Synthesis of Side-Chain Polyrotaxane by Radical Polymerizations of Pseudorotaxane Monomers Consisting of Crown Ether Wheel and Acrylate Axle Bearing Bulky End-Cap and Ammonium Group

Toshikazu Takata,* Hiroaki Kawasaki, Nobuhiro Kihara, and Yoshio Furusho

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

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ABSTRACT: The mixing of an acrylate **1a** bearing secondary ammonium salt moiety and terminal di-*tert*-butylphenyl group with dibenzo-24-crown-8 (DB24C8) afforded the pseudorotaxane monomer **2a**. The association constant K_a was 18 L mol^{-1} in $CDCl_3$ at 25 °C. An equimolar mixture of **1a** and DB24C8 was heated at 60 °C for 20 h in benzene (0.5 M) in the presence of AIBN to give side-chain-type polyrotaxane in 66% yield. The incorporation ratio of the rotaxane unit, which is denoted by *R*, in the polyrotaxane was 0.42. The *R* value increased as the polymerization temperature decreased or the dielectric constant of the solvent decreased. The effect of the molar ratio [DB24C8]/[**1a**] on the *R* value was complicated since DB24C8 itself enhanced the polarity of the system. The *R* value increased until [DB24C8]/[**1a**] reached 1.0 in benzene, chlorobenzene, and 1,2-dichloroethane. When [DB24C8]/[**1a**] > 1, however, the *R* value increased gradually as [DB24C8]/[**1a**] increased in polar solvent such as 1,2-dichloroethane, while the *R* value rather decreased in less polar solvent such as benzene. The copolymerization of **2a** and styrene afforded the corresponding copolymer. The composition of the rotaxane unit could be controlled by the feed ratio of styrene, while the ratio of complexation of the ammonium group, i.e., rotaxane content to total acrylate, remained almost constant. The acylative neutralization of the resulting polyrotaxane afforded a nonionic polyrotaxane.

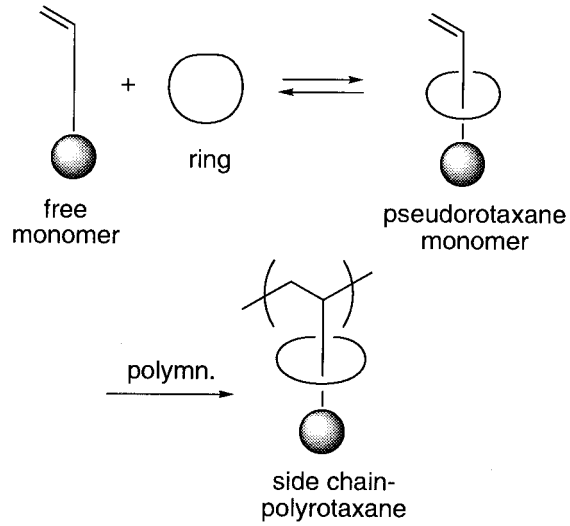
Introduction

Interlocked compounds such as rotaxanes and catenanes are characterized by the mechanical bonding by which plural numbers of component molecules interlock with each other so that the interlocked compound cannot fragment into each component without breaking any covalent bonding.[1−8] Because of the unconventional properties of mechanical bonding, polymers having mechanical bonding such as polyrotaxanes are believed to have extraordinary thermal, electric, photochemical, mechanical, and rheological properties.[9−20] Recently, applications of polyrotaxanes to a novel molecular electronics device[21] and a novel drug releasing system[22] have been examined.

Polyrotaxanes are roughly categorized into two types: main-chain-type polyrotaxane and side-chain-type polyrotaxane.[10,20] Since they have completely different topologies, they are expected to display different physical behaviors. Among the various side-chain-type polyrotaxanes, polymers with one wheel per side chain are among the most simple and versatile. Since various molecular devices have been proposed using interlocked compounds,[23−29] such side-chain-type polyrotaxanes make the molecular device arrays on polymer chains possible.

Ritter et al. first prepared side-chain-type polyrotaxane with small molecular cyclic components by the end-capping of a pseudorotaxane via a polymer reaction.[30] This method has been widely used in the preparation of various side-chain-type polyrotaxanes.[16,31−38] More recently, Ritter[39−41] and we[42] have independently reported the preparation of side-chain-type polyrotaxanes by the polymerization of pseudorotaxanes bearing polymerizable functional groups (Scheme 1). Thus, when an axle monomer with an attractive interaction site is mixed with a complementary ring molecule, the corresponding pseudorotaxane monomer can be formed. If the terminal substituent is bulky enough, the polymerization of the pseudorotaxane monomer results in the corresponding side-chain-type polyrotaxane. More attention should be given to the polymerization method for its advantageous characteristics including[1] facile and certain introduction of rotaxane units into polymers,[2] easy synthesis of various rotaxanes,[3] simple control of rotaxane unit content in the polymer chain, and[4] modification of polymerization behavior by rotaxane formation. These features are thought to present a valuable asset for the synthesis of polyrotaxane by the radical polymerization.

Scheme 1



* To whom all correspondence should be addressed.

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We have reported various syntheses of rotaxanes consisting of ammonium salts and crown ethers. Pseudorotaxane **2**, which was formed by mixing acrylate **1** with dibenzo-24-crown-8 (DB24C8), could be end-capped by radical polymerization[42] or conjugate addition reaction.[43] The acylative end-capping of hydroxy group-terminated pseudorotaxane was also reported.[44] We have demonstrated that these rotaxanes show extraordinary intramolecular hydrogen bonding between the ammonium group and crown ether components[45] and that the axle component reacts under strong influence of the wheel component.[46] These results motivated us to investigate the effect of reaction conditions on the polymerization behavior of pseudorotaxane **2** and the control of hydrogen bonding in the resulting polyrotaxane **3**. In this paper, we wish to report the details of the polymerization and copolymerization of **2** and the structural modification of **3**.

