201C, JAI JAIGEL-1H). Molecular weight and its distribution were estimated by size exclusion chromatography (SEC) on a JASCO HSS-1500 system equipped with consecutive TOSOH TSKgel GMHXL and G5000HXL eluted with $CHCl_3$ at a flow rate of 1.0 mL/min calibrated by polystyrene standards. DSC was performed on a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under a N_2 atmosphere at a flow rate of 50 mL/min to determine the glass transition temperature T_g. Thermogravimetry (TG) was performed on a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under a N_2 atmosphere (flow rate of 50 mL/min) to determine the decomposition temperature T_{d5} at which 5% weight loss was observed. High-resolution mass spectra (FAB-HRMS) were taken by an ICP-MS (Seiko Instruments, SPQ-9000) at the Center for Advanced Materials Analysis, Tokyo Institute of Technology, on request.

Synthesis of [2]Rotaxane (4). Axle component **2** (442 mg, 1.10 mmol) was dissolved with CH_2Cl_2 (4 mL) and acetonitrile (200 μL). The solution of axle component was predried over $CaSO_4$ (800 mg) at room temperature for 1 h. Diethynyl(crown ether) **1** (454 mg, 0.91 mmol) was added to the solution of axle component and stirred for 12 h. 3,5-Dimethylphenyl isocyanate (137 μL, 2.73 mmol) and dibutyltin dilaurate (104 μL, 0.16 mmol) were added to the mixture. The resulting mixture was stirred for 6 h and concentrated in vacuo. The reaction mixture was purified with preparative GPC (eluent: $CHCl_3$) to give [2]rotaxane **4** as colorless solid (658 mg, 69.2%); mp 113.7−115.2 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.36 (brd, NH), 7.24−7.20 (m, ArH, 2H), 7.14 (d, J = 8.1 Hz, ArH, 2H), 6.98−6.94 (m, ArH, 4H), 6.78−6.75 (m, ArH, 6H), 6.63−6.59 (m, ArH, 3H), 4.99 (s, 2H), 4.57 (t, J = 6.9 Hz, 2H), 4.41 (t, J = 6.9 Hz, 2H), 3.99−3.96 (m, 8H), 3.69−3.65 (m, 8H), 3.44−3.42 (m, 8H), 2.98 (s, 2H), 2.18 (s, 6H), 2.08 ppm (s, 6H). ^{13}C NMR (100 MHz, 298 K, CD_2Cl_2): δ 153.5, 148.6, 147.4, 139.1, 138.9, 138.5, 131.8, 131.7, 131.1, 129.7, 128.3,

Table 1. Click Polymerization of [2]Rotaxane 5 and [3]Rotaxane 7 with Homoditopic Nitrile *N*-Oxides 8′ and 11[a]

entry	monomer	nitrile *N*-oxide	concn (M)	polymer	yield (%)	M_w[b]	M_n[b]	M_w/M_n[b]	T_g[c] (°C)	T_{d5}[d] (°C)	T_{d10}[d] (°C)
1	**5**	**8′**	0.2	**9**	79	12 000	4300	2.8	64.9	247	278
2	**5**	**8′**	0.5	**9**	96	16 700	6300	2.6	75.4	273	294
3	**5**	**11**	1.0	**12**	87	19 200	9300	2.1	157.3	305	328
4	**7**	**8′**	0.5	**10**	84	6 600	4600	1.4	91.2	265	289
5	**7**	**11**	1.0	**13**	98	11 000	6000	1.8	105.4	284	309
6	**7** + **14**[e]	**8′**	0.5	**15**	98	7 600	6400	1.2	57.8	275	295

[a] Polymerization conditions are indicated in Scheme 6. [b] Estimated by SEC ($CHCl_3$, polystyrene standards). [c] Glass transition temperature was obtained at a heating rate of 10 °C/min under N_2 (flow rate 50 mL/min). [d] 5% and 10% weight loss temperatures were obtained at a heating rate of 10 °C/min under N_2 (flow rate 50 mL/min). [e] The feed ratio of **7**:**15** was 50:50 (mol/mol).

126.9, 126.4, 125.4, 116.7, 116.2, 115.3, 112.5, 83.5, 76.5, 71.2, 70.5, 68.6, 66.1, 53.1, 52.7, 21.5, 21.3 ppm. IR (NaCl) *v*: 3284 (C≡C−H), 2920 (C−H, str, asym), 2877 (C−H, str, sym), 2102 (C≡C) 1723 (C=O, urethane), 841 (P−F, asym), 557 cm^{-1} (P−F, sym). FAB-HRMS, *m*/*z* calcd for $C_{54}H_{63}N_2O_{10}^+$ [M−PF_6^-] 899.4477; found 899.4483.

Synthesis of *N*-Acetylated [2]Rotaxane (5). Triethylamine (67 μL, 0.48 mmol) and acetic anhydride (91 μL, 0.96 mmol) were added to a solution of **4** (100 mg, 0.10 mmol) in CH_3CN (800 μL). The mixture was stirred at 40 °C for 24 h, and the resulting mixture was extracted with CH_2Cl_2. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude **5** was purified by preparative GPC to give **5** (90.4 mg, 96.1%) as colorless solid; mp 93.5−94.8 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.25−8.22 (m, 2H, NH), 7.31−7.24 (m, 2H ArH), 7.09−7.06 (m, 2H, ArH), 6.99−6.88 (m, 8H, ArH), 6.82−6.75 (m, 3H, ArH), 6.55 (d, *J* = 6.6 Hz, 1H, ArH), 5.62 (s, 2H), 4.53−4.47 (m, 2H), 4.32−4.31 (m, 2H), 4.16−4.12 (m, 8H), 3.90−3.74 (m, 8H), 3.50−3.93 (m, 8H), 2.99 (s, 2H), 2.30−2.28 (m, 6H), 2.19−2.14 (m, 9H) ppm. ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 170.9, 153.7, 149.2, 147.9, 139.3, 138.4, 138.1, 137.9, 137.7, 137.2, 136.4, 135.1, 134.2, 128.9, 127.7, 127.4, 126.0, 125.6, 125.3, 123.9, 123.4, 115.2, 113.9, 111.5, 83.7, 75.6, 69.8, 69.4, 68.2, 65.7, 50.4, 47.7, 21.6, 21.2, 21.1 ppm. IR (NaCl) *v*: 3304 (C≡C−H), 2921 (C−H, str, asym), 2880 (C−H, str, sym), 2102 (C≡C), 1725 (C=O, urethane), 1644 cm^{-1} (C=O, amide). FAB-HRMS, *m*/*z* calcd for $C_{56}H_{64}N_2O_{11}$ $[M]^+$ 940.4510; found 940.4538.

