Polymer Journal, Vol. 36, No. 11, pp. 927—932 (2004)

NOTES

Synthesis of Side-Chain Polyrotaxane *via* Radical Polymerizations of Vinylic Pseudorotaxane Monomers Having Paraquat-type Macrocycle as a Wheel Component

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(Received May 19, 2004; Accepted August 17, 2004; Published November 15, 2004)

KEY WORDS Side-Chain Polyrotaxane / Radical Polymerization / Pseudorotaxane Monomer / Paraquat-type Macrocycle /
[DOI 10.1295/polymj.36.927]

Interlocked molecules such as rotaxanes have a striking feature of mechanical bond.[1] Because of the unconventional characteristics of the mechanical bonds, polyrotaxanes are expected to exhibit unusual viscoelastic properties such as a very large loss modulus, a low activation energy for viscous flow, and a rapid stress relaxation.[2,3] Applications of polyrotaxanes to a novel molecular electronic device[4] and new gel systems[5,6] have recently been examined.

Polyrotaxanes that have been prepared so far are roughly classified into two types, *i.e.*, main-chain and side-chain types both of which have covalently linked polymer backbones. These polyrotaxanes are distinguished from those with topologically linked polymer backbones like poly[3]rotaxane, the first polyrotaxane bearing non-covalent main chain.[7] Ritter *et al.* and we have recently reported versatile and efficient methods for the preparation of side-chain type polyrotaxanes by radical polymerization of vinylic pseudorotaxane monomers (Scheme 1).[8,9] Ritter *et al.* utilized the pseudorotaxane based on a cyclodextrin–aliphatic chain motif,[8] whereas our system relied on the pseudorotaxane based on a crown ether–*sec*-ammonium salt motif.[9,10]

The pseudorotaxane monomer strategy in side-chain type polyrotaxane synthesis has been demonstrated to have some advantageous characteristics including facile and certain introduction of rotaxane units into polymers, easy synthesis of various polyrotaxanes, simple control of rotaxane unit content by copolymerization with other vinyl monomers, and modification of polymerization behavior by rotaxane formation.[9,10] It is a quite important task to explore other pseudorotaxane motifs for the design of new pseudorotaxane monomers and polyrotaxanes.[8,9] In this paper, we report the synthesis of side-chain polyrotaxanes by radical polymerization of vinylic pseudorotaxane monomers consisting of hydroquinol-derived axle having acrylate group and a paraquat-type tetracationic macrocycle.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR measurements were performed on JEOL JNM-GX-270 and JNM-L-400 spectrometers in $CDCl_3$ with tetramethylsilane as an internal reference. IR spectra were recorded on a JASCO FT-IR model 230 spectrometer. Molecular weight was estimated by GPC on a JASCO Gulliver System equipped with three polystyrene gel columns (Tosoh TSKgel G5000H_{XL}, G4000H_{XL}, and G2500H_{XL}) at 35 °C, using $CHCl_3$ as an eluent (flow rate, 1.0 mL min^{-1}).

*Synthesis of 3,5-Di-t-butylbenzoic Acid Ester (**2**).* To a CH_2Cl_2 (4.3 mL) solution of diol **1**[11] (1.20 g, 4.27 mmol) and Et_3N (3.40 g, 34.8 mmol) was added a CH_2Cl_2 (4.3 mL) solution of 3,5-di-*t*-butylbenzoyl chloride[12] (1.00 g, 4.27 mmol). The mixture was stirred for 3 h, diluted with ether (50 mL), washed with 2 M HCl (20 mL × 2), 10% NaOHaq (20 mL × 1), water (20 mL × 1), and brine (20 mL × 2), dried ($MgSO_4$), and evaporated to dryness. The residue was chromatographed over silica gel (CH_2Cl_2) to give monoester **2** in 39% yield as colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.90 (d, $J = 2$ Hz, 2H, ArH of endcap), 7.62 (t, $J = 2$ Hz, 1H, ArH of endcap), 6.83 (s, 4H, *p*-phenylene), 4.50 (m, 2H, CH_2), 4.10–3.60 (m, 14H, CH_2), 1.34 (s, 18H, *t*-Bu). FT-IR (film) ν 3502 (ν_{O-H}), 1716 ($\nu_{C=O}$) cm^{-1}.

