Synthesis and Characterization of Poly[3]rotaxane through the Mizoroki-Heck Coupling Polymerization of Divinyl-functionalized [3]Rotaxane

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Main chain-type poly[3]rotaxanes were synthesized according to the rotaxation-polymerization protocol by the polymerization of a divinyl [3]rotaxane monomer through the Mizoroki-Heck coupling with a diiodoarene. [3]Rotaxane **5** consisting of two monovinyl dibenzo-24-crown-8-ether wheels (**2**) and *sec*-ammonium salt (**3**) as an axle component was synthesized in 86% yield by a typical urethane end-capping reaction of the axle terminal hydroxyl group with bis(4-isocyanophenyl)methane in the presence of a catalytic amount of di-*n*-butyltin dilaurate. Quantitative *N*-acetylation of **5** yielded mono(vinylphenyl)-functionalized wheel-containing [3]rotaxane monomers **6**. The mobility of the wheel components in [3]rotaxanes was evaluated by the two-dimension NOESY spectra of **5** and **6**. The main-chain type poly[3]rotaxanes **8** were obtained in high yields by the Mizoroki-Heck-type polycondensation of **6** and diiodoarenes **7** in the presence of a palladium catalyst (Pd(OAc)₂). The structures of the polyrotaxanes were determined mainly by NMR and GPC, while the IR spectra showed that vinylene groups formed mainly took the *trans* configuration. Properties of the polyrotaxanes such as solubility and thermal stability were evaluated.

KEY WORDS: Main Chain-Type Rotaxane / [3]Rotaxane / Mizoroki-Heck Coupling / Poly(arylene-vinylene) /

Interlocked polymers,^{1–20} a novel class of polymers containing mechanical linkages consisting of wheels and/or axle components, are expected to display unique properties such as mechanical and rheological ones. Among polyrotaxanes as one of the interlocked polymers (Figure 1), both poly[2]-rotaxane^{21–33} and poly[3]rotaxane^{34,35} are specially unique as characterized by their structural feature that the polymer main chain has no successive covalent bond. The repeating units of these polymers are bound by mechanical bonds. Meanwhile, there is few report on polyrotaxane with the backbone consisting of mechanical bonds, *i.e.*, topologically linked polymer backbone, in contrast to poly[2]catenanes.^{36–46}

We previously reported the synthesis of poly[3]rotaxane utilizing the reversible cleavage-recombination process of the disulfide bond in the presence of a catalytic amount of thiol under thermodynamic control.³⁴ Further, we have recently disclosed the synthesis of poly[2]rotaxane by the polymerization of a bifunctional rotaxane monomer *via* the Sonogashira coupling reaction,⁴⁷ while a few poly[2]rotaxanes were synthesized by the thermodynamic process.^{21,22,24–28} There are two possible ways accessing the main chain-type poly[3]-rotaxane: one goes through the initial rotaxation followed by the polymerization (Figure 2, route A), whereas the other undergoes the initial coupling of wheel followed by the rotaxation to poly[3]rotaxane (Figure 2, route B), as shown in Figure 1. Our previous paper³³ described the synthesis of a polyrotaxane by rotaxation of ditopic wheel component utilizing the dynamic covalent chemistry of disulfide linkage, along Route B.

Figure 1. Structures of typical polyrotaxanes.

In this paper, the synthesis of poly[3]rotaxanes by polycondensation *via* the Mizoroki-Heck coupling of divinyl-functionalized [3]rotaxane and diiodoarenes, according to the rotaxation-polymerization protocol along Route A.