Synthesis of [3]Rotaxane (6). Axle component **2** (220 mg, 0.52 mmol) was dissolved in CH_2Cl_2 (3.0 mL) and acetonitrile (300 μL). The solution of **2** was predried over $CaSO_4$ (600 mg) at room temperature for 1 h. Monoethynyl (crown ether) **3** (250 mg, 0.52 mmol) was added to the solution and stirred for 12 h. *m*-Phenylene diisocyanate (45.6 mg, 0.28 mmol) and dibutyltin dilaurate (40 μL) were added to the mixture. The resulting mixture was stirred for 24 h and concentrated under reduced pressure. The reaction mixture was purified with preparative GPC (eluent: $CHCl_3$) to give **6** (377 mg, 76.0%, colorless solid); mp 133.1−134.4 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 7.41 (brd, NH), 7.29−7.24 (m, 4H, ArH), 7.16 (s, 2H, ArH), 7.14 (s, 2H, ArH), 7.13−7.06 (m, 4H, ArH), 6.97 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H, ArH), 6.80−6.75 (m, 12H, ArH) 6.70−6.67 (m, 4H, ArH), 6.63 (d, *J* = 8.8 Hz, 2H, ArH), 4.99 (s, 4H), 4.56 (t, *J* = 6.8 Hz, 4H), 4.41 (t, *J* = 6.8 Hz, 4H), 4.00−3.97 (m, 16H), 3.70−3.66 (m, 16H), 3.41 (s, 16H), 3.00 (s, 2H), 2.06 ppm (s, 12H). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 153.4, 148.25, 147.3, 147.00, 138.3, 131.6, 131.3, 131.2, 130.6, 129.5, 128.0, 126.4, 126.1, 121.6, 115.8, 114.9, 112.6, 112.3, 83.3, 76.4, 70.6, 70.1, 68.3, 52.5, 52.3, 21.1 ppm. IR (NaCl) *v*: 3285 (C≡C−H), 2924 (C−H, str, asym), 2877 (C−H, str, sym), 2102 (C≡C), 1730 (C=O, urethane), 842 (P−F, asym), 558 cm^{-1} (P−F, sym). FAB-HRMS, *m*/*z* Calcd for $C_{94}H_{112}N_4O_{20}^+$ [M−PF_6^-] 1616.7859; found 1616.7870.

Synthesis of *N*-Acetylated [3]Rotaxane (7). [3]Rotaxane **6** (110 mg, 0.06 mmol), triethylamine (41.0 μL, 0.29 mmol), and acetic anhydride (55.0 μL, 0.58 mmol) were dissolved in acetonitrile (800 μL). The resulting mixture was stirred at 40 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2. The resulting mixture was washed with 3 M aqueous HCl and saturated aqueous Na_2CO_3. The organic layer was dried over $MgSO_4$, filtered, evaporated, and dried in vacuo. The crude mixture was purified preparative GPC (eluent: $CHCl_3$) to give **7** as pale yellow solids (89.8 mg, 88.0%); mp 102.3−103.6 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.69 (brd, NH), 7.66−7.41 (m, 4H, ArH), 7.17−7.00 (m, 8H, ArH), 6.92−6.89 (m, 6H, ArH), 6.80 (m, 8H, ArH), 6.74−6.72 (m, 4H, ArH), 6.68 (m, 2H, ArH), 5.42−5.08 (m, 4H), 4.53−4.27 (m, 8H), 4.04−4.02 (m, 16H), 3.79−3.64 (m, 16H), 3.34−3.32 (m, 16H), 2.98 (s, 2H), 2.50−2.28 (m, 12H) 2.20−2.14 ppm (m, 6H). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 171.1, 153.6, 148.3, 148.0, 138.1, 138.0, 137.2, 136.4, 129.1, 129.0, 127.7, 127.5, 126.0, 125.7, 125.2, 124.0, 120.6, 111.9, 111.5, 83.8, 75.7, 69.5, 69.3, 68.2, 68.0, 65.4, 50.4, 47.6, 21.6, 21.2 ppm. IR (NaCl) *v*: 3285 (C≡C−H), 2924 (C−H, str, asym), 2877 (C−H, str, sym), 2102 (C≡C), 1730 (C=O, urethane), 1646 cm^{-1} (C=O, amide). FAB-HRMS, *m*/*z* Calcd for $C_{98}H_{114}N_4O_{22}$ $[M]^+$ 1698.7925; found 1698.8000.

Typical Experimental Procedure for Reaction of Hydroxamoyl Chloride 8 and [2]Rotaxane Monomer 5 (9). Molecular sieve 4 Å (172 mg) was added to a solution of hydroxamoyl chloride **8**[38,39] (22.0 mg, 0.09 mmol) and [2]rotaxane **5** (86.0 mg, 0.09 mmol) in dimethylformaldehyde (DMF: 182 μL) at room temperature. The resulting slurry was stirred at room temperature and 80 °C for 30 min and for 48 h, respectively. The mixture was dissolved in $CHCl_3$ and filtered, and the filtrate precipitated into MeOH. The precipitates were collected by filtration and dried in vacuo to give poly[2]rotaxane **9** (97.0 mg, 96.0%) as a pale yellow solid. **9** (Table 1, entry 2): M_w 16 700; M_n 6300; M_w/M_n 2.6 (estimated by SEC based on PSt standards) T_g 75.4 °C; T_{d5} 273 °C; T_{d10} 294 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.31−8.27 (m, 2H, NH), 7.95 (brd, 1H, ArH), 7.59 (brd, 1H, ArH), 7.39−7.33 (m, 3H, ArH), 6.99−6.75 (m, 13H, ArH), 6.68 (s, 2H, ArH), 6.52−6.51 (m, 1H, ArH), 6.68 (brd, 2H), 4.52−4.37 (m, 4H), 4.26−4.20 (m, 8H), 3.93−3.80 (m, 8H), 3.55−3.43 (m, 8H), 2.24−2.21 (m, 6H), 2.14−2.11 ppm (m, 9H). IR (NaCl) *v*: 2922 (C−H, str, asym), 2878 (C−H, str, sym), 2102 (C≡C), 1635 cm^{-1} (C=O, amide).

The polymerization of **8** with [3]rotaxane monomer **7** was carried out according to the same procedure (Table 1, entries 3 and 4) yielding poly[3]rotaxane **10** (84%) as a pale yellow solid. **10**: M_w 6600; M_n 4600; M_w/M_n 1.4 (estimated by SEC based on PSt standards) T_g 91.2 °C; T_{d5} 265 °C; T_{d10} 289 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.79 (brd, 2H, NH), 7.87−7.52 (m, 4H, ArH), 7.20−7.15 (m, 4H, ArH), 7.00−6.68 (m, 20H, ArH), 6.60 (brd, 2H, ArH), 5.36−5.06 (brd, 4H), 4.45−4.25 (m, 8H), 4.01 (brd, 16H), 3.76 (brd, 4H), 3.33 (brd, 16H), 2.25−2.26 (m, 12H), 2.15−2.05 ppm (m, 6H). IR (NaCl) *v*: 2924 (C−H, str, asym), 2877 (C−H, str, sym), 1727(C=O, urethane), 1644 cm^{-1} (C=O, amide).