Experimental Section

General. ^{1}H NMR spectra were recorded on a JEOL JNM-GX270 and a JEOL JNM-LA400 spectrometer. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Polymers were isolated and purified by a JAICO LC-908 HPLC system with JAIGEL 1 (20 mm diameter × 600 mm) and JAIGEL 2 (20 mm diameter × 600 mm) columns using $CHCl_3$ as eluent. Molecular weight was calibrated by polystyrene standards. 3,5-Di-*tert*-butyltoluene was prepared according to the literature.[47] Carbon tetrachloride was distilled just before use. Commercial grade triethylamine and styrene were used after distillation from calcium hydride. Other chemicals were of reagent grade and were used without further purification. Initiators were kept in a freezer.

3,5-Di-*tert*-butylbenzaldehyde (4). A solution of 89.0 g (440 mmol) of 3,5-di-*tert*-butyltoluene, 78.3 g (440 mmol) of *N*-bromosuccinimide, and 850 mg (3.5 mmol) of benzoyl peroxide in carbon tetrachloride (280 mL) was refluxed for 2.5 h. The precipitate was filtered off, and the filtrate was washed with water. The organic layer was dried over magnesium sulfate and evaporated. The yellow residue was dissolved in 60% ethanol (180 mL), to which 30% formalin (43 mL) and 65.5 g (470 mmol) of hexamethylenetetramine were added. The mixture was refluxed for 5 h. The reaction mixture was extracted by ether. The organic layer was washed with 6 M hydrochloric acid, water, saturated sodium hydrogen carbonate solution, and then brine, dried over anhydrous magnesium sulfate, and evaporated to give a pale yellow solid. The crude aldehyde was recrystallized from hexane to give 48.0 g (50%) of 3,5-di-*tert*-butylbenzaldehyde (**4**) as colorless crystals.

mp 84−85 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 10.0 (1H, s, C*H*O), 7.72−7.73 (3H, m, Ar*H*), 1.37 (18H, s, CH_3).

3-(3,5-Di-*tert*-butylphenylmethylamino)-1-propanol (5). A solution of 4.1 g (55 mmol) of 3-amino-1-propanol and 12 g (55 mmol) of **3** in toluene (100 mL) was refluxed for 3.5 h in a flask equipped with a Dean−Stark apparatus. After evaporation of the solvent, 4.2 g (110 mmol) of sodium borohydride was added portionwise to a solution of the residue in methanol (300 mL) with vigorous stirring within 1 h at room temperature. After evaporation of the solvent, the residue was poured into 2 M hydrochloric acid. Sodium hydroxide solution was added to basify the solution, and the solution was extracted with benzene. The organic layer was washed successively with water, saturated sodium hydrogen carbonate solution, and then brine, dried over anhydrous magnesium sulfate, and evaporated to give 14.2 g (93%) of **5** as colorless oil, which eventually solidified. The product was used in the next step without further purification.

mp 57.0−58.0 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.33 (1H, t, J = 1.8 Hz, Ar*H*), 7.14 (2H, d, J = 1.8 Hz, Ar*H*), 3.83 (2H, t, J = 5.5 Hz, CH_2OH), 3.79 (2H, s, ArCH_2NH), 3.14 (2H, br, O*H* and N*H*), 2.94 (2H, t, J = 5.2 Hz, NHCH_2CH$_2$), 1.74 (2H, m, NHCH$_2$CH_2CH$_2$OH), 1.37 (18H, s, CH_3).

***tert*-Butyl *N*-(3,5-Di-*tert*-butylphenylmethyl)-*N*-(3-hydroxypropyl)carbamate (6).** To a solution of 11.1 g (40 mmol) of **5** and 50 mg (0.41 mmol) of 4-(dimethylamino)-pyridine in chloroform (340 mL) was added 9.2 g (42 mmol) of di-*tert*-butyl dicarbonate. The mixture was stirred at room temperature for 1 h, washed with 2 M hydrochloric acid, and then water, dried over anhydrous magnesium sulfate, and evaporated. The residue was chromatographed (silica gel, eluent; dichloromethane) to give 14.0 g (93%) of **6** as colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$): δ 7.33 (1H, t, J = 1.8 Hz, Ar*H*), 7.08 (2H, d, J = 1.8 Hz, Ar*H*), 4.37 (2H, s, ArCH_2N), 3.55 (2H, t, J = 5.5 Hz, CH_2OH), 3.40 (2H, m, NCH_2CH$_2$), 3.30 (1H, br, O*H*), 1.60 (2H, m, NHCH$_2$CH_2CH$_2$OH), 1.49 (9H, s, CH_3), and 1.31 (18H, s, CH_3). IR (NaCl): 3450 (ν_{OH}), 1684 ($\nu_{C=O}$) cm^{-1}. Anal. Calcd for $C_{23}H_{39}NO_3$: C, 73.17; H, 10.41; N, 3.71. Found: C, 72.74; H, 10.66; N, 3.64.

***tert*-Butyl *N*-(3-Acryloyloxypropyl)-*N*-(3,5-di-*tert*-butylphenylmethyl)carbamate (7a).** To a solution of 3.0 g (8.0 mmol) of **6** and 1.2 g (12 mmol) of triethylamine in THF (85 mL) was added 1.1 g (12 mmol) of acryloyl chloride. The mixture was stirred at room temperature for 5 h. The reaction mixture was poured into 2 M hydrochloric acid and extracted with ether. The extract was washed with water and then brine, dried over anhydrous magnesium sulfate, and evaporated. The residue was chromatographed (silica gel, eluent; ethyl acetate/hexane (1/7 v/v)) to give 1.76 g (51%) of **7a** as colorless oil.

^{1}H NMR (270 MHz, $CDCl_3$): δ 7.32 (1H, m, Ar*H*), 7.07 (2H, m, Ar*H*), 6.39 (1H, dd, J = 17.1 and 1.8 Hz, CH=CH_2), 6.10 (1H, dd, J = 17.1 and 10.4 Hz, C*H*=CH$_2$), 5.81 (1H, dd, J = 10.4 and 1.8 Hz, CH=CH_2), 4.41 (2H, m, ArCH_2N), 4.16 (2H, m, CH_2OCO), 3.30 (2H, m, NCH_2CH$_2$), 1.87 (2H, m, CH$_2$CH_2-CH$_2$), 1.47 (9H, s, CH_3), and 1.31 (18H, s, CH_3). Anal. Calcd for $C_{26}H_{41}NO_4$: C, 72.35; H, 9.57; N, 3.25. Found: C, 72.39; H, 9.52; N, 3.44.