EXPERIMENTAL

Measurement

¹H and ¹³C NMR spectra were recorded on a JEOL GTX-400 spectrometer using CDCl₃ as the solvent with tetramethylsilane as the internal standard. FT-IR spectra were recorded on a JASCO FT-IR-230 spectrophotometer. Preparative 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). Melting points were measured by a Stuart Scientific SMP3. Molecular

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Figure 2. Synthetic strategy of poly[3]rotaxane.

weight and its distribution were estimated by GPC on a JASCO Gulliver system equipped with two consecutive linear polystyrene gel columns (Tosoh TSKgel G5000H_{XL}, G4000H_{XL}) at 30 °C (flow rate 0.085 mL/min) using polystyrene standards and chloroform as the eluent. The glass transition temperature (T_g) was determined with a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under nitrogen atmosphere (flow rate 50 mL/min). The thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under nitrogen atmosphere (flow rate 50 mL/min). High-resolution mass spectra were obtained by a ICP-MS (Seiko Instruments, SPQ-9000) at the Center for Advanced Materials Analysis, Tokyo Institute of Technology.

Materials

Tributylamine and CH₂Cl₂ were dried over calcium hydride and purified by distillation. Commercially available NaH, acetic anhydride, triethylamine, Pd(OAc)₂ (Wako Chemical Co., Ltd.), methyltriphenylphosphonium bromide, tri(*o*-tolyl)-phosphane, dry DMF (Aldrich Chemical Co., Ltd.), and tributylphosphane (Tokyo Kasei Co., Ltd.) were used as received. Solvents other than CH₂Cl₂ were commercially available and used without further purification.

Monovinyl Dibenzo-24-crown-8-ether (Monovinyl DB24C8) (2). To a solution of 4-formylcatechol (3.45 g, 25.0 mmol) and cesium carbonate (81.4 g, 250 mmol) in dry THF (500 mL) was added ditosylate **1** (18.8 g, 27.5 mmol) dissolved in dry THF (200 mL). The mixture was refluxed for 3 d. After cooling the mixture to room temperature, the mixture was extracted with chloroform. The chloroform layer was washed with 10% K₂CO₃ aq. and H₂O, separated, dried over anhydrous MgSO₄, and evaporated to dryness. The residual product was purified by silica gel column chromatography (CHCl₃ → CHCl₃: MeOH (100/2)) to give monoformyl DB24C8 (8.46 g, 71%) as a white solid. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.82 (s, 1H, CHO), 7.44–7.32 (m, 3H, ArH), 6.96–6.82 (m, 4H, ArH),

4.25–4.11 (m, 8H, crown-CH₂), 3.98–3.89 (m, 8H, crown-CH₂), 3.86–3.79 (m, 16H, crown-CH₂) ppm.

To a solution of methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol) in dry CH₂Cl₂ (60 mL) was added NaH (0.480 g, 12.0 mmol) and the mixture was stirred for 10 min. To the mixture was slowly added a solution of monoformyl DB24C8 (1.91 g, 4.00 mmol) dissolved in dry CH₂Cl₂ (60 mL) over a period of 1 h. The resulting mixture was stirred for 14 h and subsequently quenched by the addition of H₂O (30 mL). The organic layer was separated, dried over anhydrous MgSO₄, evaporated to dryness. The residual solid material was purified by silica gel column chromatography (eluent: CH₂Cl₂ and then CH₂Cl₂-MeOH (25/1)) to give monovinyl DB24C8 **2** (1.65 g, 87%) as a white solid. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.95–6.72 (m, 7H, Ar-H), 6.61 (m, 1H, vinyl-CH), 5.57 (m, 1H, vinyl-H), 5.12 (m, 1H, vinyl-H), 4.18–4.10 (m, 8H, crown-CH₂), 3.93–3.87 (m, 8H, crown-CH₂), 3.83–3.80 (m, 8H, crown-CH₂) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 148.78, 148.72, 136.20, 131.04, 121.24, 119.78, 113.99, 113.57, 111.77, 111.38, 76.68, 71.03, 69.72, 69.69, 69.65, 69.29, 69.23, 69.20 ppm; IR (KBr): 3065 (ν_{C-H} vinyl), 1125 (ν_{C-O-C}) cm⁻¹.