Typical Experimental Procedure for Reaction of Nitrile *N*-Oxide 11 and [2]Rotaxane Monomer 5 (12). Nitrile *N*-oxide **11** (49.2 mg 0.085 mmol) was added to a solution of [2]rotaxane **5** (80.0 mg, 0.085 mmol) in $CHCl_3$ (86 μL) at room temperature. The resulting slurry was stirred at 60 °C for 48 h. The mixture was precipitated into cold diethyl ether. The precipitates were collected by filtration and dried in vacuo to give poly[2]rotaxane **12**

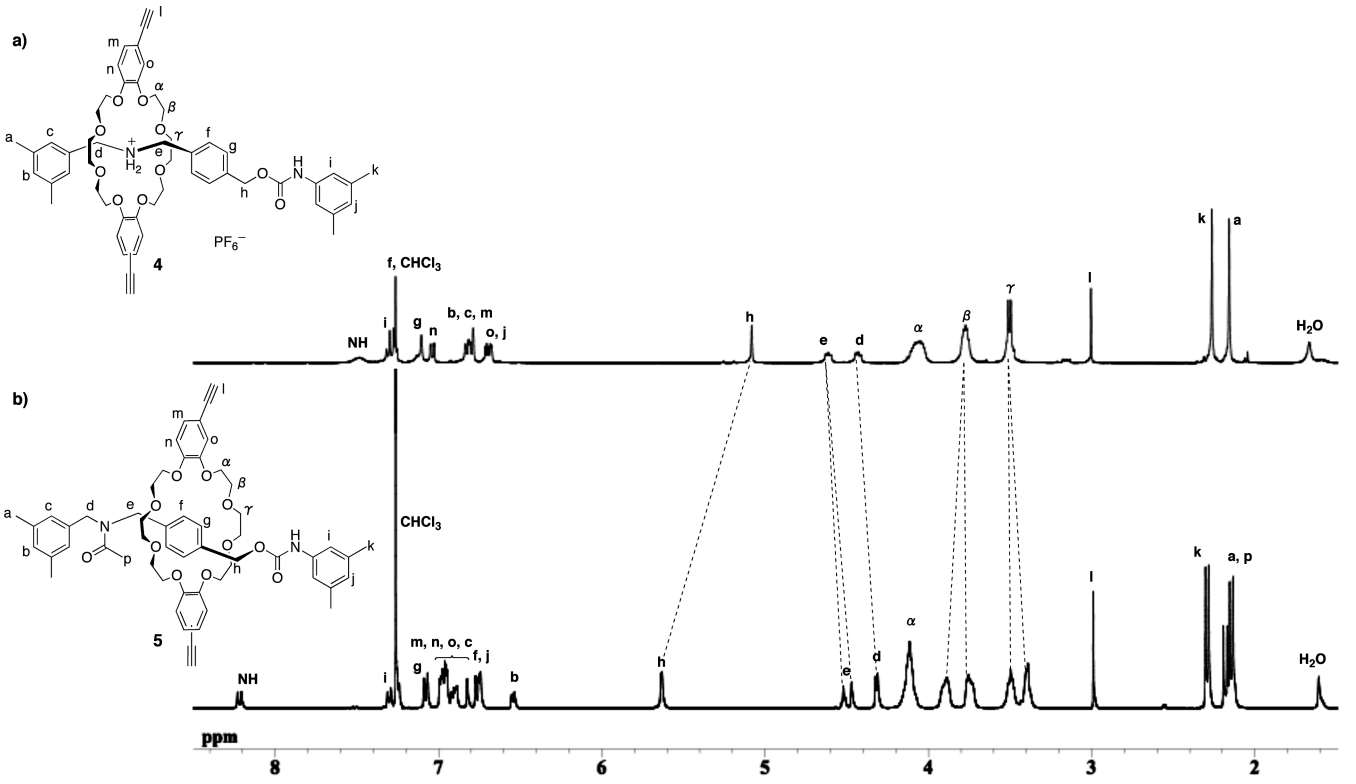
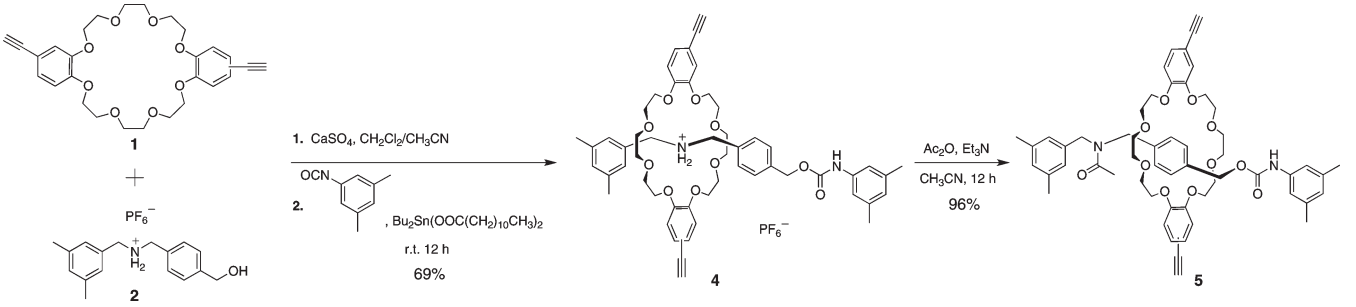


Figure 1. Partial ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of (a) [2]rotaxane **4** and (b) *N*-acetylated [2]rotaxane **5**.

Scheme 3. Synthesis of [2]Rotaxane Monomer 5



(113 mg, 87.4%) as a pale yellow solid. **12**: M_w 19 200; M_n 9300; M_w/M_n 2.1 (estimated by SEC based on PSt standards) T_g 157.3 °C; T_{d5} 305 °C; T_{d10} 328 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.26−8.23 (m, 2H, NH), 7.38−7.34 (m, 4H, ArH), 7.20−7.16 (m, 2H, ArH), 6.99−6.65 (m, 14H, ArH), 6.62 (s, 2H, ArH), 6.49−6.47 (m, 2H, ArH), 5.69−5.67 (m, 2H), 4.50−4.28 (m, 4H), 4.21−4.17 (m, 8H), 3.92−3.83 (m, 14H), 3.51−3.40 (m, 8H), 2.25−2.23 (m, 6H), 2.13−2.08 (m, 21H), 1.69−1.67 ppm (m, 6H). IR (NaCl) *v*: 2923 (C−H, str, asym), 2880 (C−H, str, sym), 1725 (C═O, urethane), 1643 cm^{-1} (C═O, amide).