***tert*-Butyl *N*-(3-Methacryloyloxypropyl)-*N*-(3,5-di-*tert*-butylphenylmethyl)carbamate (7b). 7b** was synthesized in 71% yield in a similar manner as **7a**, except that methacryloyl chloride was used instead of acryloyl chloride.

Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.32 (1H, m, Ar*H*), 7.07 (2H, m, Ar*H*), 6.09 (1H, m, =CH_2), 5.54 (1H, m, =CH_2), 4.42 (2H, s, ArCH_2N), 4.15 (2H, m, CH_2OCO), 3.29 (2H, m, NCH_2CH$_2$CH$_2$), 1.93 (3H, m, =C−CH_3), 1.89 (2H, m, CH$_2$CH_2CH$_2$), 1.48 (9H, s, CH_3), and 1.31 (18H, s, CH_3). Anal. Calcd for $C_{27}H_{43}NO_4$: C, 72.77; H, 9.73; N, 3.14. Found: C, 72.48; H, 9.90; N, 3.03.

***N*-(3,5-Di-*tert*-butylphenylmethyl)-*N*-(3-acryloyloxypropyl)ammonium Hexafluorophosphate (1a).** To a solution of 1.73 g (4.0 mmol) of **7a** in chloroform (60 mL) was added 3.0 g (26 mmol) of trifluoroacetic acid, and the mixture was stirred at room temperature for 48 h. The reaction mixture was evaporated, and the residue was dissolved in dichloromethane. The organic layer was washed with saturated ammonium hexafluorophosphate aqueous solution and then brine, dried over anhydrous magnesium sulfate, and evaporated to give 1.47 g (77%) of **1a** as colorless crystal. Since **1a** polymerized upon heating before melting **1a** showed no melting point.

^{1}H NMR (270 MHz, $CDCl_3$): δ 7.45 (1H, m, Ar*H*), 7.35 (2H, m, Ar*H*), 6.32 (1H, dd, J = 17.1 and 1.2 Hz, CH=CH_2), 6.03 (1H, dd, J = 17.1 and 10.4 Hz, C*H*=CH$_2$), 5.80 (1H, dd, J = 10.4 and 1.2 Hz, CH=CH_2), 4.20 (2H, t, J = 6.1 Hz, CH_2OCO), 4.14 (2H, m, ArCH_2NH$_2$), 3.04 (2H, m, NH$_2$CH_2CH$_2$), 2.19 (2H, m, CH$_2$CH_2CH$_2$), and 1.32 (18H, s, CH_3). Anal. Calcd for $C_{21}H_{34}F_6NO_2P$: C, 52.83; H, 7.18; N, 2.93. Found: C, 52.64; H, 7.36; N, 3.03.

***N*-(3,5-Di-*tert*-butylphenyl)methyl-3-(methacryloyloxy)propylammonium Hexafluorophosphate (1b). 1b** was synthesized in 81% yield in a similar manner as **1a**, except that **7b** was used instead of **7a**.

mp 138.2−139.3 °C (dec). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.40 (2H, br, NH_2), 7.52−7.28 (3H, m, Ar*H*), 6.03 (1H, s, =CH_2), 5.56 (1H, m, =CH_2), 4.22 (2H, t, J = 5.5 Hz, CH_2OCO), 4.15 (2H, s, ArCH_2N), 3.03 (2H, m, NCH_2CH$_2$CH$_2$), 2.19 (2H, m, CH$_2$CH_2CH$_2$), 1.86 (3H, s, =C−CH_3), and 1.32 (18H, s, CH_3).

Anal. Calcd for $C_{22}H_{36}F_6NO_2P$: C, 53.76; H, 7.38; N, 2.85. Found: C, 53.28; H, 7.17; N, 2.94.

Polymerization of 2. Typical Procedure. A solution of 48 mg (0.1 mmol) of **1a**, 45 mg (0.1 mmol) of DB24C8, and 1 mg (0.003 mmol) of 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) in 0.2 mL of benzene was placed in a glass tube, and the tube was degassed and sealed in vacuo. The mixture was heated at 40 °C for 20 h. After the volatiles were removed in vacuo, the residue was purified by preparative GPC to isolate higher molecular weight fractions (>5000, PSt standards). Polyrotaxane **3** (45 mg, 64% yield as 51% incorporation ratio of rotaxane unit) was obtained as pale yellow solid.

Effect of [DB24C8]/[1a] to the *R* Value. To a solution of 48 mg (0.1 mmol) of **1a** and 1 mg (0.003 mmol) of AIBN in 0.2 mL of solvent was added a suitable amount of DB24C8 (see Figure 2) in a glass tube. The tube was degassed and sealed in vacuo. The polymerization was carried out at 60 °C for 20 h, and the reaction mixture was treated as described above. In the experiment without solvent, *tert*-butyl hydroperoxide was used instead of AIBN, and polymerization was carried out with 224 mg (0.5 mmol) of DB24C8 at 110 °C (melting point of DB24C8 is 105 °C) for 20 h.

Copolymerization of 2a with Styrene. General Procedure. A mixture of **1a**, styrene, DB24C8, and AIBN (amount, see Table 2) was dissolved in 0.2 mL of benzene in a glass tube. The total amount of **1a** and styrene was set to 0.1 mmol. The amount of DB24C8 used was 1 equiv of **1a**. The amount of AIBN was 3 μmol. The tube was degassed, sealed in vacuo, and heated at 60 °C for 20 h. The reaction mixture was treated as described above.

