Supramolecular Polymers

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Graft Polyrotaxanes: A New Class of Graft Copolymers with Mobile Graft Chains**

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Polyrotaxanes (PRs) have been at the forefront of polymer and related materials-science research throughout this decade.[1] In their pioneering work, Gibson and co-workers reported various structural possibilities regarding PR molecular architectures.[1b] In addition to main-chain-type PRs,[2–4] poly[*n*]rotaxanes,[5] daisy-chain-type PRs,[6] and dendritic PRs[7,8] have attracted much attention as novel classes of polymers with flexible main chains the repeating units of which are mechanically connected. Cross-linked PRs[9] are also simple but quite attractive classes of PRs for applications in functional materials.[3a,10,11] On the other hand, we proposed a novel class of graft copolymers the graft chains of which are mechanically bound to the main chain by rotaxane skeletons and we referred to them as "graft polyrotaxanes (GPR)."[12] Depending on the function of their graft chains, there are two types (Figure 1): 1) GPR-A has graft chains as the axle components that translate through cavities in the main chain, thus change in the length of the graft chains is coupled with their movement. 2) GPR-B has graft chains linked to the wheel components that translate along and circumrotate around the axle polymer, thus delocalizing their positions and varying the density of the graft chains on the axle polymer.

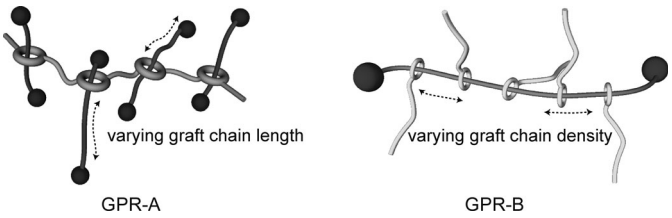
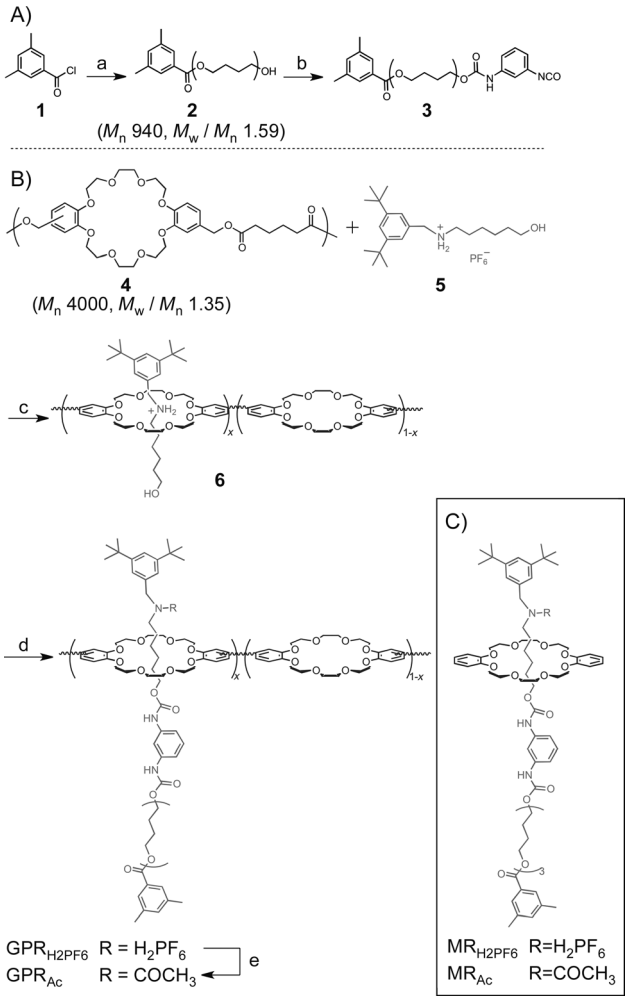


Figure 1. Structures of two graft polyrotaxanes (GPRs): GPR-A with varying graft chain length and GPR-B with varying graft chain density.

We are intrigued by these unique structures, because graft length and density should significantly affect the physical and mechanical properties of graft polymers, including their solution properties, surface properties, and microstructure. However, GPR-A has not yet been reported, unlike GPR-B, which several groups, including our own, have synthesized.[12,13] We describe herein the synthesis of GPR-A by applying the grafting-onto protocol to a poly(pseudorotaxane) and analyze its structural characteristics and dynamic behavior.