[3]Rotaxane 5. To a solution of a mixture of **2** (449 mg, 0.946 mmol) and *sec*-ammonium salt **3**⁵⁰ (345 mg, 0.860 mmol) in CHCl₃ (1.0 mL) was added bis(4-isocyanatophenyl)methane (108 mg, 0.430 mmol) and di-*n*-butyltin dilaurate (DBTDL, 26.0 μL, 43.0 mmol) at an ambient temperature. The resulting mixture was stirred for 24 h and concentrated by evaporation. The resulting residue was dissolved in CH₂Cl₂ (20 mL) and washed with 10 mL of saturated NH₄PF₆ aq. The organic layer was dried over anhydrous MgSO₄ and evaporated. The residual solid material was purified by silica gel column chromatography (eluent: CH₂Cl₂ and then CH₂Cl₂-MeOH (100/1, v/v)) to give [3]rotaxane **5** (741 mg, 86%) as a yellow solid. Mp 134.5–136.6 °C; ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.44 (br s, 2H, NH), 7.27 (br, 2H, NH₂), 7.25 (m, 8H, Ar-H), 6.94 (m, 6H, Ar-H), 6.85–6.60 (m, 18H), 6.50 (m, 2H, vinyl-H), 5.52 (m, 2H, vinyl-H), 5.04 (m, 2H, vinyl-H), 4.96 (s, 4H), 4.54 (m, 4H), 4.36 (m, 4H), 4.09–3.91 (m, 16H), 3.71 (s, 2H), 3.75–3.59 (m, 16H), 3.46–3.29 (m, 16H), 2.05 (s, 12H) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 153.45, 147.34, 147.18, 138.19, 137.56, 136.15, 136.95, 131.32, 130.49, 129.43, 129.14, 127.79, 126.50, 121.54, 119.87, 118.80, 112.55, 112.48, 112.35, 109.88, 70.53, 70.04, 68.19, 68.04, 65.71, 52.50, 52.19, 40.43, 21.07 ppm; IR (KBr) 3065 (ν_{C-H} vinyl), 1728 (ν_{C=O} ester), 843 (ν_{P-F}), 557 (ν_{P-F}) cm⁻¹; high-resolution mass spectrum, *m/z* Calcd. for C₁₀₁H₁₂₂N₄O₂₀ [M]⁺ 1710.8652; found: 1710.8649;

***N*-Acetylated [3]Rotaxane 6.** A mixture of **5** (356 mg, 0.177 mmol), acetic anhydride (72.4 mg, 0.709 mmol), and triethylamine (179 mg, 1.77 mmol) in dry DMF (1.4 mL) was stirred at room temperature for 12 h. The mixture was diluted with CH₂Cl₂ (10 mL), washed with 1 M hydrochloric acid and saturated sodium carbonate, and dried over anhydrous MgSO₄. The organic layer was evaporated and the resulting crude product was purified by preparative GPC to give **6** (225 mg,

Scheme 1.

71%) as a white solid. Mp 94.4–96.2 °C; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.58 (br s, 2H, NH), 7.40 (m, 8H, Ar-H), 6.98–6.70 (m, 20H, Ar-H), 6.66–6.58 (m, 2H, vinyl-H), 5.55 (s, 2H), 5.51 (m, 2H, vinyl-H), 5.10 (m, 2H, vinyl-H), 4.49 (m, 1H), 4.44 (m, 1H), 4.28 (m, 2H), 4.10 (m, 8H), 3.82 (m, 6H), 3.71 (m, 4H), 3.36 (m, 8H), 2.29 (m, 6H), 2.27 (m, 6H), 2.15 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 170.98, 170.85, 153.60, 148.32, 148.29, 148.26, 148.23, 138.42, 137.94, 137.45, 137.31, 137.12, 136.42, 136.39, 136.28, 135.25, 134.69, 134.24, 130.38, 130.35, 129.01, 128.92, 128.87, 127.70, 127.50, 127.41, 125.91, 125.65, 123.89, 120.61, 119.20, 118.08, 117.98, 111.86, 111.59, 69.56, 69.44, 68.08, 67.97, 67.89, 65.60, 65.49, 50.35, 50.30, 47.58, 40.58, 21.62, 21.60, 21.18, 21.14 ppm; IR (KBr) 3065 (ν_{C-H} vinyl), 1725 (ν_{C=O} ester), 1647 (ν_{C=O} amide) cm⁻¹; high-resolution mass spectrum *m/z* Calcd. for C₁₀₅H₁₂₄N₄O₂₂Na [M + Na]⁺ 1815.8605; found 1815.8594.