Acetylation of 3a. To a solution of 29 mg of **3a** (rotaxane content = 44%, with a total 86 μmol of ammonium salt group) in benzene (0.1 mL) were added 36 μL (260 μmol) of triethylamine and 25 μL (260 μmol) of acetic anhydride, and the mixture was stirred for 48 h. The reaction mixture was washed by saturated ammonium chloride solution, saturated sodium hydrogen carbonate solution, and then brine, dried over anhydrous magnesium sulfate, and evaporated to give 10 mg of acetylated polyrotaxane as pale yellow solid.

IR (NaCl); 1729 ($\nu_{C=O}$), 1643 ($\nu_{C=O}$) cm^{-1}.

Results and Discussion

Synthesis of Monomer. (Meth)acrylates **1** were prepared as illustrated in Scheme 3. The oxidation of 3,5-di-*tert*-butyltoluene[47] to aldehyde **4** followed by reductive amination afforded amino alcohol **5**. After the amino group was protected by a Boc group to give **6**, acylation by (meth)acryloyl chloride gave (meth)acrylate **7**. Finally, **7** was deprotected by trifluoroacetic acid (TFA), and the anion exchange of the resulting TFA salt afforded hexafluorophosphate **1**. The analytical data as well as the spectral data of **7** and **1** were consistent with their structure.

Equilibrium of Monomers. Since pseudorotaxane monomer **2** is present in an equilibrium with nonrotaxane monomer **1**, the simple homopolymerization of **2** does not proceed but copolymerization with **1** occurs. The concentration of **1** and **2** in the system depends on the thermodynamic nature of the equilibrium and the reaction conditions such as amount of DB24C8, temperature, and property of the solvent used. If the rate of interconversion between **1**+DB24C8 and **2** is comparable with that of polymerization, the kinetic nature of the equilibrium also affects the copolymerization of **1** and **2**.

Figure 1 shows the ^{1}H NMR spectra of **1a** (a) before and after the addition of 1 equiv of DB24C8 (b) in $CDCl_3$. A new set of signals assignable to pseudorotaxane **2a** (**1a**−DB24C8 complex) appeared in the spectrum of the mixture, while the signals of both free DB24C8 and **1a** remained present. Among these signals, noteworthy are

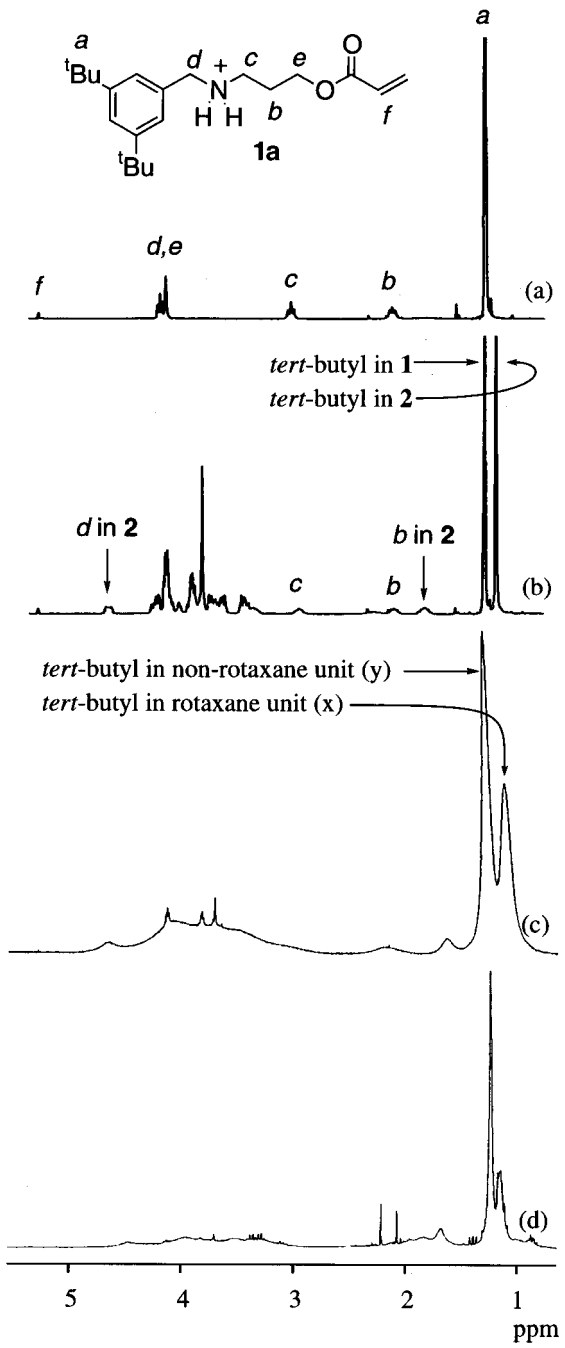


Figure 1. Partial ^{1}H NMR (270 MHz, 25 °C) spectra of (a) **1a** ($CDCl_3$), (b) an equimolar mixture of **1a** and DB24C8 ([**1a**] = [DB24C8] = 1.5×10^{-1} L mol^{-1}, $CDCl_3$), (c) **3a** obtained in benzene at 60 °C with 1 equiv of DB24C8 (R = 0.42, $CDCl_3$), and (d) **4** obtained by the treatment of **3** with excess amount of acetic anhydride and triethylamine ($CDCl_3$).

tert-butyl and benzylic methylene protons. The signals of *tert*-butyl protons are observed at 1.30 ppm for **1a** (uncomplexed) and 1.20 ppm for **2a** (complexed). The upfield shift observed for **2a** can be accounted for by the shielding effect of the benzene ring of DB24C8. On the other hand, the signal of benzylic methylene protons of **2a** is observed at 4.7 ppm as a complex multiplet, while that of **1a** is observed at 4.1 ppm as a singlet. The type of change observed in the benzylic methylene proton signal is characteristic of rotaxane consisting of benzylammonium salt and DB24C8.[48−52]

The association constant K_a of **1** with DB24C8 can be easily evaluated from the intensities of both com-