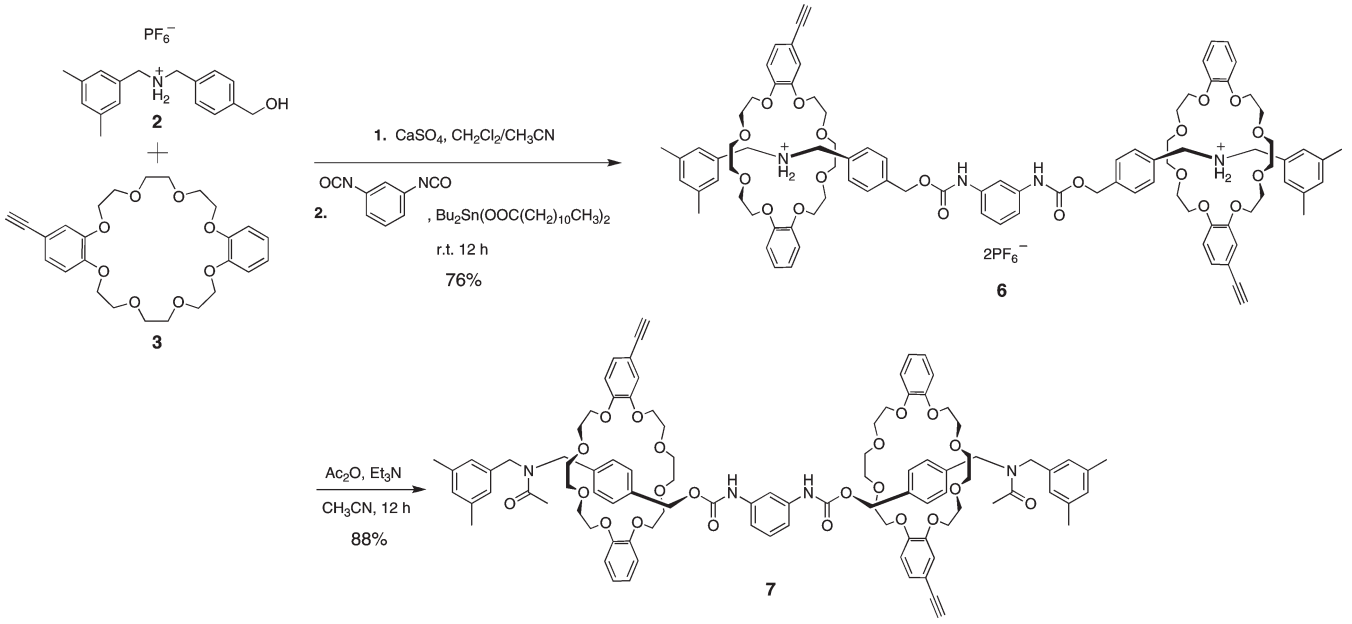
The polymerization of **11** with [3]rotaxane monomer **7** was carried out according to the same procedure (Table 1, entry 6). **13** (98%): M_w 11 000; M_n 6000; M_w/M_n 1.8 (estimated by SEC based on PSt standards) T_g 105.4 °C; T_{d5} 279 °C; T_{d10} 303 °C. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ 8.74−8.72 (m, 2H, NH), 7.77−7.69 (brd, 4H, ArH), 7.38−7.05 (m, 10H, ArH), 6.90−6.87 (m, 10H, ArH), 6.80−6.77 (m, 8H, ArH), 6.71−6.65 (m, 4H, ArH), 6.64−6.62 (m, 2H, ArH), 6.59−6.53 (m, 2H, ArH), 6.12−6.02 (m, 2H, ArH), 5.39−5.04 (m, 4H), 4.51−4.24 (m, 8H), 4.01−3.93 (m, 16H), 3.82 (s, 6H), 3.68−3.65 (m, 16H), 3.34−3.32 (m, 16H), 2.26−2.24 (m, 12H), 2.17−2.08 (m, 18H), 1.76−1.74 ppm (m, 6H). IR (NaCl) *v*: 2923 (C−H, str, asym), 2877 (C−H, str, sym), 1730(C═O, urethane), 1644 cm^{-1} (C═O, amide).

Results and Discussion

Synthesis of Rotaxane Monomers. Diethynyl-functionalized crown ether **1** was prepared from difomyl dibenzo-24-crown-8 ether (DB24C8)[46] by the Corey−Fuchs reaction.[47,48] The treatment of the diformyl crown ether with CBr_4 and Ph_3P in CH_2Cl_2 afforded bis(dibromoethynyl) DB24C8 and was followed by the treatment with BuLi to yield **1** (54%) in two steps. Monoethynyl-functionalized crown ether **3** was synthesized from monoformyl DB24C8 in 86% yield in a similar manner. The structures of **1** and **3** were fully determined by IR, ^{1}H NMR, and ^{13}C NMR spectra.[47]

Scheme 3 shows the synthetic route to [2]rotaxane **4** according to the urethane end-capping protocol[49] of pseudorotaxane, consisting of **1** as a wheel component and *sec*-ammonium salt **2** as an axle component, with 3,5-dimethylphenyl isocyanate in the presence of a catalytic amount of dibutyltin dilaurate (DBTDL). [2]Rotaxane **4** was obtained as colorless solids in 69% yield. Subsequent acetylation reaction of **4** afforded *N*-acetylated [2]rotaxane **5** in 96% yield. The ^{1}H NMR spectrum of **4** (Figure 1a) strongly supported its interlocked structure. In accordance with our previous result,[27] the signals of benzylic protons neighboring

Scheme 4. Synthesis of [3]Rotaxane Monomer 7



sec-ammonium group showed the characteristic split pattern (H_e and H_d), while their chemical shifts were largely downfield-shifted from 3.91 and 3.90 ppm of **2** to 4.57 and 4.41 ppm, respectively, by the rotaxanation to **4**. The downfield shift is clearly explained by the generation of CH−O interaction due to the rotaxanation.[47] Additionally, the methyl protons on the phenyl group of the axle **2** (H_a) was shifted to upfield (from 2.26 to 2.16 ppm) because of the shielding effect of the benzene ring of the crown ether moiety.

The ^{1}H NMR of **5** (Figure 1b) was confirmed by large downfield shift from 5.08 (**4**) to 5.63 ppm of the signal of the ester benzylic methylene protons (H_h), being most indicative of the movement of crown ether wheel from the ammonium group to ester bonding site. Two sets of split signals of the benzylic protons (H_e and H_d) neighboring the nitrogen atom are attributed to the *S-trans* and *S-cis* stereoisomerism of the amide group formed by the acetylation, but not to the diastereotopic relation caused by the asymmetric nitrogen atom. All proton signals including acetylenic and aromatic signals supported the rotaxane structure of **5**.

As shown in Scheme 4, [3]rotaxane **6** was synthesized by treating a mixture of **3** and **2** with *m*-phenylene diisocyanate in presence of a catalytic amount of DBTDL in a similar manner to **4**. [3]Rotaxane **6** was obtained as a colorless solid in 76% yield. The treatment of **6** with acetic anhydride and triethylamine gave *N*-acetylated [3]rotaxane **7** as the bisacetylene-functionalized monomer in 88% yield.[50]

The inspection of ^{1}H NMR spectral data (Figure 2a) confirmed the interlocked structure of **6** from the typical chemical shifts for the rotaxanation (e.g., signals d and e), similar to the case of **4**. Because [3]rotaxane **6** was a mixture of two isomers based on the asymmetry of the wheel **3** originating from the ethynyl substitution, the spectrum of **6** was slightly broadened (Figure 2a).

In the ^{1} H NMR spectrum of **7** (Figure 2b) the typical downfield shifts[28] of signals of h and i by the *N*-acetylation was confirmed similar to the case of [2]rotaxane **5**. This result supported the movement of the crown ether wheel from the ammonium group to urethane part. Moreover, two split signals of benzylic protons (H_e and H_d) neighboring amide nitrogen of **7** showed a similar stereoisomerism as **5**. The structure of **7** was fully determined by the ^{1}H NMR, IR, and high-resolution mass spectra (FAB-HRMS).