*Synthesis of Acrylic Acid Ester (**3**).* To a THF

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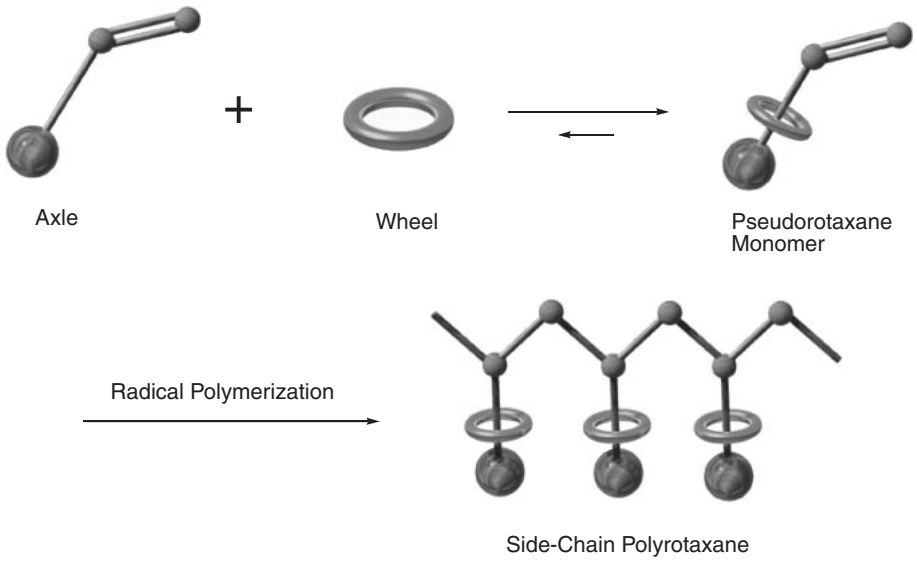


Scheme 1.

(9.0 mL) solution of monoester **2** (0.84 g, 1.6 mmol) and Et_3N (0.25 g, 2.5 mmol) was added acryloyl chloride (0.23 g, 2.5 mmol). The mixture was stirred for 1 h at room temperature. The mixture was acidified with 2 M HCl (100 mL) and extracted with ether (100 mL × 1). The extract was washed with water (30 mL × 1) and brine (30 mL), dried ($MgSO_4$), and evaporated to dryness. The residue was purified with silica gel chromatography (CH_2Cl_2) to afford acrylate **3** in 41% yield as a colorless oil. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.90 (d, $J = 2$ Hz, 2H, ArH of endcap), 7.62 (t, $J = 2$ Hz, 1H, ArH of endcap), 6.72 (s, 4H, *p*-phenylene), 6.42 (dd, $J = 17$ Hz, 2 Hz, 1H, OCOCH=C$\underline{H}_2$ (*cis* to C=O)), 6.14 (dd, $J = 17$ Hz, 10 Hz, 1H, OCOC$\underline{H}$=CH_2), 5.83 (dd, $J = 10$ Hz, 2 Hz, 1H, OCOCH=C$\underline{H}_2$ (*trans* to C=O)), 4.54–4.48 (m, 2H, CH_2O), 4.37–4.31 (m, 2H, CH_2O), 4.13–4.04 (m, 2H, CH_2O), 3.94–3.78 (m, 2H, CH_2O), 1.34 (s, 18H, *t*-Bu). FT-IR (film) ν 1722 ($\nu_{C=O}$), 1635 ($\nu_{C=C}$) cm^{-1}.