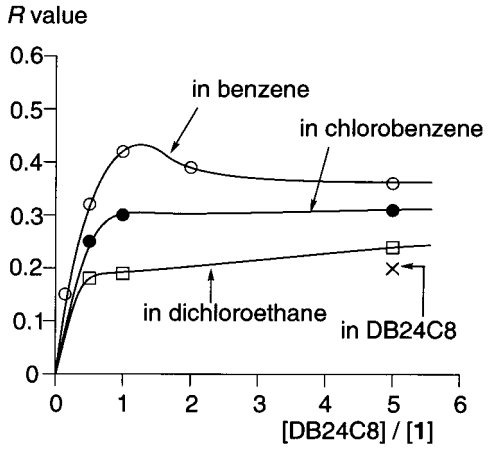


Figure 2. Effect of [DB24C8]/[**1a**] on the *R* value. Polymerizations were carried out in benzene (○), chlorobenzene (●), and dichloroethane (□) ([**1a**] = 0.5 mol/L) at 60 °C for 20 h using 3 mol % of AIBN as an initiator. Polymerization without solvent (×) was carried out at 110 °C using 3 mol % of *tert*-BuOOH as an initiator.

plexed and uncomplexed *tert*-butyl proton signals. The K_as were determined at 25 °C in $CDCl_3$: 18 M^{-1} for **1a** and 12 M^{-1} for **1b**. The K_as of **1** and DB24C8 were smaller than those of similar unhindered benzylammonium salts and DB24C8 because of the steric hindrance of bulky 3,5-di-*tert*-butylphenyl group and the intramolecular hydrogen bonding between ammonium and (meth)acrylate groups.[46,49,52] However, 72% of **1a** is, for example, present as the pseudorotaxane form **2a** when equimolar DB24C8 is added in 0.5 M $CDCl_3$ solution of **1a**. Thus, **2a** is stable enough to behave as the major species in the system.

The fact that the ^{1}H NMR signals of **1** and **2** were observed separately indicates that the rate of threading and dethreading in $CDCl_3$ is slower than the time scale of the ^{1}H NMR (millisecond order in this case). When C_6D_6 was used as the solvent, the signals of **1** did not separate by the addition of DB24C8 but rather shifted. This observation indicates that the equilibrium is faster in C_6D_6 than in $CDCl_3$. The evaluation of K_a in C_6D_6 by ^{1}H NMR titration was unsuccessful because the chemical shift of **1** depended on its concentration. In any case, the system reached an equilibrium within a minute when the temperature or concentration was changed. Therefore, the rate at which the equilibrium is reached is far faster than the polymerization rate (minutes−hour order), and the system maintains this equilibrium during polymerization.

Polymerization of 2. The basic features of the radical polymerization of **2** were studied by heating an equimolar mixture of **1** and DB24C8 (0.5 M) at 60 °C for 20 h in benzene in the presence of AIBN. Since the isolation of polyrotaxane **3** by precipitation was unsuccessful because of coprecipitation of the monomer or DB24C8, **3** was isolated by preparative GPC.

When **1a** was used as axle monomer, **3a** was obtained in 66% yield as a fraction of molecular weight over 5000 (PSt standards). The ^{1}H NMR spectrum of **3a** shows that the olefinic proton signals of the acrylate group disappeared while the main chain methylene group appeared around 1 ppm as a broad signal. The signals of the *tert*-butyl protons were observed separately at 1.15 and 1.26 ppm (Figure 1c). These signals corresponded to those of **1a** and **2a**. Further, the homopolymer of **1a** prepared independently showed the ^{1}H NMR signal of its *tert*-butyl protons at 1.26 ppm. Therefore, **3a** consists of both rotaxane (from **2a**) and non-rotaxane (from **1a**) units. The *tert*-butyl protons in rotaxane units showed a higher chemical shift than those in the non-rotaxane units, consistent with the ^{1}H NMR results of **1a** and **2a** discussed above. The *R* value [$x/(x + y)$], which indicates the incorporation ratio of rotaxane unit in the polymer, was calculated to be 0.42 from the intensities of the ^{1}H NMR signals of *tert*-butyl protons under the polymerization condition. The reproducibility of the *R* values was under the error level of the ^{1}H NMR experiments (ca. 5%) throughout the following runs.

The polymerization of **1b** in the presence of DB24C8 was carried out under similar conditions. The corresponding polyrotaxane **3b** (MW > 5000) was obtained in 76% yield. The composition of **3b** could be evaluated in the same manner, and the *R* value was 0.34. As the first approximation, the *R* value reflected the value of K_a or the ratio of [**2**]/[**1**].

Generally, K_a between ammonium salt and crown ether decreases as solvent polarity increases or temperature rises. Although solvent polarity has been evaluated by various parameters, the most suitable parameter for pseudorotaxane formation has not yet been confirmed. Further, the conformation of polymer chains in a solvent can affect the polymerization behavior. Thus, the effects of solvent and temperature on the radical polymerizations of **2a** were investigated. The results are summarized in Table 1 with specific solvent parameters.[53]

The *R* value increased as the polymerization temperature decreased, in accordance with the fact that pseudorotaxane formation is favored at lower temperatures. When the polymerization was carried out at 40 °C using 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) as an initiator, the *R* value was 0.51, the highest value observed in this system. The choice of solvent also largely affected the *R* value. Although the effect of donor number (DN) of solvent has been discussed in analogous pseudorotaxane systems,[48,49,51,54] the *R* value did not correspond to DN in the present system. Instead, the dielectric constant (ϵ_r) of the solvent was related to the *R* value: the *R* value generally increased as ϵ_r of solvent decreased. It is very impressive that a high *R* value was obtained in 1,4-dioxane despite its larger DN value. A similar solvent effect has been observed in the preparation of rotaxane consisting of crown ether and ammonium salt.[43] While primary ammonium salts form complexes with crown ethers mainly by the hydrogen-bonding interaction, the ion−dipole interaction plays an important role as well in pseudorotaxane consisting of secondary ammonium salt and crown ether. A higher DN prevents the hydrogen-bonding interaction, and a higher ϵ_r prevents the ion−dipole interaction. Therefore, the use of a low ϵ_r solvent increased K_a in the **1a**−DB24C8 system and consequently also raised the *R* value. Since the DN value of the solvent also affected K_a, the *R* value did not correlate simply with ϵ_r.