Click Polymerization. General scheme for click polymerization of diynes and homoditopic nitrile *N*-oxide (**8′**) which is generated in situ from 1,3-bis(dicarbohydroxamoyl dichloro)benzene (**8**) is illustrated (Scheme 5).[38] The polymerization was carried out by heating an equimolar mixture of **8** and **5** or **7** in the presence of MS 4 Å in DMF for 48 h because MS 4 Å was the most effective base as we previously reported.[43] Poly[2]rotaxane **9** and poly[3]rotaxane **10** were obtained through the polycycloaddition of **8′** with **5** and **7**, respectively (Scheme 6). The results of the polymerization are summarized in Table 1. While the polymerization at a low concentration (0.2 M) of **5** afforded the polymer **9** with a modest molecular weight (entry 1, M_w 12 000, M_w/M_n 2.8) in a slightly low yield (79%), the higher concentration (0.5 M) of **5** provided **9** with a higher molecular weight in a high yield (entry 2, M_w 16 700, M_w/M_n 2.6, 96%).

Meanwhile, the click polymerization of [3]rotaxane **7** under the same conditions (0.5 M) afforded poly[3]rotaxane **10** in a 84% yield, although the molecular weight was rather low (entry 4, M_w 6600, M_w/M_n 1.4).

The polymerization using kinetically stabilized homoditopic nitrile *N*-oxide **11**[45] instead of *in situ*-formed one **8′** (Scheme 6) was carried out by heating a mixture of **11** and **5** or **7** in refluxing $CHCl_3$ for 48 h. Poly[2]rotaxane **12** was obtained as a white solid from **5** in 87% yield (entry 3, M_w 19 200, M_w/M_n 2.1), while poly[3]rotaxane **13** was synthesized from **7** in 98% yield as a white solid with molecular weight of M_w 11 000 (entry 5, M_w/M_n 1.8).

Thus, both poly[2]rotaxane (**9** or **10**) and poly[3]rotaxane (**12** or **13**) were prepared using either unstable (**8′**) or stable (**11**) homoditopic nitrile *N*-oxides with diethynyl-functionalized [2]- and [3]rotaxane monomers (**5** and **7**). It is concluded that the present click polycycloaddition proceeds very smoothly with accompanying C−C bond formation without any catalyst.

The structures of polyrotaxanes (**9**, **10**, **12**, and **13**) were mainly determined by ^{1}H NMR (Figures 3 and 4) and IR spectra (Figures SI-31 and SI-32)[47] in addition to the SEC results. The ^{1}H NMR spectrum of **9** was quite similar to that

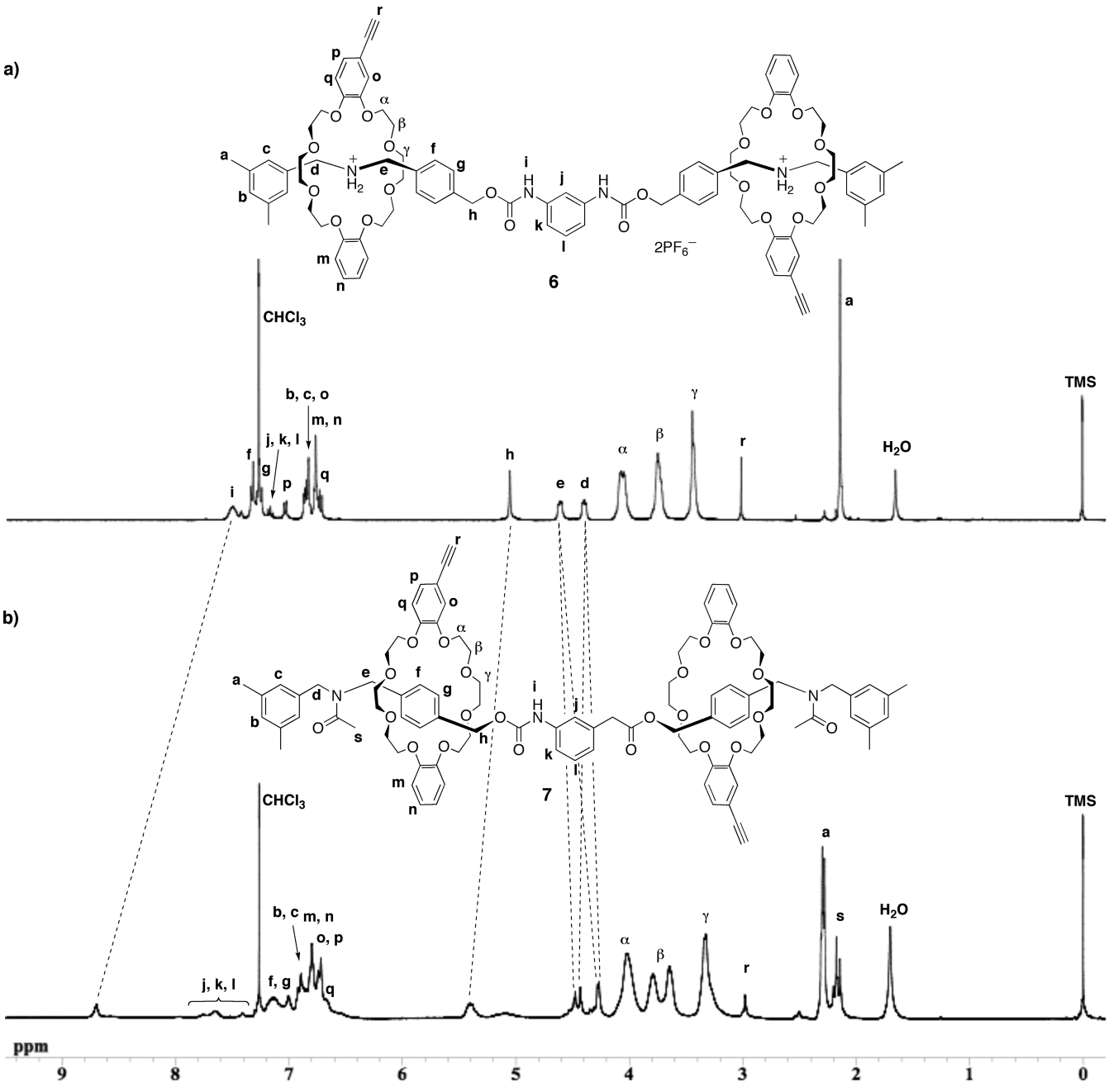
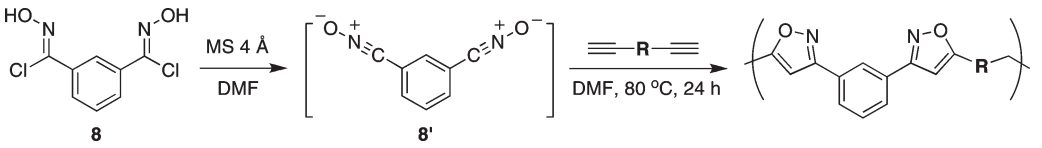