Polymerization (A Typical Procedure). A mixture of **6** (17.9 mg, 10.0 μmol), **7a** (3.30 mg, 10.0 μmol), Pd(OAc)₂ (1.10 mg, 5.00 μmol), tributylamine (4.7 μL), and P(*o*-tolyl)₃ (1.50 mg, 5.00 μmol) was dissolved in 120 μL of dry DMF. The mixture was heated at 90 °C for 48 h under Ar atmosphere. The mixture was cooled to room temperature and then precipitated by pouring into methanol (100 mL). The resulting precipitate was collected by filtration, washed with methanol several times, and dried *in vacuo* to give poly[3]rotaxane **8a** (15.1 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.11 (m, 4H, Ar-H), 7.81–7.49 (m, 8H, 7.18–6.58 (m, 14H), 6.00 (s, 2H), 4.52 (m, 2H), 4.37 (m, 2H), 4.23–4.04 (m, 8H), 3.86–3.59 (m, 8H), 3.32 (m, 4H), 3.08–2.85 (m, 4H), 2.29 (m, 6H), 2.28 (m, 6H), 2.06 (m, 3H) ppm; IR (KBr) 1710 (ν_{C=O} ester), 1647 (ν_{C=O} amide) cm⁻¹. Molecular weight and thermal property of **8** are listed in Table I.

RESULTS AND DISCUSSION

Synthesis of [3]Rotaxane Monomer **6**

Styrenic vinyl-functionalized wheel **2** was prepared in 62% overall yield by the reaction of an oxyethylene chain-containing ditosylate **1** with 4-formylcatechol to monoformyl dibenzo-24-crown-8-ether followed by the conversion of the formyl

group to the vinyl group by the Wittig reaction, as shown in Scheme 1.⁴⁸ The structure of **2** was determined by the ¹H NMR and IR spectra.

Synthesis of [3]rotaxane **6** was carried out according to the urethane end-capping protocol⁴⁹ of intermediary pseudorotaxane **4** formed *in situ* (Scheme 2). A mixture of vinyl-functionalized crown ether wheel **2** and hydroxy-terminated *sec*-ammonium salt **3** was allowed to stand at room temperature to form the threading complex pseudorotaxane **4**. The mixture was then treated with bis(4-isocyanatophenyl)methane as an end-capping agent for two moles of *in situ*-formed **4** in the presence of a catalytic amount of DBTDL (Scheme 2).

Rotaxane **5** was obtained as yellow solid in 86% isolated yield. Comparison of the ¹H NMR spectrum of **5** with that of the free components wheel **2** and axle **3** confirms its interlocked structure, especially from the typical chemical shift changes in ¹H NMR where the all signals were assignable (Figure 3). The most designating characteristics in the spectra involve the signals of the benzylic protons neighboring the *sec*-ammonium group of the axle (H_d and H_e), which are largely downfield-shifted (from 3.91, 3.90 ppm to 4.66, 4.22 ppm) by the rotaxation. The clear downfield shift can be explained by the generation of the CH-O interaction of the benzylic protons by the complexation with the crown ether wheel.^{48–52} The methyl proton signal on the phenyl ring of the axle (H_a) is shifted to upfield, because of the shielding effect of the benzene ring of the crown ether wheel. Since [3]rotaxane **5** is a mixture of two diastereomers based on the lowered symmetry of the wheel **2** due to the vinyl substitution, the spectrum of **5** is not very simple, as shown in Figure 3.