Based on these results, the polymerization of **2a** was investigated at −45 °C initiated by irradiation in the presence of AIBN. Low melting point solvents were used for the investigation. The system was homogeneous throughout the polymerization. Unfortunately, the *R* values were not very high. Although comparing the *R* values in different solvents is not normally useful, the low *R* value observed in toluene at −45 °C was perplex-

Table 1. Radical Polymerization of 2a: Effects of Solvent and Temperature[a]

solvent	temp/°C	initiator	yield[b]/%	R[c]	DN[d]/kcal mol^{1}	ϵ_r[e]	δ[f]/J$^{1/2}$ cm$^{-3/2}$
benzene	80	ACHCN[g]	63	0.40	0.1	2.27	18.8
benzene	60	AIBN	66	0.42	0.1	2.27	18.8
benzene	40	AMDVN[h]	64	0.51	0.1	2.27	18.8
chlorobenzene	60	AIBN	62	0.30	3.3	5.62	19.8
1,2-dichloroethane	60	AIBN	53	0.19	0.0	10.37	20.0
1,4-dioxane	60	AIBN	67	0.34	14.8	2.21	19.7
dichloromethane	−45	AIBN-$h\nu$[i]	65	0.30	1.0	8.93	20.2
toluene	−45	AIBN-$h\nu$[i]	86	0.44	0.1	2.38	18.8

[a] Polymerizations were carried out at [**1a**] = [DB24C8] = 0.5 mol L^{-1} for 20 h using 3 mol % of initiator. [b] Isolated by preparative GPC (MW > 5000). [c] Incorporation ratio of rotaxane unit: $x/(x + y)$. [d] Donor number (ref 53). [e] Dielectric constant (ref 53). [f] Solubility parameter (ref 53). [g] 2,2′-Azobis(cyclohexanecarbonitrile). [h] 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile). [i] Irradiation with a 200 W high-pressure mercury lamp through a Pyrex filter.

Table 2. Radical Copolymerization of 2a with Styrene[a]

feed				composition				
1a	DB24C8	styrene	yield[b]/%	x	y	z	R[c]	S[d]
10	10	90	31	5	10	85	0.05	0.34
30	30	70	65	15	22	63	0.15	0.40
50	50	50	83	19	30	51	0.19	0.39
70	70	30	80	25	40	35	0.25	0.39
90	90	10	53	35	52	13	0.35	0.41
100	100	0	66	42	58	0	0.42	0.42

[a] Polymerizations were carried out in benzene at 60 °C for 20 h using 3 mol % of AIBN as an initiator. [b] Isolated by preparative GPC (MW > 5000). [c] Incorporation ratio of rotaxane unit: $x/(x + y + z)$. [d] Ratio of complexation of ammonium group: $x/(x + y)$.

ing because benzene and toluene have similar solvent parameters. Viscosity or the change of polarity of the solvents at lower temperatures might affect the R value.

Because of the ionic structure of **3a**, the relationship between the solubility parameter δ and the R value should be discussed. The solubility parameter was, however, scarcely related to the R values. We have reported that the ionic character of the secondary ammonium salts essentially disappears by rotaxane formation with crown ether because of the strong intramolecular hydrogen bonding.[45] In this case, a hydrophobic hexafluorophosphate ion is used as the counteranion of **1a**. Therefore, polyrotaxane **3a** does not behave as a typical ionic polymer, and the conformation of the polymer chain in the solvent barely affects the R value.

It was expected that the R value would increase as the ratio [DB24C8]/[**1**] increased. Thus, the polymerizations at varying [DB24C8]/[**1a**] ratios were carried out using benzene, chlorobenzene, and 1,2-dichloroethane as solvents at 60 °C ([**1a**] = 0.5 mol/L). The results are summarized in Figure 2. The R value steadily increased until the [DB24C8]/[**1a**] ratio reached 1.0 in every solvent. However, a significant increase of the R value was not observed when [DB24C8]/[**1a**] > 1. The R value slightly increased as [DB24C8]/[**1a**] increased in 1,2-dichloroethane. In contrast, the R value rather decreased in benzene. In chlorobenzene, the use of excess DB24C8 showed essentially no effect on the R value. Obviously, the decrease of the R value by excess crown ether is more remarkable in lower ϵ_r solvent. To confirm the effect of excess crown ether, polymerization was carried out in molten DB24C8 (5 equiv) without solvent. Although polymerization was carried out at a temperature high enough to possibly decrease the R value (110 °C), the ratio of [**2a**]/[**1a**] should be maximum in molten DB24C8. As a result, the R value was 0.20, thus lower than any R value obtained in the solution polymerizations. These results suggest that DB24C8 takes on two opposite roles in the polymerization system; first, it acts as a component of the pseudo- and polyrotaxane where more DB24C8 leads to an increase in the ratio of [**2a**]/[**1a**] and the R value, and second, it behaves as highly polar compound in the system where an excess amount of DB24C8 increases the ϵ_r of the system to decrease the ratio of [**2a**]/[**1a**] and the R value. Although polymerization in molten crown ether has been reported in polyrotaxane synthesis,[55] the use of excess amounts of crown ether rather prevents the (poly)rotaxane formation in this case. We can conclude that the polymerization in less polar solvent with 1 equiv of crown ether results in a higher R value.

