Radically Polymerizable Pseudorotaxane Monomers: Versatile Building Units for Side Chain Polyrotaxane Synthesis

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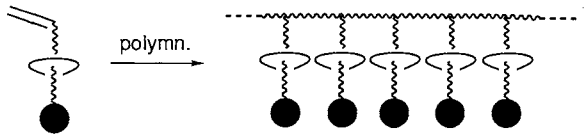
Side chain polyrotaxanes were synthesized from radically polymerizable pseudorotaxane monomers (DB24C8·**1**) which were composed of secondary ammonium salts having (meth)acryl group at one end and bulky stopper at the other end (**1a** and **1b**) and dibenzo-24-crown-8 (DB24C8). Both radical polymerization of DB24C8·**1** and copolymerization of DB24C8·**1a** with styrene afforded corresponding polymers having rotaxane moieties in the side chains (**2a**, **2b**, and **3**).

Topological bonding-comprising supramolecules such as polyrotaxanes and polycatenanes have recently occupied much attention, mainly because of the unconventional unique properties expected from their interesting molecular structures. As for polyrotaxanes, a limited number of preparation methods is available due to the difficulty in construction of such mechanical bondings as the essential elements.[1-8] Although a number of main chain polyrotaxanes have been prepared so far,[1-8] there is no report on side chain polyrotaxane, other than those of Ritter *et al.*[6] and Osakada *et al.*[7b,7c] Among a few methods for preparation of side chain polyrotaxanes,[2] polymerization of pseudorotaxane monomer is one of the most promising versatile methods (Scheme 1), because (i) a variety of monomers is applicable, (ii) physical properties and content of rotaxane unit can be controlled by (co)polymerization with comonomers, and (iii) polymer is one of the most effective end-capping groups.

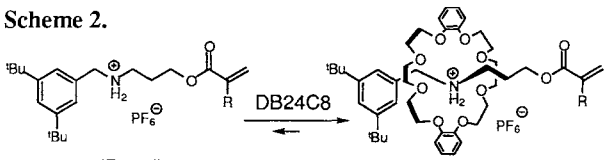
Scheme 1.



Recently, we have synthesized pseudorotaxanes consisting of (meth)acrylate skeletons which are suitable for synthesis of side chain polyrotaxanes through radical polymerization, by utilizing secondary ammonium - crown ether system developed by Stoddart *et al.*[9] Recent Ritter's report on preparation of side chain polyrotaxane[6f] strongly prompted us to present our recent results on the synthesis of side chain polyrotaxanes by radical (co)polymerizations of the pseudorotaxane monomers.

Pseudorotaxanes (DB24C8·**1**) were prepared by adding an equimolar amount of DB24C8 to (meth)acrylate endowed with secondary ammonium and end-capping groups (**1**)[10] in $CDCl_3$. The ^1H NMR spectrum of the mixture displayed a new set of resonances assignable to the pseudorotaxane, besides those of both free DB24C8 and **1**. The structure was eventually confirmed by comparing with those of the corresponding polyrotaxane mentioned later. This result is consistent with the secondary ammonium-crown ether pseudorotaxane system[9] where activation barriers for both the complexation and decomplexation steps are so high that threading and dethreading are sufficiently slower than the ^1H NMR time scale.

Scheme 2.



1a (R = H)
1b (R = CH_3)

DB24C8·**1a** (R = H)
DB24C8·**1b** (R = CH_3)

Among the ^1H NMR signals noteworthy is a set of two *tert*-butyl singlets which are assigned to **1** (uncomplexed, 1.30 ppm) and DB24C8·**1** (complexed, 1.20 ppm), respectively (Figure 1). Meanwhile, the benzylic proton signals of DB24C8·**1** were shifted to higher magnetic field (4.67 ppm) as compared with those of free **1**, due to [C-H···O]hydrogen bonding between the benzylic proton and DB24C8. Association constants *Ka* of **1a** and **1b** with DB24C8 were evaluated to be 18 and 12 $L \cdot mol^{-1}$, respectively, based on the ^1H NMR spectra at 298 K in $CDCl_3$ (*Ka* = [DB24C8·**1**]/[DB24C8][**1**]).

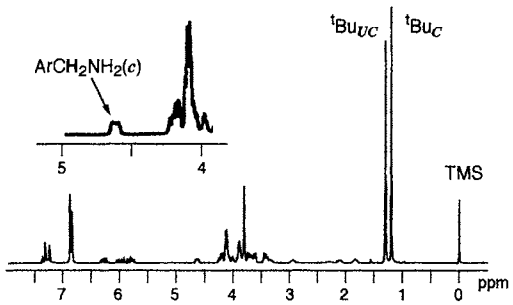
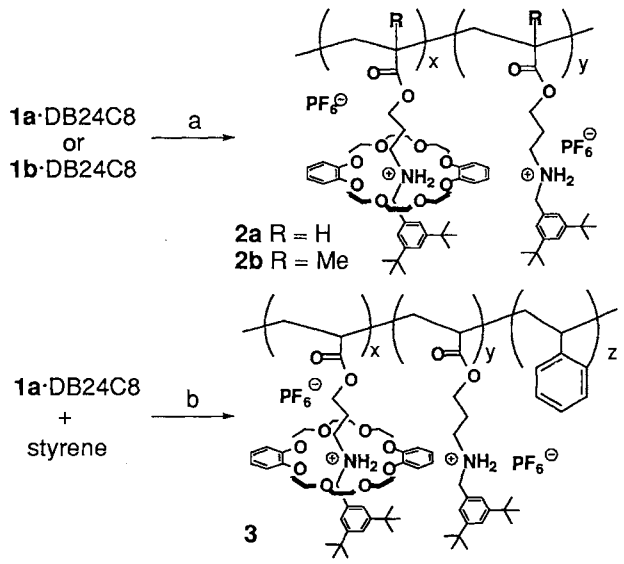


Figure 1. The ^1H NMR (270 MHz, $CDCl_3$) spectrum of an equimolar mixture of DB24C8 and **1a** at 298 K (both 1.5×10^{-1} $L \cdot mol^{-1}$). The subscripts ***c*** (or (*c*)) and ***uc*** denote the complexed and uncomplexed species.