*A Typical Procedure for Polymerization of Pseudorotaxane Monomer (**6**·PF$_6$).* A mixture of acrylate **3** (278 mg, 0.500 mmol), cyclophane **4**·PF_6[11] (550 mg, 0.500 mmol), AIBN (10 mg, 0.06 mmol), and acetonitrile (5.0 mL) was heated in a sealed tube under Ar atmosphere at 70 °C for 20 h. The mixture was allowed to cool to room temperature and evaporated to dryness to give a mixture of polyrotaxane (**6**·PF_6) and unincorporated wheel (**4**·PF_6) as a red solid. ^{1}H NMR (DMSO-d_6, 270 MHz) δ 9.4 (d, $J = 6$ Hz, 8H, H_α of **4**·PF_6), 9.2 (br s, 8H, H_β of wheel), 8.7 (d, $J = 6$ Hz, 8H, H_β of **4**·PF_6), 8.3 (br s, 8H, H_β of wheel), 7.8 (br s, 8H, *p*-phenylene of wheel), 7.7 (s, 8H, *p*-phenylene of **4**·PF_6), 7.7–7.5 (m, 3H, ArH of endcap), 6.7 (br s, 8H, *p*-phenylene of axle), 5.8 (br s, 8H, CH_2 of wheel), 5.7 (s, 8H, CH_2 of wheel), 4.5–3.0 (m, 16H, CH_2O of axle), 2.5 (br s, 1H, CH of the main chain), 1.3–1.0 (br s, 20H, *t*-Bu and CH_2 of the main chain). From the ^{1}H NMR spectrum, the *R* value (the incorporation ratio of rotaxane unit) was determined to be 10%. FT-IR (KBr) ν 2965, 1718, 1637, 1508, 1450, 1238, 1153, 840 (PF_6), 781, 642, 557 (PF_6), 530 cm^{-1}.

*Isolation of Polyrotaxane (**6**·Cl).* A mixture of **6**·PF_6 and **4**·PF_6 in H_2O–sat.NH_4Claq–MeOH (1/1/2 (v/v/v)) was refluxed for 1 d. The mixture was cooled to room temperature and filtered to give polyrotaxane (**6**·Cl) as a red solid. ^{1}H NMR (DMSO-d_6, 270 MHz): see Figure 2(v). FT-IR (KBr) ν 2960, 1722, 1631, 1508, 1454, 1363, 1238, 1132, 1062, 946, 827, 773, 707, 541, 526 cm^{-1}.

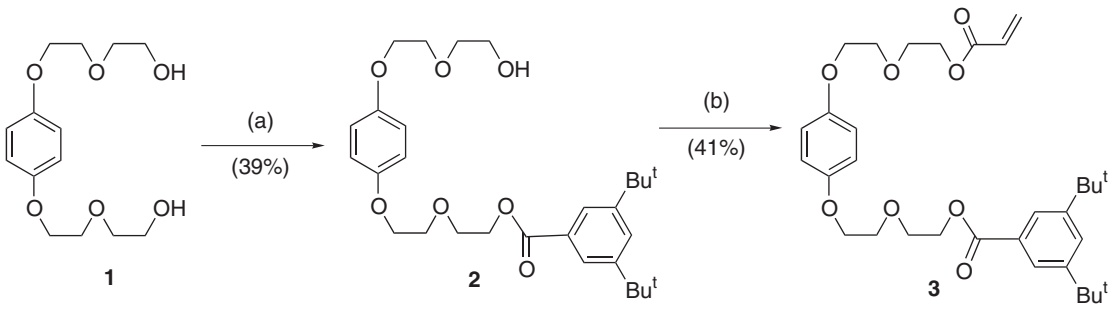
RESULTS AND DISCUSSION

Synthesis of Axle and Wheel Components

Axle having an acryl end (**3**) was synthesized as illustrated in Scheme 2. Monoesterification of **1** with 3,5-di-*t*-butylbenzoyl chloride lead to the corresponding monoester (**2**),[11] which was converted to **3** by acylation with acryloyl chloride. Paraquat-type tetracationic macrocycle (**4**·PF_6) as the wheel component was prepared according to the Stoddart's method.[11]