The treatment of **5** with excess amount of triethylamine and acetic anhydride gave *N*-acetylated [3]rotaxane **6** in 71% yield (Scheme 2), in good accordance with the reported result.^{51,52} In the ¹H NMR of **6** (Figure 3), the signal of the urethane *O*-benzylic methylene and urethane NH protons (H_h and H_i) showed a large downfield shift from 4.96 and 7.44 to 5.55 and 8.58, respectively. This is most indicative of the rotaxane structure,⁵² because of the crown ether moved from being around the ammonium group to the urethane bonding site. Two split signals of the benzylic protons (H_d and H_e) neighboring to the amide nitrogen would be attributed to the *syn-anti*

Scheme 2.

Figure 3. ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of (a) wheel component **2**, (b) axle component **3**, (c) [3]rotaxane **5**, and (d) *N*-acetylated [3]rotaxane **6**. The signal *z* denotes that of *N*-acetyl methyl protons of **6**.

Figure 4. Partial two-dimensional ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of (a) [3]rotaxane **5** and (b) *N*-acetylated [3]rotaxane **6**.

Scheme 3.

stereoisomerism of the amide group formed by the acetylation, but not to the diastereotopic relation caused by the asymmetric nitrogen atom. Thus, all proton signals including vinylic signals other than the aromatic signals of **6** are assignable as those of the proposed rotaxane structure.

The mobility of the wheel component on the axle component in the [3]rotaxane **5** and **6** was examined by painstaking analysis of two-dimensional NOESY ^1H NMR spectra (Figure 4). In the case of [3]rotaxane **5**, the H_s and H_t signals on the wheel component indicated the presence of strong NOEs with H_f and H_b in the axle component, respectively, however the H_s and H_t on the wheel component of [3]rotaxane **6** showed no correlation with other protons. This result suggests that the wheel components of [3]rotaxane **6** are freely moving along the axle component, being consistent with the disappearance of the strong attractive interaction between the components by the *N*-acetylation.

Polymerization

The Mizoroki-Heck coupling⁵³ is a widely used carbon-carbon bond forming reaction catalyzed by Pd(0) between aryl halide and olefinic compound in the presence of a hindered amine, and thereby was chosen for the present polymerization.

Table I. Polycondensation of [3]rotaxane **6** with dihaloarene **7** under the Mizoroki-Heck coupling condition^a

Entry	Dihalo-arene	Temp. (°C)	Polym.	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	7a	90	8a	82	18	7.3	2.5	90	247	271
2	7a	60	8a	40	5.6	3.9	1.4	—	—	—
3	7b	90	8b	88	14	4.4	3.1	88	286	308
4	7b	60	8a	34	3.4	2.6	1.3	—	—	—

^aPolymerization conditions: [[3]rotaxane **6**] = [dihaloarene **7**] = 0.1 M, 48 h, in DMF. ^bDetermined by GPC (CHCl_3 , polystyrene standards). ^cGlass transition temperature obtained by DSC at a heating rate of 10 °C/min under nitrogen (N_2 flow rate: 50 mL/min) in the second scan. ^d5% Weight loss temperature obtained by TGA at a heating rate of 10 °C/min under nitrogen (N_2 flow rate: 50 mL/min).

Poly[3]rotaxane **8** was obtained by the polycondensation through the Pd(0)-catalyzed coupling of *N*-acetylated [3]rotaxane monomer **6** and diiodoarene **7** in DMF for 48 h in the present of $n\text{-Bu}_3\text{N}$ (Scheme 3). The results are summarized in Table I. Polymers **8a** and **8b** were obtained as solid in 80% and 88% yields, respectively, under the polymerization at 90 °C. However, the polymerization at 60 °C afforded only low molecular weight polymers in low yields. Each of **8** had a unimodal GPC profile showing the molecular weight M_w 14,000 (**8a**) and 18,000 (**8b**) with the molecular weight distribution of 2.5 and 3.1, respectively.