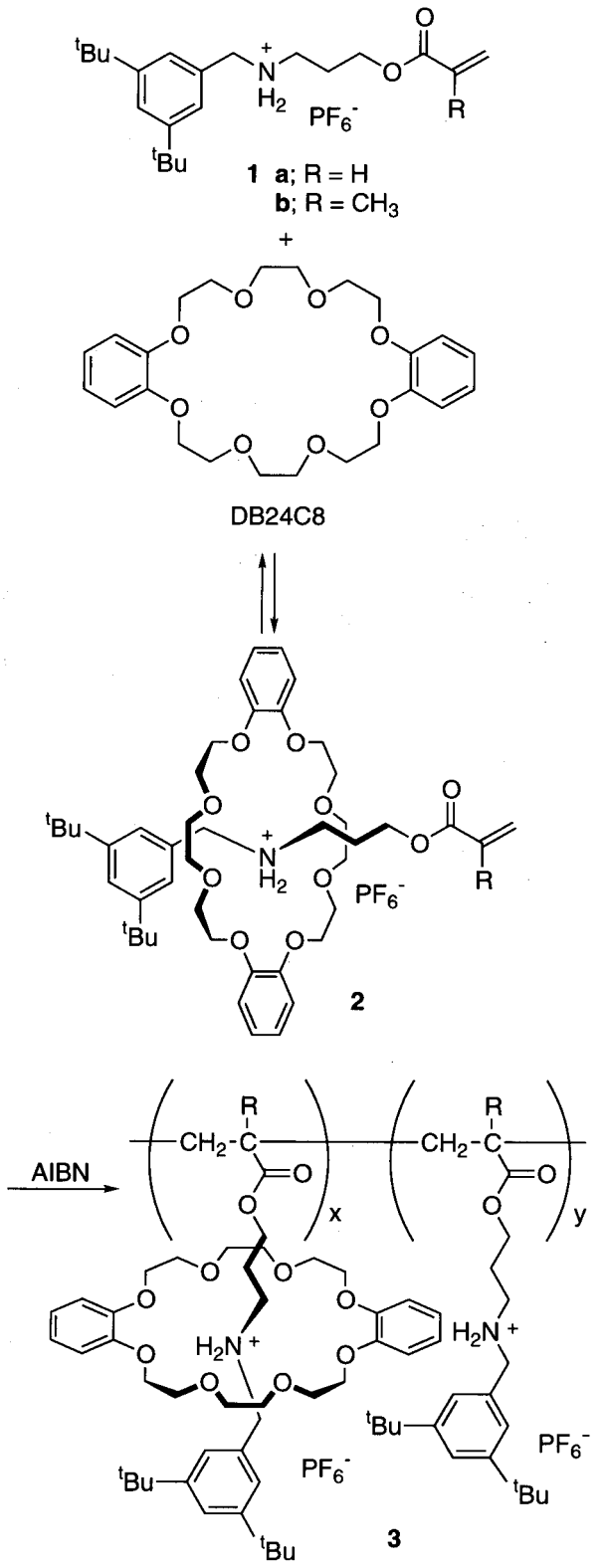
Copolymerization with Styrene. The maximum R value observed in the polymerization of **2a** (a mixture of **1a** and DB24C8) was 51%. Since this value is quite close to 50%, the following scheme seems plausible: although **2a** is more reactive than **1a**, a sequence whereby the rotaxane units adjoin to each other is unfavorable because of the steric repulsion of the bulky crown ether ring in **2a**, leading to alternating copolymerization. If this speculation can be proven operative, the copolymerization of **2a** with a sterically less hindered monomer can increase the ratio of the rotaxane unit against the free ammonium unit. Meanwhile, the radical copolymerization of **2** with other vinyl monomers is interesting from the viewpoint of control of the R value and modification of common polymers by the introduction of the rotaxane structure.

The copolymerizations of **2a** and styrene were carried out in benzene: a mixture of **1a**, DB24C8 (equimolar to **1a**), and styrene in benzene in a sealed tube was heated at 60 °C for 20 h in the presence of AIBN (Scheme 4). The polymeric materials formed (MW > 5000) were isolated by preparative GPC. The structure and composition of the copolymer were determined by ^{1}H NMR spectra. In the copolymerization system, the R value was defined as $x/(x + y + z)$, where z is the composition of the styrene unit. Further, the degree of the complexed ammonium group (S) was calculated as $S = x/(x + y)$. The results are summarized in Table 2.

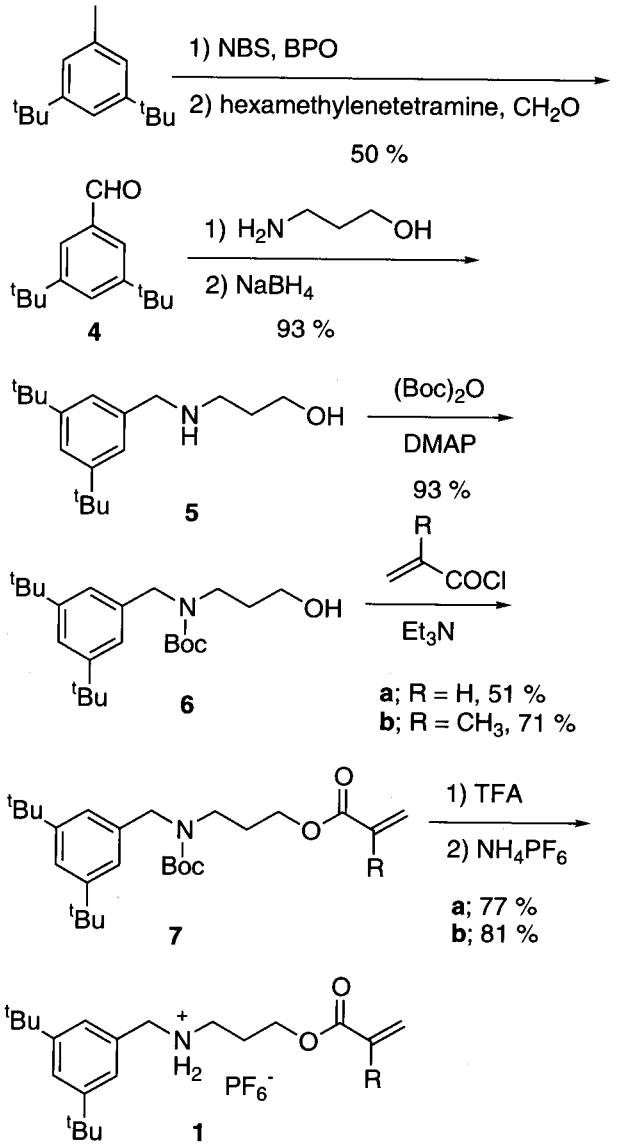
The composition of the styrene unit corresponded very well to the feed ratio of styrene, whereas the R value simply decreased as the feed ratio of styrene increased. Therefore, the incorporation of the rotaxane unit into the polymer can be readily controlled by copolymerization.

