Ferrocene-containing Side Chain Polyrotaxanes Obtained by Radical Copolymerization of Styrenes with Acrylamide with a [2]Rotaxane Structure

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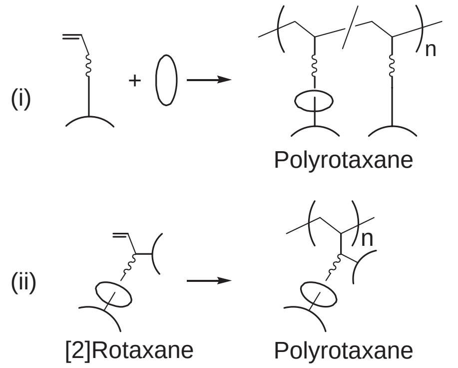
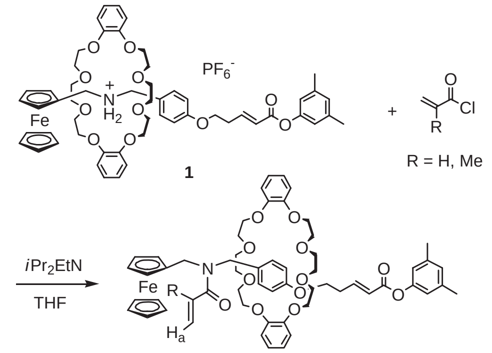
Radical copolymerization of styrenes and a [2]rotaxane monomer composed of ferrocene-containing *N*,*N*-dialkylacrylamide and dibenzo[24]crown-8-ether (DB24C8) yielded side chain polyrotaxanes.

Polyrotaxanes which contain multiple rotaxane units in the molecule have been reported to exhibit unique thermal and photochemical properties.[1–4] Radical polymerization of acrylate was employed to introduce the rotaxanes to the side chains of the polymer; a mixture of acrylic monomers with a bulky stopper and macrocyclic compounds such as cyclodextrin, crown ether, and cyclic viologen produces the side chain polyrotaxanes in the presence of radical initiator (Scheme 1(i)).[5–8] These polyrotaxanes, however, contain branches without rotaxane structure due to insertion of monomer without pseudorotaxane structure during the polymer growth. Polymerization of a monomer with [2]rotaxane structure would produce polymers in which every monomer unit contains a side chain with interlocked structure (Scheme 1(ii)). In this paper, we report radical copolymerization of styrenes and a [2]rotaxane composed of dibenzo[24]crown-8-ether (DB24C8) and acrylamide derivative to produce the side chain polyrotaxanes as well as the properties of the rotaxane-functionalized polystyrenes.

[2]Rotaxane monomer **2** was synthesized by acylation of the nitrogen of cationic rotaxane [{(Fe(C$_5$H$_4$)(C$_5$H$_5$))CH$_2$NH$_2$CH$_2$-C$_6$H$_4$-4-OCH$_2$CH$_2$CHCHCOO-C$_6$H$_3$-3,5-Me$_2$}(DB24C8)]-(PF$_6$) (**1**) with acryloyl chloride in THF/*i*-Pr$_2$EtN (eq 1).[9–11] A similar reaction of methacryloyl chloride with **1** gave **3**. The IR spectrum of **2** shows peaks at 1728 and 1647 cm^{-1}, which are assigned to C=O stretching vibration of the ester and amide groups, respectively. Figure 1a shows the ^{1}H NMR spectrum of **2**. The ^{1}H NMR signals at δ 5.63 and 5.76 are assigned to vinyl hydrogen (H$_a$ in eq 1) of **2** with s-cis and s-trans conformational structures of the amide group. Rotaxane **2** keeps its interlocked structure in toluene-d_8 and dmso-d_6 ([**2**] = 5 mM) at 100 °C for 24 h, which was evidenced by ^{1}H NMR spectroscopy.