The structure of **8** was characterized by IR and ^1H NMR spectra in addition to the GPC result. FT-IR spectra showed the characteristic absorption peak of the vinyl group at 3065 cm^{-1} which largely decreased after the polymerization. At the same time, a weak absorption peak at 961 cm^{-1} corresponding to the out-plane bending made of the *trans*-vinylene groups appeared, suggesting that the generated vinylenes group takes mainly *trans* configuration.⁵⁴ The ^1H NMR spectrum (Figure 5) is quite similar to that of rotaxane monomer **6** except for the aromatic and vinyl signals, although most signals are broadened. Small vinylic methylene signals H_m and H_n appeared around 5.51 and 5.10 ppm, respectively, were attributed to those of the vinyl group of polymer terminal end, which significantly decreased as the polymerization progressed. Detailed information on the degree of polymerization (DPs) was obtained by the end group analysis of the ^1H NMR

Figure 5. Partial ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of (a) [3]rotaxane **6** and (b) poly[3]rotaxane **8b**. The signals * around 5.6 and 5.1 ppm denote the terminal vinyl proton signals of the polymer chain.

spectrum (Figure 5). The signal integration of the terminal vinyl protons (5.54 and 5.10 ppm) was compared with that of the methyl protons (2.29 and 2.27 ppm) of the end-capping groups. As a result, the averaged DPs of **8a** and **8b** were estimated to be DP 8.0 and 5.4, which corresponded to the M_n value of 7,500 and 5,200, respectively, being comparable with the GPC data of M_n 7,300 and 4,400, respectively (Table I).

Properties of Poly[3]rotaxane **8**

Both poly[3]rotaxanes **8a** and **8b** were soluble in ordinary organic solvents such as dichloromethane, chloroform, and THF, but insoluble in methanol and *n*-hexane. Based on their high solubility, transparent polymer films could be prepared on a glass by casting from their chloroform solution, although no strong self-standing film was obtained, probably due to the low degree of polymerization.

Thermal properties of **8** were evaluated by TGA and DSC (Table I). Good thermal stability was confirmed from the weight loss temperatures at 247 and 286 °C (5% weight loss) for **8a** and **8b**, respectively. Thermal events around the temperature of 90 and 88 °C range as observed by DSC during the heating scans could be attributed to the glass transitions (T_g).

Thus, this paper has demonstrated the synthesis of divinyl [3]rotaxane monomer and its derivation to poly[3]rotaxanes **8** possessing the rotaxanated polymacrocyclic structure in the main chain according to the rotaxanation-polymerization protocol. The polyrotaxane is categorized as one of the polymers having no successive covalent bond in the polymer main chain. The polymerization was carried out by the poly(Mizoroki-Heck coupling) of styrenic vinyl-functionalized

wheel-containing [3]rotaxane **6** with dihaloarenes **7** such as diiodoarenes in the presence of a catalytic amount of $\text{Pd}(\text{OAc})_2$ to yield poly(phenylene-vinylene)-type polymers **8**. The main-chain type poly[3]rotaxanes **8** obtained in high yields showed a molecular weight range of M_w 14,000–18,000 (M_n 4,400–7,300) with molecular weight distributions of 2.5–3.1, whereas film-forming property based on their good solubility in ordinary organic solvents was confirmed, in addition to their good thermal stability. The present successful synthesis of the main chain-type polyrotaxanes based on the rotaxanation-polymerization protocol provides an efficient entry to polyrotaxanes, since this method suggests the possibility of preparing the main chain-type polyrotaxanes possessing many type of backbones by the polycondensation without the application of thermodynamic process.