Pseudorotaxane Monomer

The pseudorotaxane monomer (**5**·PF_6) was prepared *in situ* by adding an equimolar amount of **3** to a CD_3CN solution of **4**·PF_6. Upon addition of **3**, the ^{1}H NMR signals of aromatic protons a and b in **4**·PF_6 exhibited upfield shifts (*ca.* −0.02 ppm and *ca.* −0.20 ppm for a and b, respectively), while that



Scheme 2. Synthesis of Axle (**3**). Reagents and conditions: (a) 3,5-bis(di-*t*-butyl)benzoyl chloride, Et_3N, CH_2Cl_2, rt; (b) acryloyl chloride, Et_3N, CH_2Cl_2, rt.

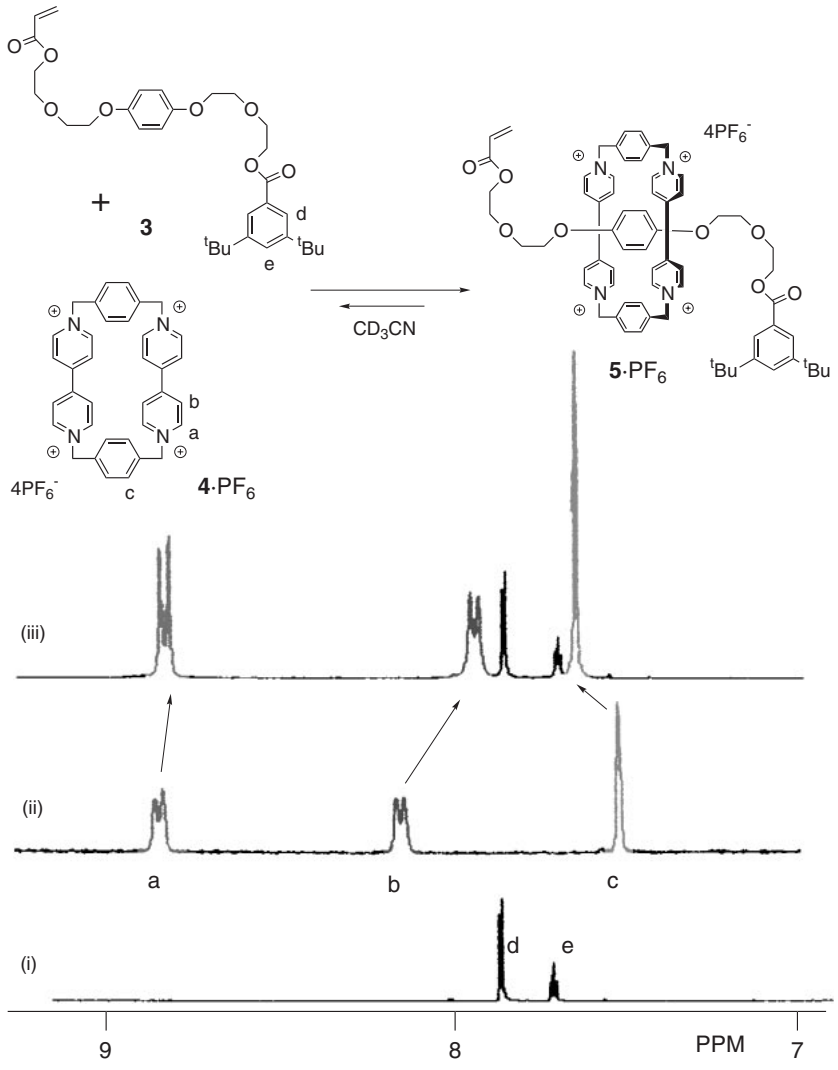


Figure 1. Partial ^1H NMR spectra (270 MHz, CD_3CN, 298 K) of (i) axle (**3**), (ii) wheel (**4**·PF_6), and (iii) pseudorotaxane monomer (**5**·PF_6).