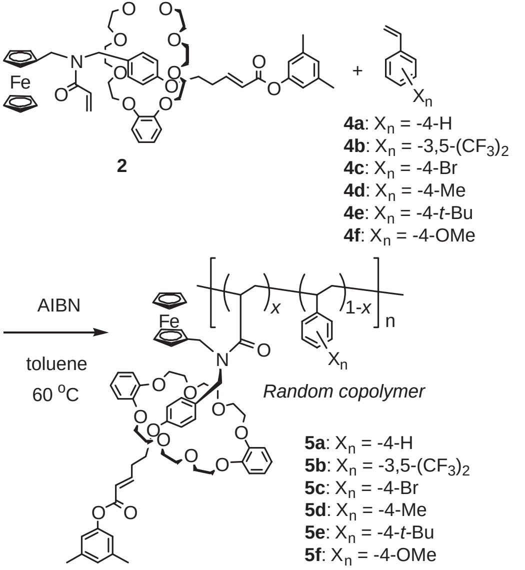
Scheme 1. Synthetic strategies toward side chain polyrotaxanes.



(1)

2: R = H (48%)
3: R = Me (53%)

Copolymerization of **2** with styrene (**4a**) in the presence of AIBN (azobisisobutyronitrile) at 60 °C for 20 h in toluene produces the polyrotaxane **5a** containing the two monomer units randomly (eq 2). Figure 1b shows the ^{1}H NMR spectrum of **5a**. The signals at δ 2.26 (Me), 1.59 (CH$_2$-main chain), and 3.4–4.0 (CH$_2$-DB24C8) indicate copolymerization of **2** and **4a**.[12] The ratio of the rotaxane unit to styrene unit, *x*, varies from 0.18–0.41 depending on the ratio of the monomer used, as summarized in Table 1 run 1–4. Molecular weight (M_n) of the polyrotaxane **5a** ranges from 2000 to 6700 with the molecular weight distribution (M_w/M_n) of 1.35–1.54.



4a: X$_n$ = -4-H
4b: X$_n$ = -3,5-(CF$_3$)$_2$
4c: X$_n$ = -4-Br
4d: X$_n$ = -4-Me
4e: X$_n$ = -4-*t*-Bu
4f: X$_n$ = -4-OMe

(2)

5a: X$_n$ = -4-H
5b: X$_n$ = -3,5-(CF$_3$)$_2$
5c: X$_n$ = -4-Br
5d: X$_n$ = -4-Me
5e: X$_n$ = -4-*t*-Bu
5f: X$_n$ = -4-OMe

Reaction of **2** in the presence of AIBN results in recovery of unreacted monomer (run 5), probably due to the steric hindrance of DB24C8 which prevents homopolymerization of the axle molecule. Copolymerization of **2** with substituted styrenes **4b**–**4f** yields corresponding polyrotaxanes **5b**–**5f** (run 6–10) in

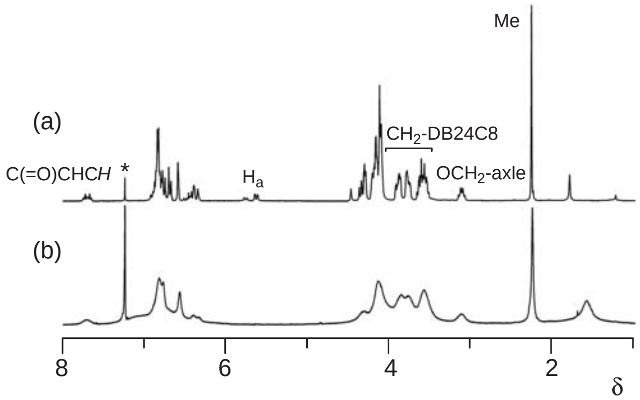


Figure 1. ^{1}H NMR spectra of (a) **2**, and (b) **5a** (run 3 of Table 1) (300 MHz, $CDCl_3$, rt). The peak with asterisk indicates residual solvent ($CHCl_3$).