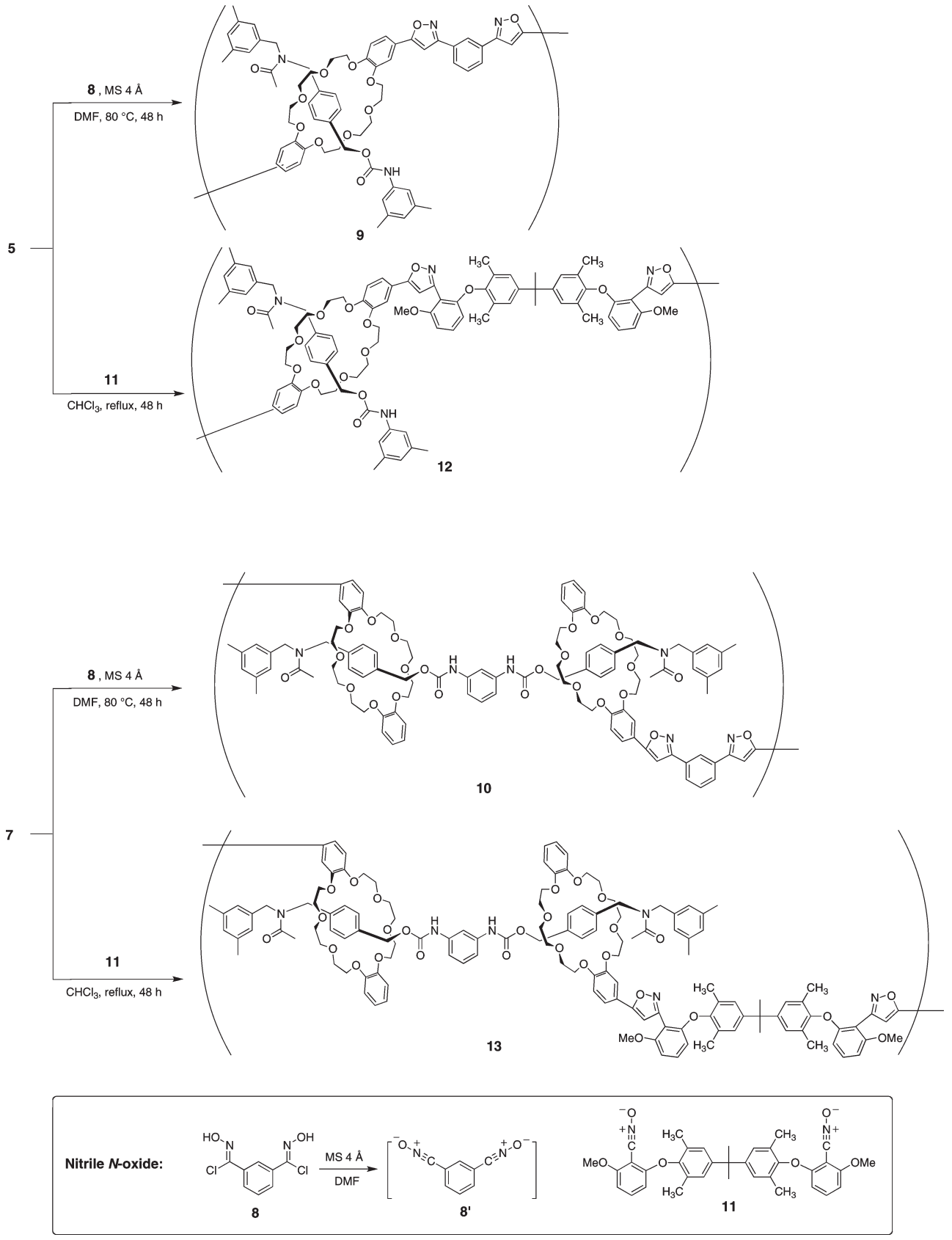
Figure 2. ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of (a) [3]rotaxane **6** and (b) *N*-acetylated [3]rotaxane **7**.

Scheme 5. Synthesis of Polyisoxazole by Polycycloaddition of 8′ Generated from 8 and Diyne Monomer



of [2]rotaxane monomer **5** except for the newly appearing aromatic signals (**r**, **s**, and **t**) and heteroaromatic proton signal **q** at 6.68 ppm, in addition to the disappearance of ethynyl proton signal **l** at 2.99 ppm, although most signals are slightly broadened (Figure 3). Moreover, the IR spectrum of **9** showed the disappearance of characteristic absorption at 2102 cm^{-1} originated from ethynyl group of [2]rotaxane monomer **5** (Figure SI-31).[47] These significant spectral changes along with the SEC result (Table 1, entry 2) suggests the formation of poly[2]rotaxane **9** via the click polymerization of **5** and **8′**.[47] A similar ^{1}H NMR spectral change was observed for **12** to support the proposed structure. The disappearance of ethynyl proton signal **l** of **5** at 2.99 ppm corresponded well to the appearance of the characteristic signal at 6.62 ppm of the isoxazole moiety. Likewise, the IR spectrum of **12** showed the disappearance of ethynyl absorption at 2102 cm^{-1} originating from [3]rotaxane monomer **7** (Figure SI-32).[47]

Scheme 6. Polymerization of [2]Rotaxane Monomer 5 (top) and [3]Rotaxane Monomer 7 (bottom) by Click Polymerization Using Homoditopic Nitrile *N*-Oxides



Although most signals were broadened (Figure 4), the ^{1}H NMR spectra of poly[3]rotaxanes **10** and **13** were similar to that of [3]rotaxane monomer **7**, except for the aromatic (**s**, **t**, and **u**), heteroaromatic **r′**, and ethynyl proton signals **l**. Similar to the spectral change of Figure 3, the disappearance of ethynyl proton signal **l** of **5** at 2.98 ppm was consistent with