We designed GPR_{H2PF6} as a GPR-A that possesses both a poly(crown ether) main chain and a poly(tetrahydrofuran) (poly(THF)) graft chain (Scheme 1). Prior to the synthesis of



Scheme 1. A) Synthesis of graft chain. Reagents and conditions: a) AgOTf (1.0 equiv), THF, 0 °C, 3 min then H_2O, 77% yield; b) *m*-phenylene diisocyanate (5.0 equiv), CH_2Cl_2, 25 °C, 12 h, quantitative; B) Synthesis of graft polyrotaxane; reagents and conditions: c) CH_2Cl_2, 25 °C, 12 h; d) **3** (2.0 equiv), $Bu_2Sn(OCOC_{11}H_{23})_2$ (3 mol%), CH_2Cl_2, 25 °C, 12 h; e) Ac_2O (3.0 equiv), Et_3N (6.0 equiv), DMF, 60 °C, 72 h, 94%; C) Structures of model [2]rotaxanes. OTf = trifluoromethanesulfonate, THF = tetrahydrofuran, DMF = *N*,*N*-dimethylformamide.

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GPR_{H2PF6}, a model [2]rotaxane (MR_{H2PF6}) corresponding to the repeating unit of GPR_{H2PF6} was synthesized by the typical threading-end-capping method[14] in order to investigate the relative position and mobility of the components.

Figure 2 shows the ^{1}H NMR spectra of the axle component **5** and MR_{H2PF6}. Signals corresponding to *N*-benzylic protons (s) were shifted downfield from $\delta = 4.19$ to 4.58 ppm by rotaxanation, while the *t*Bu signal was shifted upfield from $\delta = 1.31$ ppm to 1.23 ppm because of the deshielding effect of the aromatic ring of DB24C8. The results indicated that DB24C8 was located on the ammonium station owing to the strong hydrogen-bonding interaction between the components.[11b,15] We previously reported the effective removal of hydrogen bonding by *N*-acylation.[16] Thus, the ammonium moiety was *N*-acetylated with acetic anhydride to afford MR_{Ac}. In the case of MR_{Ac}, the ^{1}H NMR chemical shift of the *t*Bu protons shifted back to that observed in **5**, while most signals of the tris-THF moiety (c, f, g, and l) were shifted in comparison with those of MR_{H2PF6}. In addition, NOESY correlations between DB24C8 and the tris-THF moiety of MR_{Ac} were clearly observed.[17] Therefore, it was concluded that as a result of *N*-acetylation, DB24C8 could freely move over the whole axle component including the tris-THF moiety. Consequently, this MR system was identified as a suitable unit for the synthesis of GPR-A with mobile graft chains.

GPR_{H2PF6} was synthesized according to Scheme 1. Monofunctional poly(THF) **2** (M_n 1.3×10^3, M_w/M_n 1.53) was treated with excess *m*-phenylene diisocyanate to form grafting agent **3**.[18] Mixing poly(crown ether) **4**[11b,15] (M_n 4.0×10^3, M_w/M_n1.35) with an equimolar amount of **5**[11b,15] in CH_2Cl_2 initially formed poly(pseudorotaxane) **6** in situ. The subsequent addition of **3** afforded GPR_{H2PF6}-62 as an Et_2O-insoluble polymer (47% yield).

Detailed analysis of the ^{1}H NMR spectrum of GPR_{H2PF6}-62 and comparison with the spectra of the individual polymer components strongly supports the formation of GPR_{H2PF6}-62.[17] For example, *N*-benzylic proton signals of the axle component were shifted downfield from $\delta = 4.19$ to 4.58 ppm and each of the methylene proton signals α and γ of the DB24C8 moiety were split into two peaks by rotaxanation. These spectral changes were consistent with those observed for the main-chain-type PRs[11b,15] and the above mentioned MR_{H2PF6}. Further evidence to confirm the structure of GPR_{H2PF6}-62 was obtained by FTIR spectroscopy and MALDI-TOF mass spectrometry.[17] The rotaxanation ratio of **6** was determined to be 62% from the ^{1}H NMR integral ratio. The observed graft ratio of 62% for GPR_{H2PF6}-62 precisely correlated with the rotaxanation ratio, which suggested that all axle components incorporated into **6** were used in the graft chains of the final product GPR_{H2PF6}-62.

