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

Yuji Suzaki, Shintaro Murata, and Kohtaro Osakada*

Chemical Resources Laboratory R1-3, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

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Radical copolymerization of styrenes and a [2]rotaxane monomer composed of ferrocene-containing *N*,*N*-dialkylacryl-amide 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-8ether (DB24C8) and acrylamide derivative to produce the side chain polyrotaxanes as well as the properties of the rotaxanefunctionalized polystyrenes.

[2]Rotaxane monomer **2** was synthesized by acylation of the nitrogen of cationic rotaxane [{(Fe(C₅H₄)(C₅H₅))CH₂NH₂CH₂-C₆H₄-4-OCH₂CH₂CHCHCOO-C₆H₃-3,5-Me₂}(DB24C8)]-(PF₆) (**1**) with acryloyl chloride in THF/*i*-Pr₂EtN (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 ¹H NMR spectrum of **2**. The ¹H 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 ¹H NMR spectroscopy.



Scheme 1. Synthetic strategies toward side chain polyrotaxanes.



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 ¹H NMR spectrum of **5a**. The signals at δ 2.26 (Me), 1.59 (CH₂-main chain), and 3.4–4.0 (CH₂-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.



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. ¹H NMR spectra of (a) **2**, and (b) **5a** (run 3 of Table 1) (300 MHz, CDCl₃, rt). The peak with asterisk indicates residual solvent (CHCl₃).

Table 1. Copolymerization of styrene derivatives and rotaxane 2^{a}

Run	Styrene	[styrene] /[2]	Yield /% ^b	$M_{\rm n}~(M_{\rm w}/M_{\rm n})^{\rm c}$	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	4 a	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	4 c	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

^aReaction conditions: styrene + **2** = 0.100 mmol, AIBN = 6μ mol, solvent = toluene (0.1 mL), reaction time = 20 h, at 60 °C. ^bThe yields of polymers were calculated on the basis of the total amount of the used monomers. ^cDetermined by GPC based on polystyrene standard. ^dIncorporation ratio of rotaxane unit estimated by ¹H NMR. ^e5% weight loss temperature. ^fT_{d5} of DB24C8 = 295 °C. ^gNo 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 CH₂Cl₂ solution of *n*-Bu₄NPF₆ 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*-Pr₂EtN (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 CHCl₃, washed with water and dried over MgSO₄. Further purification by SiO₂ 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 (6µmol) 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.
- 14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/ index.html.