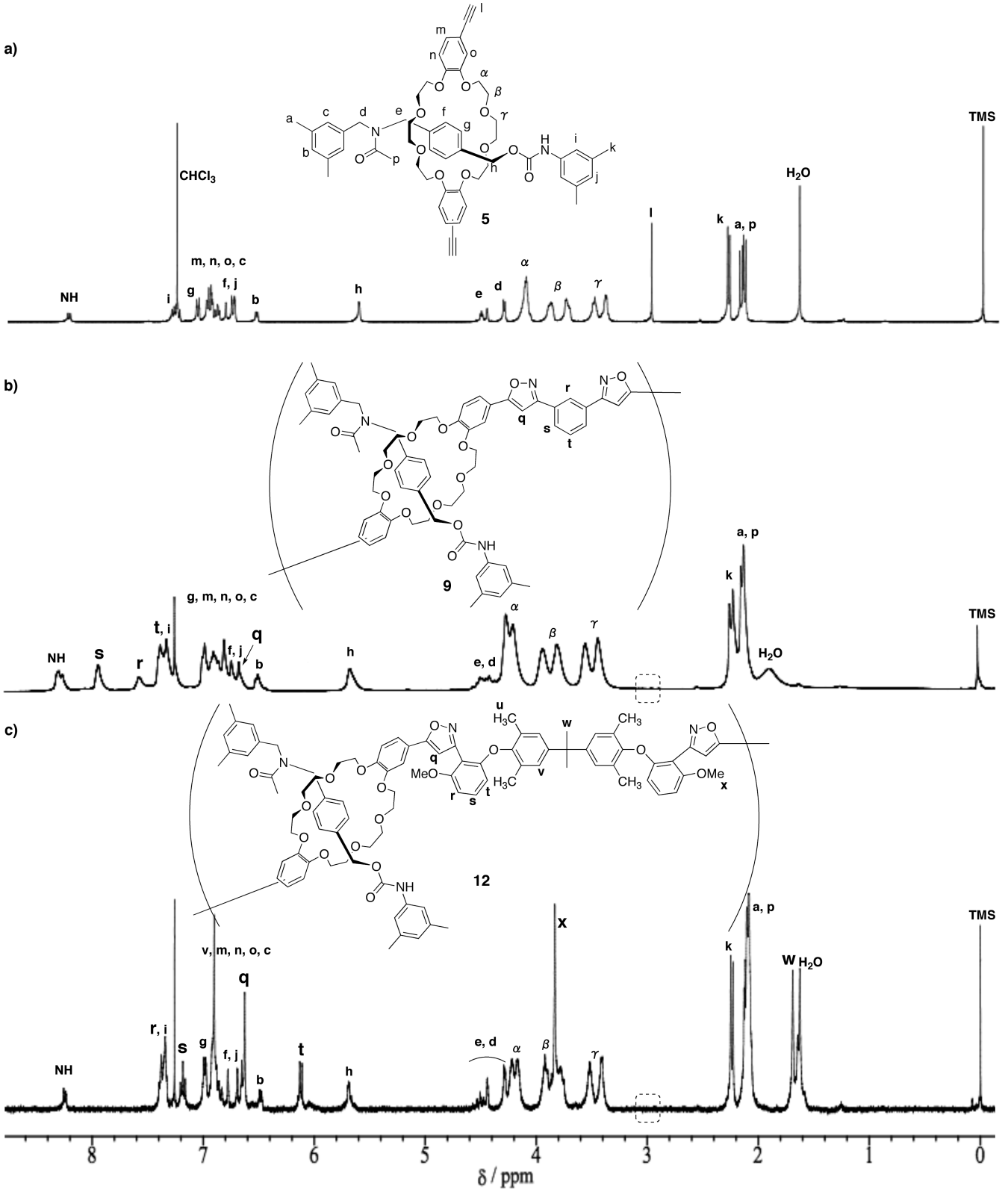


Figure 3. ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of (a) [2]rotaxane monomer **5**, (b) poly[2]rotaxane **9** (Table 1, entry 2), and (c) poly[2]rotaxane **12**.

the appearance of the characteristic signal of heteroaromatic protons (**r′**) at 6.60 ppm after the polymerization. These spectral characteristics strongly supported the structures of poly[3]rotaxanes **10** and **13**.[47]

For the control of polymer structure, copolymerization of [3]rotaxane **7** and acetylene-terminated polytetrahydrofuran **14** (M_n 1300) was examined (Scheme 7). Diethynyl polytetrahydrofuran **14** was synthesized by S_N2 reaction of polytetrahydrofuran and propargyl bromide.[44] An equimolar mixture of **7** and **14** was subjected to polycycloaddition with nitrile *N*-oxide (**8′**) under the same conditions as mentioned above. The copolymer **15** was obtained in 90% yield (Table 1, entry 6). From the IR, ^{1}H NMR, and SEC analyses of **15**, it was revealed that the copolymerization successfully

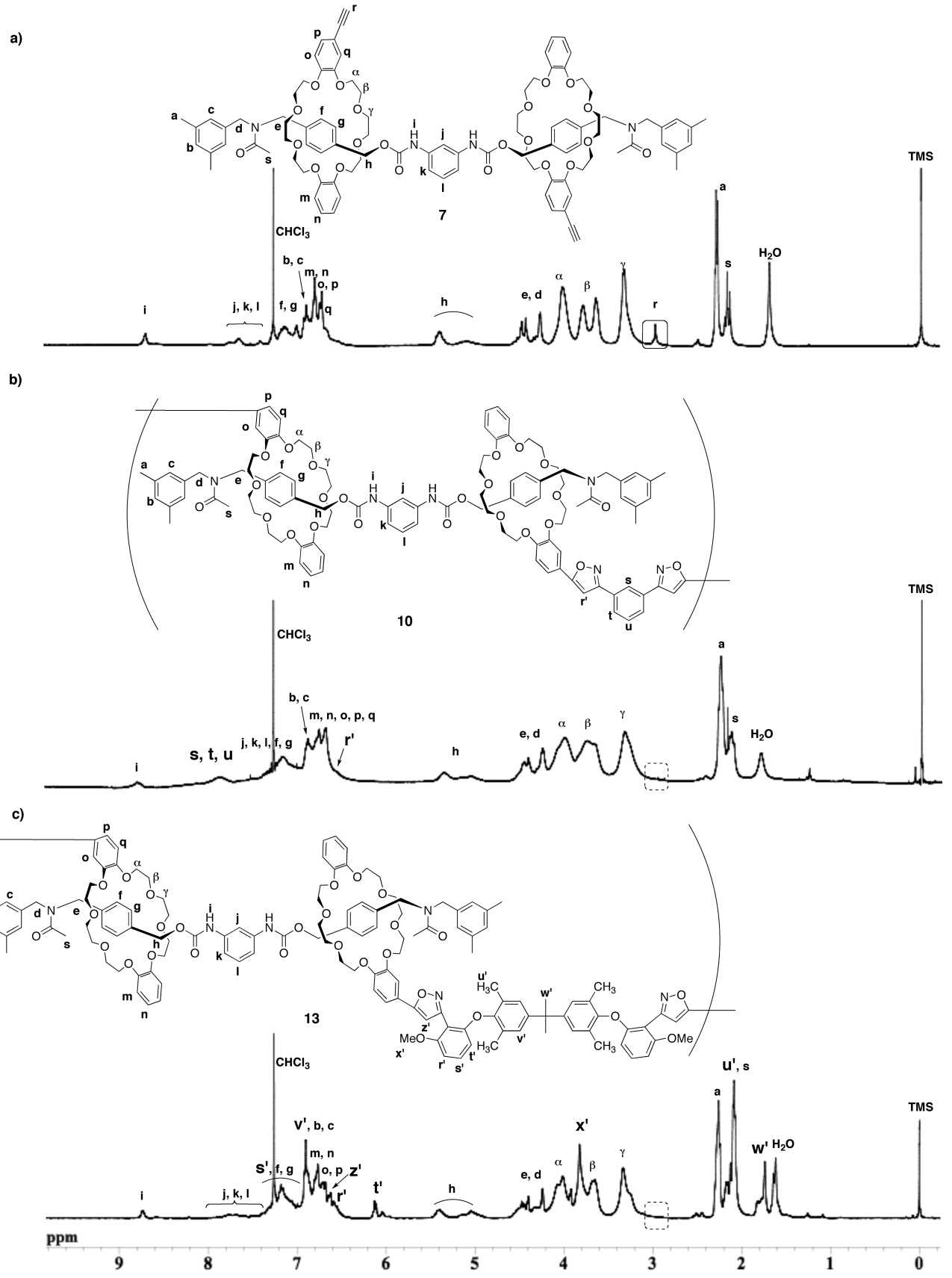
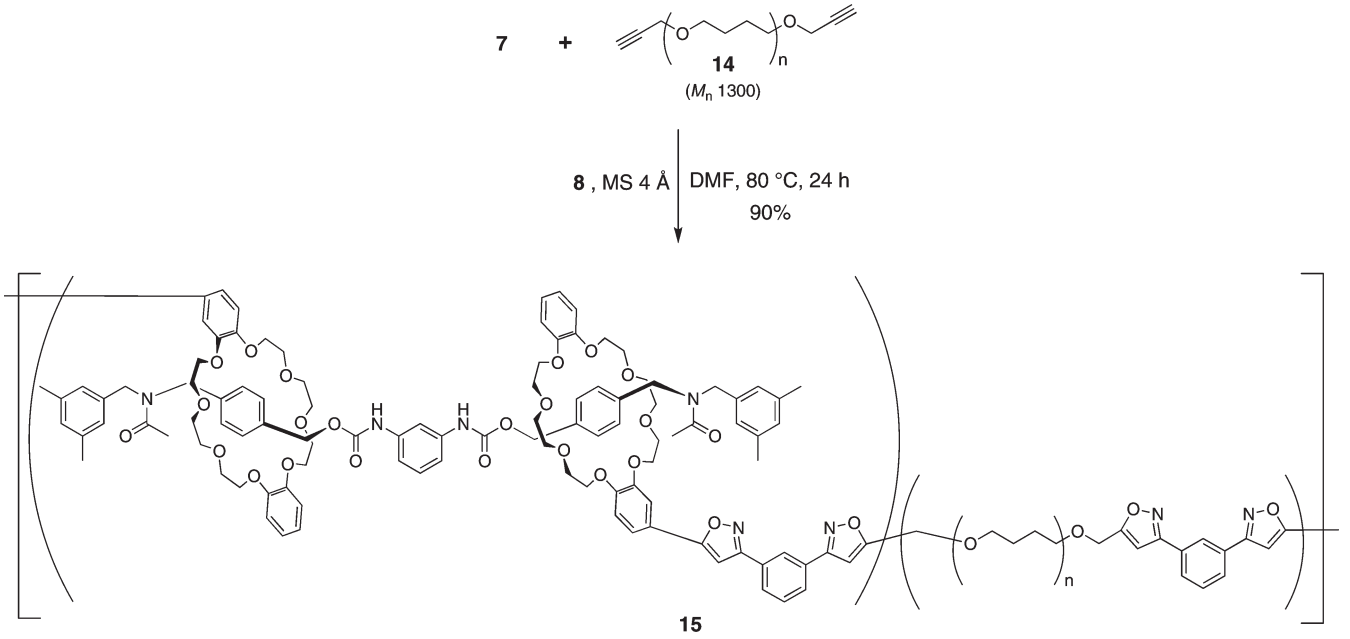