Meanwhile, the S values were essentially constant, being hardly affected by the feed ratio of styrene. This result means that the terminal styrene radical does not prefer to react with **2a** although styrene is a sterically less hindered monomer than **2a**.[56] Therefore, the polymerization behavior of **2a** is simply accounted for by

Scheme 2



Scheme 3



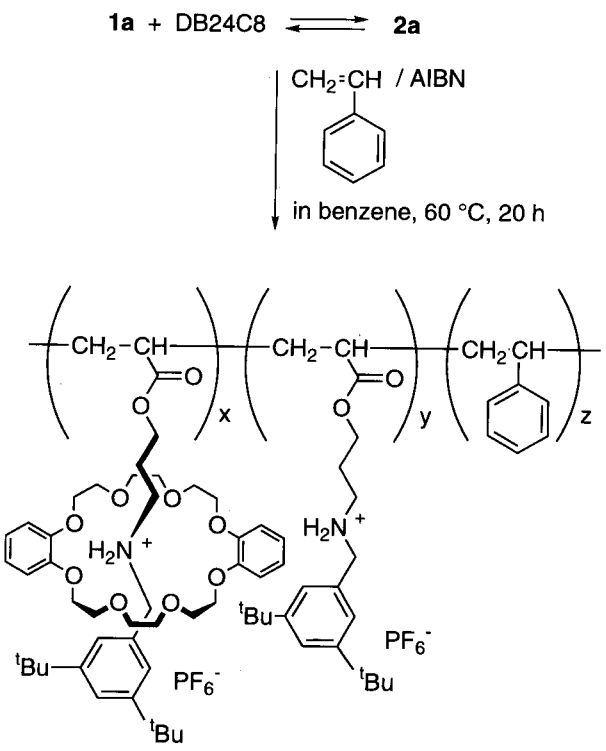
relative concentration and reactivity of **1a** and **2a**; i.e., the steric effect of **2a** is negligible.

Acylative Neutralization of Polyrotaxane. The ammonium salt surrounded by crown ether of the rotaxane structure shows extremely low acidity. Although neutralization of the ammonium group in rotaxane by ordinary bases is impossible, acylation in the presence of excess amount of triethylamine takes place slowly.[45] Thus, the acylative neutralization of **3a** was investigated to obtain nonionic polyrotaxanes (Scheme 5). Polyrotaxane **3a** ($R = 0.44$) was treated with excess amounts of triethylamine and acetic anhydride at room temperature.

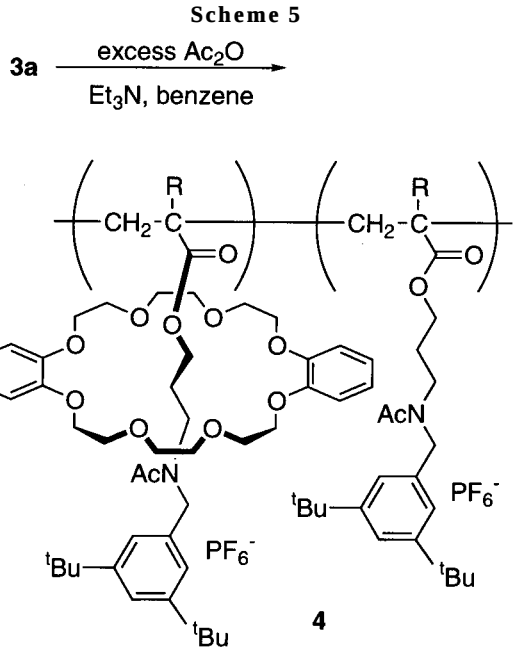
The acylation proceeded slowly, and the reaction was completed after 48 h. The strong IR band at 1643 cm^{-1} indicated the introduction of acetamide structure. Further, the IR peaks corresponding to the PF_6 anion almost disappeared, indicating that the ammonium group was quantitatively converted to an amide structure. The ^1H NMR spectrum of acetylated polyrotaxane **4** is shown in Figure 1d. The acetyl protons appeared as a broad signal around 2 ppm. The signal of *tert*-butyl protons in non-rotaxane unit changed its chemical shift by acylation to a higher field because the electron-withdrawing ammonium group was neutralized. Meanwhile, the upfield shift of the *tert*-butyl protons in the rotaxane unit was very small because acylative neutralization drives off the DB24C8 component from the 3,5-di-*tert*-butylphenyl terminal to decrease the shielding effect of the benzene ring in the DB24C8 component.

Since the DB24C8 component in **4** is not restricted in motion by hydrogen-bonding interaction with ammonium salt, nonionic polyrotaxane **4** can demonstrate

Scheme 4



Scheme 5



physical properties characteristic of the rotaxane structure.[57] The physical properties of these polyrotaxanes will be reported elsewhere.

Summary

We have demonstrated the details of the radical (co)-polymerizations of pseudorotaxane **2** present as a mixture with *sec*-ammonium salt **1**+DB24C8 in an equilibrium. We conclude that the radical polymerization of pseudorotaxane monomers, i.e., end-capping of pseudorotaxanes by polymer chain during polymerization, is an effective method to prepare side-chain polyrotaxanes. Rotaxane content can be controlled by solvent, temperature, and concentration of component molecules. It can also be controlled by copolymerization. Since this type of polymerization can be regarded as the copolymerization of a pseudorotaxane monomer and a free monomer present in an equilibrium, the polymerization behavior is complicated. For instance, an increase in concentration of the ring molecule does not simply lead to an increase of rotaxane content in the polymer because the concentration change of the ring component causes a polarity change in the system.

Because of the small steric effect of the pseudorotaxane structure, the rotaxane content in the polymer was controlled mainly by the relative concentrations and reactivity between the pseudorotaxane monomers and the free monomers. If we can find a system in which equilibrium is almost completely shifted to the pseudorotaxane monomer,[44,46] we would obtain a polymer whose rotaxane content is nearly 100%.

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