of c in **4**·PF_6 showed a downfield shift (*ca.* +0.14 ppm), as shown in Figure 1. These behaviors were consistent with the ^1H NMR spectral change between the pseudorotaxane prepared *in situ* from **1** and **4**·PF_6 in CD_3CN, which was reported by Stoddart *et al.*[11] In accordance with these changes, the color change of the solution from colorless to brownish orange was observed. This is attributed to the charge transfer complex formation between the bipyridinium units and the hydroquinol ring.

Radical Polymerization of **5**·PF_6

Since the pseudorotaxane monomer (**5**·PF_6) exists in equilibrium between the axle monomer (**3**) and

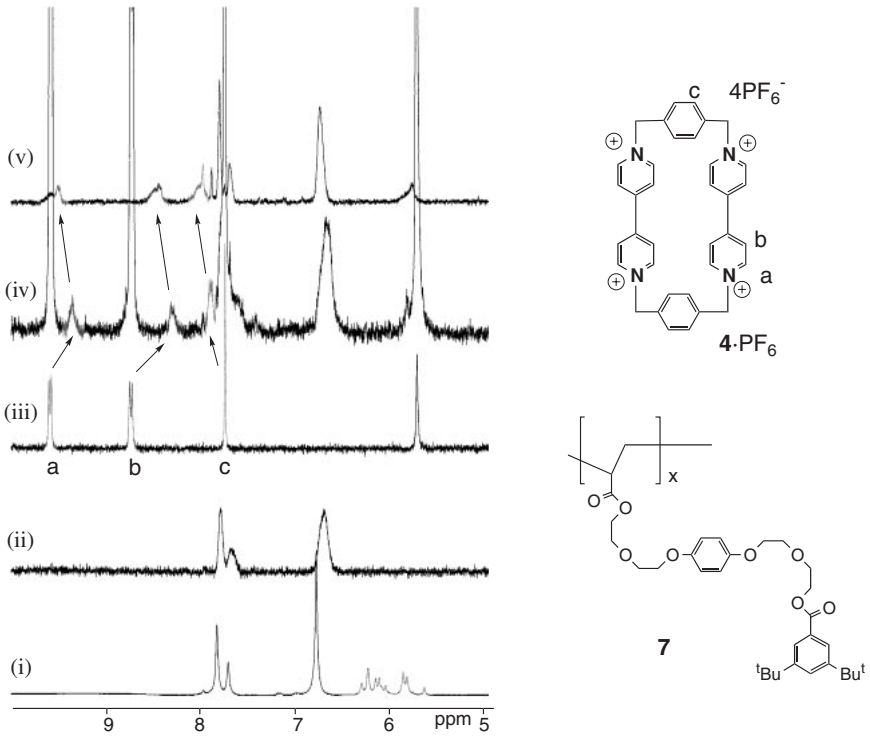


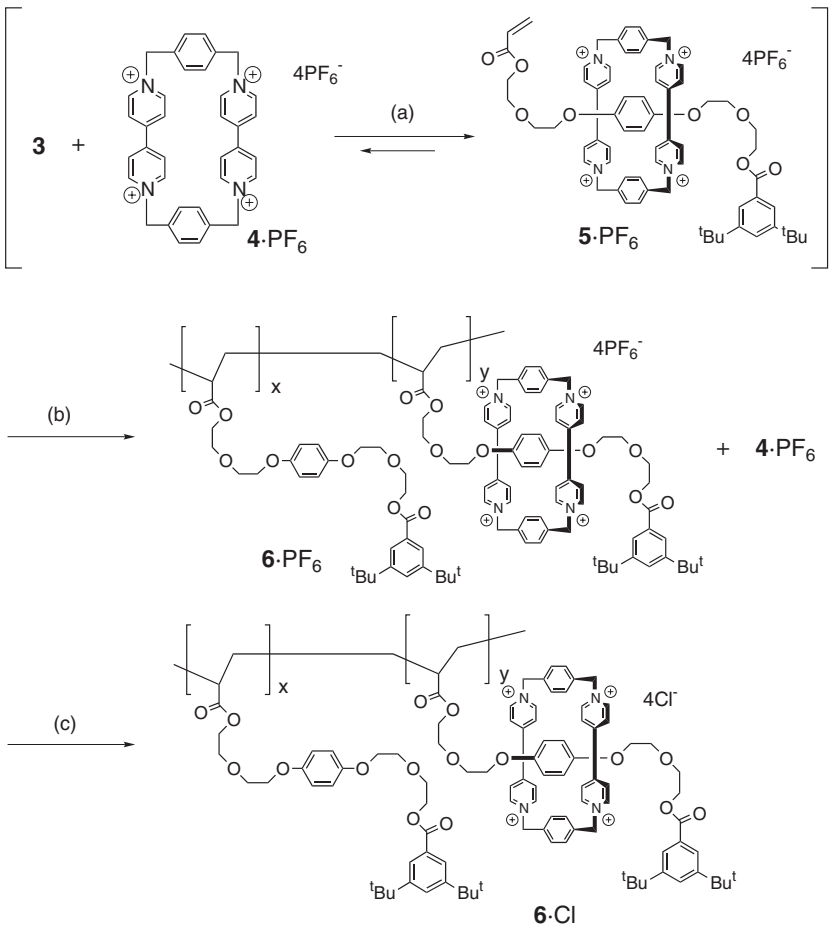
Figure 2. Partial ^{1}H NMR spectra (DMSO-d_6, 298 K, 270 MHz) of (i) axle (**3**), (ii) poly(axle) (**7**), (iii) wheel (**4**·PF_6), (iv) a mixture of polyrotaxane (**6**·PF_6) and wheel (**4**·PF_6), and (v) polyrotaxane (**6**·Cl).

4·PF_6, it is conceivable that **5**·PF_6 copolymerizes with **3** (Scheme 3). In particular, the polymerizability difference between them may largely affect the composition of the copolymers being formed.