Figure 4. ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of (a) [3]rotaxane monomer **7**, (b) poly[3]rotaxane **10**, and (c) poly[3]rotaxane **13**.

proceeded to give the corresponding copolymer with a composition ratio of 55:45 for **7** and **14**. M_w of the copolymer **15** was 7600 (entry 6, M_w/M_n 1.2, by SEC).[47] However, the ^{1}H NMR spectra of the poly[3]rotaxanes (**10**, **13**, and **15**) clearly showed the characteristic new signals originating from the isoxazole (Figure 4 and Figure SI-30)[47] along with the

Scheme 7. Copolymerization of [3]Rotaxane Monomer 7 and Acetylene-Terminated Polytetrahydrofuran 14 via Click Reaction Using 8′



significant disappearance of ethynyl proton signal after the polymerization, supporting the high degree of polymerization. Therefore, it can be suggested that the actual molecular weight of poly[3]rotaxanes is higher than the SEC-estimated molecular weight because the SEC standard such as polystyrenes, solvent, and morphology of polymers in solution state usually affect the molecular weight of polymer in SEC.

Properties of Poly[2]rotaxanes and Poly[3]rotaxanes. All polyrotaxanes prepared (**9**, **10**, **12**, **13**, and **15**) were soluble in ordinary organic solvents such as CH_2Cl_2, $CHCl_3$, THF, and DMF but insoluble in MeOH, diethyl ether, and hexane. The good solubility was attributed to their amorphous nature presumably caused by the flexible rotaxane moieties in the main chain. On the basis of high solubility, the transparent and self-standing polymer films could be prepared on a glass by casting from the $CHCl_3$ solution (film thickness: ca. 35 μm).

Thermal properties of the polyrotaxanes were evaluated by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC). The 5% weight loss temperatures (T_{d5}) of **9** and **10** were 273 and 265 °C, respectively, indicating the thermal stability of the polymer structure including the isoxazole skeleton (Table 1, entries 2 and 3). Because those of **12**, **13**, and **15** were 305, 284, and 275 °C, respectively, the polyrotaxanes obtained from stable nitrile *N*-oxide **11** (**12** and **13**) were slightly thermally stable.

The glass transition temperatures (T_g) of **9**, **10**, **12**, and **13** were in a range of 75−157 °C by DSC analysis (Table 1, entries 2, 3, 5, and 7). The polymers **12** and **13** showed higher T_g value (**12**: 157 °C; **13**: 105 °C) than those of **9** (75 °C) and **10** (91 °C). Again, higher thermal stability of the polyrotaxanes from stable nitrile *N*-oxide **11** was confirmed. The reason for such stability may come from the introduction of a hard segment, the bisphenol A moiety of **11**. On the other hand, the single and lower T_g value of copolymer **15** (57.8 °C) compared with poly[3]rotaxane **10** (91.2 °C) indicated the efficient random copolymerization and formation of soft segment-incorporated polymer.

Conclusions

This study has demonstrated the main chain-type poly[2]rotaxanes (**9** and **12**) and poly[3]rotaxanes (**10**, **13**, and **15**) synthesized by the new click polymerizations of wheel-functionalized rotaxane monomers and stable and unstable nitrile *N*-oxides according to the rotaxanation−polymerization protocol. Remarkable advantages of the click reaction using nitrile *N*-oxide in comparison with that reaction using azide and ethynyl compounds, as stated in the Introduction, have also been utilized in the present polymerization to prepare highly functionalized polymers like poly[2]rotaxanes and poly[3]rotaxanes. In particular, the simple addition reaction accompanying the C−C bond formation without a catalyst is quite useful for the polymer synthesis that usually favors metal catalyst-free conditions to avoid metal contamination to polymer. We will further investigate the significance and usefulness of the click reaction using nitrile *N*-oxide in the construction of various integrated molecules and materials.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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