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REFERENCES

- H. W. Gibson, M. C. Bheda, and P. T. Engen, *Prog. Polym. Sci.*, **19**, 843 (1994).
- F. Vögtle, T. Dunnwald, and T. Schmidt, *Acc. Chem. Res.*, **29**, 451 (1996).
- H. W. Gibson, in "Large Ring Molecules" Semlyen, J. A. Semlyen, Ed., John Wiley and Sons: New York, 1996, chapt. 6, p 191.
- M. C. T. Fyfe and J. F. Stoddart, *Acc. Chem. Res.*, **30**, 393 (1997).
- A. Harada, *Adv. Polym. Sci.*, **133**, 141 (1997).
- S. A. Nepogodiev and J. F. Stoddart, *Chem. Rev.*, **98**, 1959 (1998).
- "Molecular Catenanes, Rotaxanes, and Knots," J.-P. Sauvage and C. Dietrich-Buchecker, Ed., Wiley-VCH, Weinheim, 1999.
- F. M. Raymo and J. F. Stoddart, *Chem. Rev.*, **99**, 1643 (1999).
- T. Takata and N. Kihara, *Rev. Heteroat. Chem.*, **22**, 197 (2000).
- E. Mahan and H. W. Gibson, in "Cyclic polymers," 2nd ed, E. R. Semlyen, Ed., Kluwer Publishers, Dordrecht, 2000, p 415.
- T. J. Hubin and D. H. Busch, *Coord. Chem. Rev.*, **200**, 5 (2000).
- A. Harada, *Acc. Chem. Res.*, **34**, 456 (2001).
- I. G. Panova and I. N. Topchieva, *Russ. Chem. Rev.*, **70**, 23 (2001).
- T. Takata, N. Kihara, and Y. Furusho, *Adv. Polym. Sci.*, **171**, 1 (2005).
- F. Huang and H. W. Gibson, *Prog. Polym. Sci.*, **30**, 982 (2005).
- S. J. Cantrill, K. S. Chichak, A. J. Peters, and J. F. Stoddart, *Acc. Chem. Res.*, **38**, 1 (2005).
- G. Wenz, B.-H. Han, and A. Müller, *Chem. Rev.*, **106**, 782 (2006).
- T. Takata, *Polym. J.*, **38**, 1 (2006).
- R. Liu, A. Harada, and T. Takata, *Polym. J.*, **39**, 1, 21 (2007).
- K. Ito, *Polym. J.*, **39**, 6, 489 (2007).
- P. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, and D. J. Williams, *Angew. Chem., Int. Ed.*, **37**, 1294 (1998).
- P. R. Ashton, I. W. Parsons, F. M. Raymo, J. F. Stoddart, A. J. P. White, D. J. Williams, and R. Wolf, *Angew. Chem., Int. Ed.*, **37**, 1913 (1998).
- N. Yamaguchi and H. W. Gibson, *Angew. Chem., Int. Ed.*, **38**, 143 (1999).
- S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White, and D. J. Williams, *Org. Lett.*, **2**, 759 (2000).
- T. Fujimoto, Y. Sakata, and T. Kaneda, *Chem. Commun.*, 2143 (2000).
- T. Hoshino, M. Miyauchi, Y. Kawaguchi, H. Yamaguchi, and A. Harada, *J. Am. Chem. Soc.*, **122**, 9876 (2000).