The radical polymerization of **5**·PF_6 was carried out by heating an equimolar mixture of **3** and **4**·PF_6 in acetonitrile for 20 h. Evaporation of the reaction mixture gave a mixture of polyrotaxane **6**·PF_6 and **4**·PF_6 (recovered) as a red solid. The incorporation ratio of the rotaxane unit (R value, $R = 100y/(x + y)$) was determined to be 10% by its ^{1}H NMR spectrum in DMSO-d_6 (Figure 2). Since the isolation of **6**·PF_6 by precipitation was unsuccessful, counter anion exchange from hexafluorophosphate to chloride was conducted by refluxing the product mixture in H_2O–sat.NH_4Claq.–MeOH (1/1/2 (v/v/v)) for 24 h (Scheme 3). **6**·Cl was isolated in 28% yield by filtration, because **4**·Cl was soluble in water while **6**·Cl was not. **6**·Cl thus obtained was characterized by ^{1}H NMR, IR, and GPC. The absorption bands at 840 and 557 cm^{-1} due to PF_6 anion completely disappeared in the IR spectrum of **6**·Cl. The incorporation ratio (R value) of **6**·Cl was determined to be 12% by its ^{1}H NMR spectrum in DMSO-d_6 (Figure 2). The molecular weight of **6**·Cl was estimated to be an M_n of 5,000 ($M_w/M_n = 40$, $CHCl_3$, PSt standards) by GPC.