Table 1. Copolymerization of styrene derivatives and rotaxane **2**[a]

Run	Styrene	[styrene] /[**2**]	Yield /%[b]	M_n (M_w/M_n)[c]	x[d]	T_{d5} /°C[e,f]
1	**4a**	4.0	70	2000 (1.51)	0.41	259
2	**4a**	2.3	63	3100 (1.54)	0.24	277
3	**4a**	1.5	93	6700 (1.35)	0.18	249
4	**4a**	1.0	32	2600 (1.38)	0.27	189
5	**4a**	0	n.r.[g]	—	—	—
6	**4b**	1.5	65	3700 (1.56)	0.27	279
7	**4c**	1.5	50	6700 (1.34)	0.25	273
8	**4d**	1.5	59	3600 (1.54)	0.30	283
9	**4e**	1.5	69	5400 (1.58)	0.18	315
10	**4f**	1.5	75	12000 (2.30)	0.18	281

[a]Reaction conditions: styrene + **2** = 0.100 mmol, AIBN = 6 µmol, solvent = toluene (0.1 mL), reaction time = 20 h, at 60 °C. [b]The yields of polymers were calculated on the basis of the total amount of the used monomers. [c]Determined by GPC based on polystyrene standard. [d]Incorporation ratio of rotaxane unit estimated by ^{1}H NMR. [e]5% weight loss temperature. [f]T_{d5} of DB24C8 = 295 °C. [g]No reaction.

moderate yields (50–75%) with the incorporation ratio of rotaxane unit, x, of 0.18–0.30. Molecular weight of polyrotaxane varies depending on the substituent group on the aromatic ring. Copolymerization of **2** with **4f** bearing electron-donating *para*-methoxy group yields **5f** with high molecular weight (M_n = 12000, M_w/M_n = 2.30). Methacrylamide with the rotaxane structure, **3**, does not undergo polymerization nor copolymerization with styrene in the presence of AIBN.

Thermal gravimetric analyses (TGA) of polyrotaxanes **5a**–**5f** (run 3 and 6–10) show 5% weight loss in the range of T_{d5} = 249–315 °C which is higher than that of monomer **2** (244 °C) and **3** (227 °C), indicating that thermal stability of rotaxane units was improved by incorporation to the thermally stable polystyrene.[13] The cyclic voltammogram (CV) of **5a** in CH_2Cl_2 solution of n-Bu_4NPF_6 shows a redox peak pair of Fe^{III}/Fe^{II} of the ferrocenyl group at $E_{1/2}$ = 0.08 V (vs Fc^+/Fc (Fc = ferrocene), scan rate = 0.1 V s^{-1}). The redox potential is slightly higher than that of **2** ($E_{1/2}$ = 0.06 V).

In summary, we succeeded in synthesis of the side chain polyrotaxanes by using [2]rotaxane monomer bearing a radically polymerizable acrylamide as a comonomer with styrenes. Obtained polyrotaxane shows higher thermal stability than rotaxane monomer. This method provides a new means for obtaining side chain polyrotaxane with high incorporation ratio of macrocyclic unit to polymer branches.[14]

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11 To a solution of **1** (3.23 g, 2.9 mmol) in THF (10 mL) were added i-Pr_2EtN (0.88 g, 6.8 mmol) and acryloyl chloride (0.65 g, 7.2 mmol). The mixture was stirred for 2 h at room temperature, followed by evaporation of solvent. Crude product was dissolved in $CHCl_3$, washed with water and dried over $MgSO_4$. Further purification by SiO_2 column chromatography (hexane/AcOEt = 5/1 then 1/1) gave **2** (1.48 g, 1.4 mmol, 48%) as a yellow solid.

12 A mixture of **2**, styrene **4a**, and AIBN (6 µmol) was dissolved in toluene (0.1 mL). The total amount of **2** and styrene was set to 0.10 mmol. The mixture was degassed and stirred at 60 °C for 20 h, followed by addition of CH_2Cl_2 (0.1 mL). The reaction mixture was added to hexane to cause separation of yellow solid which was collected by filtration and dried in vacuo to give polyrotaxane **5a** as a pale yellow solid. A part of monomer **2** was recovered by evaporation of the filtrate.

13 Degradation of polystyrene (M_n = 3600) was reported to start above 314 °C. See: B. V. Kokta, J. L. Valade, W. N. Martin, *J. Appl. Polym. Sci.* **1973**, *17*, 1.

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