27. H. Onagi, C. J. Easton, and S. F. Lincoln, *Org. Lett.*, **3**, 1041 (2001).
28. S. J. Rowan and J. F. Stoddart, *Polym. Adv. Technol.*, **13**, 777 (2002).
29. Y. Hasegawa, M. Miyauchi, Y. Takashima, H. Yamaguchi, and A. Harada, *Macromolecules*, **38**, 3724 (2005).
30. M. Miyauchi, T. Hoshino, H. Yamaguchi, S. Kamitori, and A. Harada, *J. Am. Chem. Soc.*, **127**, 2034 (2005).
31. M. Miyauchi, Y. Takashima, H. Yamaguchi, and A. Harada, *J. Am. Chem. Soc.*, **127**, 2984 (2005).
32. A. Harada, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 5113 (2006).
33. T. Sato and T. Takata, *Macromolecules*, **41**, 2739 (2008).
34. T. Oku, Y. Furusho, and T. Takata, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 119 (2003).
35. Y. Sohgawa, H. Fujimori, J. Shoji, Y. Furusho, N. Kihara, and T. Takata, *Chem. Lett.*, **30**, 774 (2001).
36. Y. Geerts, D. Muscat, and K. Müllen, *Macromol. Chem. Phys.*, **196**, 3425 (1995).
37. J. L. Weidmann, J.-M. Kern, J.-P. Sauvage, Y. Geerts, D. Muscat, and K. Müllen, *Chem. Commun.*, 1243 (1996).
38. D. Muscat, A. Witte, W. Köhler, K. Müllen, and Y. Geerts, *Macromol. Rapid. Commun.*, **18**, 233 (1997).
39. S. Menzer, A. J. P. White, D. J. Williams, M. Belohradsky, C. Hamers, F. M. Raymo, A. N. Shipway, and J. F. Stoddart, *Macromolecules*, **31**, 295 (1998).
40. C. Hamers, F. M. Raymo, and J. F. Stoddart, *Eur. J. Org. Chem.*, 2109 (1998).
41. J. L. Weidmann, J.-M. Kern, J.-P. Sauvage, D. Muscat, S. Mullins, W. Köhler, C. Rosenauer, H. J. Räder, K. Martin, and Y. Geerts, *Chem. Eur. J.*, **5**, 1841 (1999).
42. D. Muscat, W. Köhler, H. J. Räder, K. Martin, S. Mullins, B. Müller, K. Müllen, and Y. Geerts, *Macromolecules*, **32**, 1737 (1999).
43. S. Shimada, K. Ishikawa, and N. Tamaoki, *Acta. Chem. Scand.*, **52**, 374 (1998).
44. C. Hamers, O. Kocian, F. M. Raymo, and J. F. Stoddart, *Adv. Mater.*, **10**, 1366 (1998).
45. D. L. Simone and T. M. Swager, *J. Am. Chem. Soc.*, **122**, 9300 (2000).
46. C. A. Fustin, C. Bailly, G. J. Clarkson, P. De Groote, T. H. Galow, D. A. Leigh, D. Robertson, A. M. Z. Slawin, and J. K. Y. Wong, *J. Am. Chem. Soc.*, **125**, 2200 (2003).
47. H. Sasabe, N. Inomoto, N. Kihara, Y. Suzuki, A. Ogawa, and T. Takata, *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 4154 (2007).
48. T. Sato and T. Takata, *Tetrahedron Lett.*, **48**, 2797 (2007).
49. Y. Furusho, H. Sasabe, D. Natsui, K. Murakawa, T. Takata, and A. Harada, *Bull. Chem. Soc. Jpn.*, **77**, 179 (2004).
50. H. Kawasaki, N. Kihara, and T. Takata, *Chem. Lett.*, **28**, 223 (1999).
51. N. Kihara, Y. Tachibana, H. Kawasaki, and T. Takata, *Chem. Lett.*, **29**, 506 (2000).
52. Y. Tachibana, H. Kawasaki, N. Kihara, and T. Takata, *J. Org. Chem.*, **71**, 5093 (2006).
53. Y. Lee, Y. Liang, and L. Yu, *Synlett*, 2879 (2006).
54. Y. Liu, C. Yang, Y. Li, Y. Li, S. Wang, J. Zhuang, H. Liu, N. Wang, X. He, Y. Li, and D. Zhu, *Macromolecules*, **38**, 716 (2005).