It was found that the percent grafting ratio (x) of GPR_{H2PF6} could be controlled by the feed ratio of **5** (Table 1). When 0.60 equiv of **5** were employed, x was found to be 25% (Table 1, run 1). The obtained polymer (GPR_{H2PF6}-25) was soluble in $CHCl_3$, acetone, and dimethyl sulfoxide (DMSO), but insoluble in CH_3OH and Et_2O. In contrast, with 2.0 equiv of **5**, the product GPR_{H2PF6}-100, the DB24C8 moieties of which were completely penetrated by the axle graft chain ($x = 100\%$), was soluble in most organic solvents, including CH_3OH and Et_2O. Therefore, GPR_{H2PF6}-100 was purified by preparative size exclusion chromatography (SEC) instead of fractional precipitation (Table 1, run 3), resulting in a considerable decrease in yield (37%). In addition to their solubility properties, the glass transition temperatures (T_g) of GPR_{H2PF6} polymers were also found to be dependent on the grafting ratio. GPR_{H2PF6}-25 and GPR_{H2PF6}-62 exhibited single T_g at 11.3 °C and 12.8 °C, respectively, and were similar to that of the trunk polymer **4** (11.3 °C). In contrast, GPR_{H2PF6}-100 showed two T_g at −60.5 °C and 63.2 °C. The former T_g originates from the graft chains that consistof poly(THF), while that of the latter is assigned to the trunk polymer that contains completely penetrated DB24C8 moieties, which is fully consistent with the structural characteristics of GPR_{H2PF6}.

To achieve high mobility of the graft chain of GPR_{H2PF6}, *N*-acetylation of the polymer was performed to produce GPR_{Ac} in the same manner as that of MR_{H2PF6}. Treatment of GPR_{H2PF6}-62 with acetic anhydride (Ac_2O) and triethylamine

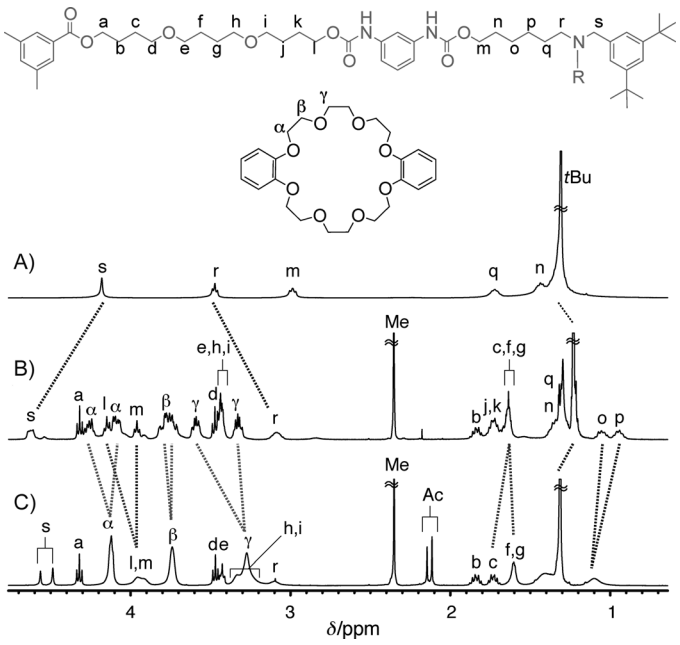

Figure 2. Partial ^{1}H NMR spectra of A) **5**, B) MR_{H2PF6}, and C) MR_{Ac} (400 MHz, 298 K, $CDCl_3$).

Table 1: Synthesis and thermal property of GPR_{H2PF6} with controlled grafting ratio.[a]

Run	[**5**] [M][b]	Product	x [%][c]	Yield [%]	T_g [°C]
1	0.60	GPR_{H2PF6}-25	25	57[d]	11.3
2	1.00	GPR_{H2PF6}-62	62	47[d]	12.8
3	2.00	GPR_{H2PF6}-100	100	37[e]	−60.5
					63.2
poly(THF)		**2**			−74.7
poly(crown ether)		**4**			11.3

[a] Reaction was performed by the initial mixing of **4** (0.50 unit-mol L^{-1}) and **5** and subsequent addition of **3** (2.0 equiv to **5**). [b] Concentration of **5**. [c] Grafting ratio. [d] Isolated as MeOH-insoluble polymer. [e] Isolated by preparative SEC.

at 60 °C for 3 days gave the *N*-acetylated product GPR_{Ac}-62 in 94 % yield. Based on the integral ratio obtained from ^{1}H NMR, the percentage conversion to the *N*-acetylation product reached 80 %.[17] The downfield shift of the *t*Bu signal from $\delta = 1.20$ to 1.31 ppm confirmed the movement of the DB24C8 wheel to the poly(THF) moiety, which concurred with the results obtained for MR_{Ac}. Thus, the results indicated the delocalization of the graft chains; the structure of GPR_{Ac}-62 was also confirmed by IR, SEC, and DSC.[17]