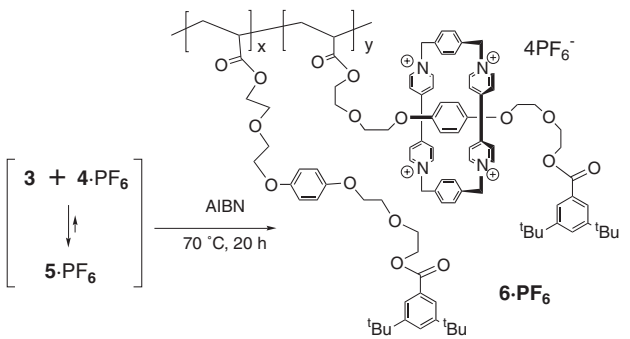
The low composition of the rotaxane unit can be accounted for by the polymerization rate difference between the acrylate **3** and the pseudorotaxane monomer **5**·PF_6 formed *in situ* in the competitive condition where these two species are in existence in an equilibrium (Scheme 3). Stoddart reported that association constant (K_a) for 1:1 complexation between a 1,4-dialkoxybenzene similar to **1** and the wheel **4** was 2220 M^{-1} (acetonitrile, 25 °C).[11] In this case, the complexation ratio is calculated to be 94%. Since in the present study the polymerization is carried out at 70 °C, the ratio would be lower than that. However, the low composition is difficult to explain only from the equilibrium because the complexation ratio is 80% even when $K_a = 200$. Therefore, it seems reasonable that the polymerization rate of **3** without the wheel is much larger than that of the pseudorotaxane monomer **5**·PF_6.

Various solvents were examined in the radical polymerization of **5**·PF_6 and the R value was determined by ^{1}H NMR (Table I). Methanol, THF, acetone, and chloroform resulted in $R = 0$, that is, no **4**·PF_6 was incorporated in the polymer side chain at all (entries 1–5). These results are attributed to the fact that **4**·PF_6 is highly insoluble in those solvents so that no **5**·PF_6 was formed. Almost same R values were observed for DMSO (9%) and acetonitrile (10%) (entries 5 and 6). The R value decrease was observed in the polymerization at a lower feed concentration of 0.01 M (entry 7) which leads to the lowered ratio of the pseudorotaxane formation. Increasing the feed



Scheme 3. Synthesis of pseudorotaxane monomer (**5**·PF_6) and side-chain polyrotaxane (**6**·PF_6). Reagents and conditions: (a) CH_3CN (0.10 M), rt; (b) AIBN (10 mol%), 70 °C, 20 h; (c) H_2O–sat. NH_4Claq–MeOH (1/1/2), reflux, 24 h.

Table I. Effects of solvent and concentration on the incorporation ratio



Entry	Solvent	Conc. (M)	AIBN (mol%)	R^a
1	MeOH	0.10	10	0
2	THF	0.10	10	0
3	Acetone	0.10	10	0
4	$CHCl_3$	0.10	10	0
5	DMSO	0.10	10	9
6	CH_3CN	0.10	10	10
7	CH_3CN	0.01	10	4
8	CH_3CN	0.50	12	5

[a]Incorporation ratio of the rotaxane units, $100y/(x + y)$, was determined by ^1H NMR.

concentration up to 0.50 M failed to enhance the *R* value, because a certain amount of **4**·PF_6 remained insoluble during the polymerization (entry 8). The *R* value decrease at high concentration can be explained by the prevention of the association to **5**·PF_6 due to the presence of highly polar compound **4**·PF_6 at high concentration. Thus, use of the solvents that could dissolve **4**·PF_6 is indispensable to get the polyrotaxane (**6**·PF_6), while polarity control of the whole system should be taken into consideration.

In summary, a new pseudorotaxane monomer **5**·PF_6 has been designed based on the paraquat-type tetracationic macrocycle–hydroquinol motif. The radical polymerization of **5**·PF_6 yielded the corresponding side-chain type polyrotaxane with *R* value up to *ca.* 10%. The *R* value highly depends on the solubility of the tetracationic macrocycle to the solvent and probably on the polarity of the whole polymerization system.

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