Radical polymerization of the pseudorotaxane monomers was carried out by heating an equimolar mixture of **1** and DB24C8 at 60 °C for 20 h in benzene (0.5 M) in the presence of AIBN. The polymeric products (**2a** and **2b**) purified by preparative GPC[10] were obtained in 66% and 76% yields, respectively. The ^1H NMR spectra of the polymers clearly indicated the formation of polyrotaxanes (**2**) which consisted of not only rotaxane unit (x) but also free ammonium unit (y) (for **2a**, Figure 2).[11] The olefinic proton signals of the (meth)acrylate group disappeared, while singlet *tert*-butyl signal of **1** at 1.32 ppm was divided into two singlets of complexed and uncomplexed species at 1.15 and 1.26 ppm, respectively. The benzylic proton signal of the rotaxane unit appeared at 4.64 ppm, like in the cases of DB24C8 · **1**.



Scheme 3. (a) AIBN, C_6H_6, 60 °C, 20 h. (b) AIBN, C_6H_6, 70 °C, 20 h.

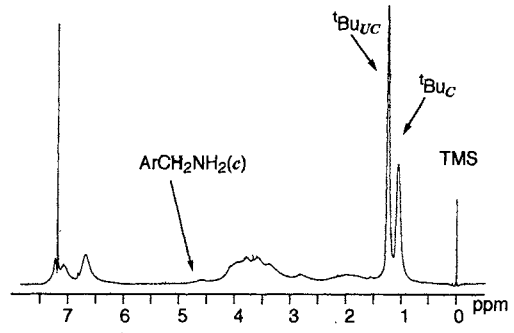


Figure 2. The ^{1}H NMR (200 MHz, $CDCl_3$, 295 K) spectrum of **2a**. The subscripts ***c*** (or (***c***)) and ***uc*** denote the complexed and uncomplexed species.

Since **1**·DB24C8 was in the slow equilibrium of Scheme 2, the rotaxane unit content was actually affected by the polymerization conditions such as solvent polarity and feed ratio, revealing that the content is readily controllable.[12]

On the other hand, to regulate the rotaxane content, copolymerization of the pseudorotaxane monomer (**1a**·DB24C8) with styrene as a comonomer (**1a**/DB24C8/styrene = 1/1/1) was conducted in C_6H_6 at 70 °C for 20 h (Scheme3). The obtained copolymers (**3**, *Mw* 2130, *Mw*/*Mn* 1.84) contained the rotaxane unit (x : y : z = 19 : 30 : 51, by ^{1}H NMR). A feed ratio dependent rotaxane content was confirmed by the detailed study.

In this paper we have demonstrated a general method for synthesizing side chain polyrotaxanes by utilizing the radically polymerizable pseudorotaxane monomers. This method can provide a wide variety of side chain polyrotaxanes with controlled number of the rotaxane units dependent of polymerization condition.

References and Notes

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10 Preparation of **1**. Reductive condensation of 3,5-di-*tert*-butylbenzaldehyde and 3-amino-1-propanol with $NaBH_4$ yielded a γ-hydroxypropyl amine. Protection of the NH group with $(Boc)_2O$ was followed by esterification of the OH group with (meth)acryloyl chloride. The (meth)acrylic ester having the protected amine group was deprotected with trifluoroacetic acid and successively treated with NH_4PF_6, giving **1**. overall yield and ^{1}H NMR data: **1a**: 34%. ^{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 Hz, 1 Hz, CH=CH_2), 6.03 (1H, dd, *J*= 17 Hz, 10 Hz, C*H*=CH$_2$), 5.80 (1H, dd, *J*= 10 Hz, 1Hz, CH=CH_2), 4.20 (2H, t, *J*= 6 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$_2$), 1.32 (18H, s, Ar-^{t}C$_4$H$_9$). **1b**: 53%. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.40 (2H, br s, N*H*$_2$), 7.52-7.28 (3H, m, Ar*H*), 6.03 (1H, s, =CH_2), 5.56 (1H, s, =CH_2), 4.22 (2H, t, *J*= 6 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, CH$_2$=C(CH_3)), 1.32 (I8H, s, ^{t}C$_4$H$_9$Ar).

11 Composition and molecular weight (PSt standards) of **2**. For **2a**, x : y = 42 : 58 (*Mw* = 769, *Mw*/*Mn* = 1.79) and for **2b**, x : y = 34 : 66 (*Mw* = 5430, *Mw*/*Mn* =2.09). The molecular weights estimated here should be much smaller than "real" ones, as seen in most polyions.

12 For example, the rotaxane content (x) in the polymerization of **1a**·DB24C8 (feed ratio DB24C8/**1a** = 1 : 1) was as follows: x = 43 in benzene, x = 30 in chlorobezene, and x = 20 in 1,2-dichlorobenzene.