To evaluate macromolecular structural changes after *N*-acetylation, the diffusion ordered spectroscopy (DOSY) NMR spectra[19] of GPR_{H2PF6}-62 and GPR_{Ac}-62 were measured (Figure 3). The broad distributions of each peak are attributed to the broad molecular weight distribution of each component. Because all peaks show a unimodal distribution of the diffusion coefficient (D), it was confirmed that graft polyrotaxanes GPR_{H2PF6}-62 and GPR_{Ac}-62 contained no impurities such as unreacted grafting agent or unthreaded axle component. From the results, we estimated the hydrodynamic radii (R_H) of GPRs by the Einstein–Stokes equation.[20] Because D for GPR_{H2PF6}-62 and GPR_{Ac}-62 had a certain distribution, we used the diffusion coefficient at the point of maximum correlation (D_p, 5.28×10^{-11} and 4.15×10^{-11} m s^{-1} for GPR_{H2PF6}-62 and GPR_{Ac}-62, respectively). Thus, the calculations give the following values: $R_H = 5.76$ nm for GPR_{H2PF6}-62 and $R_H = 7.33$ nm for GPR_{Ac}-62. The clear increase in R_H as a result of *N*-acetylation can be attributed to a change in molecular shape. GPR_{H2PF6}-62 has polyionic structure; thus, the graft chain terminal is fixed at the crown ether cavity of the main chain. The graft chain length is sufficient to allow aggregation around the backbone. As a result, the main chain acquires a somewhat folded conformation (Figure 3b). In contrast, the graft chain length of GPR_{Ac}-62 apparently increases because of the enhanced mobility or free translation of the graft chain as shown in Figure 3d. The unconstrained movement of the graft chain drives the extension of the folded structure (Figure 3d), thus resulting in the observed increase in R_H. Further, the difference in D distribution observed in Figure 3 (a and c) seems to correspond well with the higher size uniformity of GPR_{Ac}-62 than GPR_{H2PF6}-62. The present macromolecular shape change well reveals the characteristics of mobile connections served by rotaxane skeletons.

In conclusion, we have performed the first synthesis of GPR-A using the grafting-onto method and with a controllable grafting ratio. The mobility of the graft chains was observed to increase as a result of *N*-acetylation of GPR_{H2PF6} to GPR_{Ac}. This observation caused the extension of the GPR_{Ac} graft chain, and in accordance with the results of the model study, lead to an enhancement in its macromolecular size. Although GPR is similar to conventional graft copolymers with respect to its grafted structure, the nature of its structure is dynamic because of the mobile rotaxane connection. Hence, the graft copolymer structure resembles that of a polymer blend, in which each of the component polymers can move somewhat independently. Further study of the relationship between the macroscopic properties and dynamic structure of GPR is currently in progress.

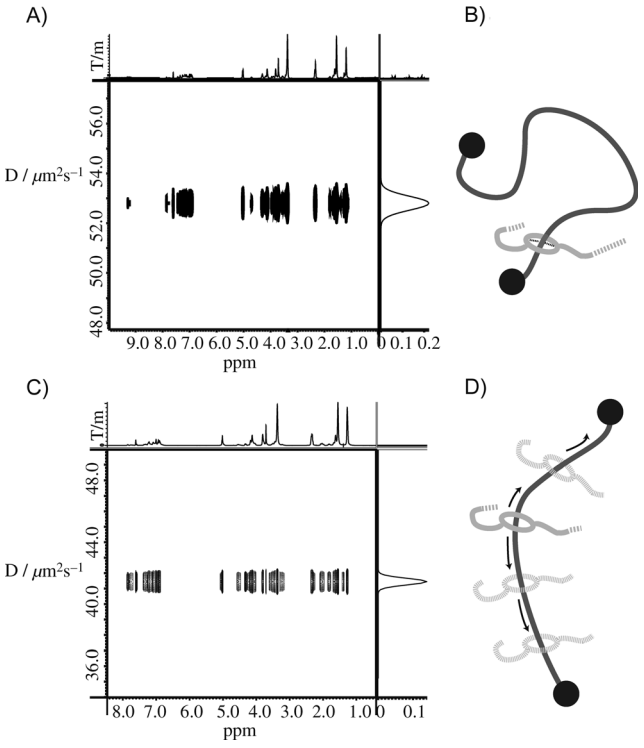

Figure 3. DOSY spectra (500 MHz, [D$_7$]DMF, 333 K) of A) GPR_{H2PF6} and C) GPR_{Ac} and B,D) their suggested molecular conformations.

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