# Synthesis of Poly(tetrahydrofuran) Polymacromonomers Having Mixed Branch Segments through Reshuffling in Electrostatic Self-Assembly and Subsequent Covalent Fixation

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ABSTRACT: A new polymacromonomer architecture with mixed branch segments of different lengths has been constructed through reshuffling of poly(tetrahydrofuran), poly(THF), segments in an electrostatic self-assembly and subsequent covalent fixation process. Thus, two types of electrostatically self-assembled polymacromonomer precursors **4a** and **4b** were prepared by the ion-exchange reaction between α-methoxy-*ω*-(*N*-phenylpyrrolidinium) poly(THF)s (**1a** and **1b**) ($M_n$ = 3000 and 6200, respectively) and a poly(sodium acrylate) (DP = 52), respectively. By reshuffling of different poly(THF) segments in the two polymer precursors, **4a** and **4b**, a new electrostatically self-assembled precursor, **4[a,b]**, was obtained. The subsequent heat treatment of **4[a,b]** effectively produced a covalently linked polymacromonomer, **5[a,b]**, having mixed branch segments through the ring-opening reaction of the pyrrolidinium salt groups in **1a** and in **1b** by carboxylate anions in the backbone poly(acrylate) component.

## Introduction

Polymacromonomers have now been recognized as a novel class of highly branched macromolecules, which can form various mesoscopically ordered structures due to their anisotropic cylindrical molecular shapes.[1−10] The synthesis of polymacromonomers has so far been limited mostly by a free radical polymerization of a macromonomer under rigorously controlled conditions.[2−4,7] Recently, however, new synthetic processes, including an atom transfer living radical polymerization[11] as well as a coupling reaction of uniform size polymer precursors for both backbone and branch segments,[12] have been successfully applied to produce polymacromonomers of well-defined backbone segment length and branch segment numbers, as well as their branch segment lengths.

We have also developed an efficient process to prepare polymacromonomers of well-defined structures by making use of an electrostatically self-assembled precursor as a critical intermediate.[13−15] Thus, poly(THF)s having an *N*-phenylpyrrolidinium salt end group and poly(sodium acrylate) were subjected to the ion-exchange reaction to produce an electrostatically self-assembled polymacromonomer precursor, which could be isolated and fully characterized by means of conventional spectroscopic techniques. The covalently linked polymacromonomer was then obtained quantitatively by the heat treatment, causing the ring-opening reaction of pyrrolidinium salt groups by a nucleophilic attack of acrylate anions to form amino-ester groups.

In this paper, we demonstrate a reshuffling process of different branch segments between two electrostatically self-assembled poly(THF) polymacromonomer precursors, to produce, by subsequent heat treatment, covalently linked poly(THF) polymacromonomers having mixed branch segments in high yields. This novel process will provide an efficient means for the synthesis of *co*polymacromonomers, in contrast to the conventional copolymerization process involving different macromonomers of incompatible nature and with repulsive interaction.[16,17]

## Experimental Section

**Reagents.** α-Methoxy-*ω*-(*N*-phenylpyrrolidinium) poly(THF)s (**1a** and **1b**, $M_n$ = 3000 and 6200, respectively) were prepared by a method reported before.[14] Poly(sodium acrylate) (DP = 52) was prepared by the living anionic polymerization of *tert*-butyl acrylate and subsequent saponification and neutralization.[18,19] Sodium benzoate (Koso Chemical Co., Ltd.) and sodium terephthalate (Tokyo Chemical Industry Co., Ltd.) were used as received. THF was dried over sodium benzophenone ketyl and distilled just before use. Trifluoromethanesulfonic anhydride (triflic anhydride) was distilled from $P_2O_5$ just before use. Unless otherwise noted, materials were obtained from commercial sources.

**Preparation of α-Benzyloxy-*ω*-(*N*-phenylpyrrolidinium) Poly(THF) (1c).** α-Benzyloxy-*ω*-(*N*-phenylpyrrolidinium) poly(THF) was prepared from a living poly(THF) produced by a benzyl trifluoromethanesulfonate as an initiator, prepared in situ from benzyl alcohol and triflic anhydride in the presence of 2,6-di-*tert*-butylpyridine,[20] and a subsequent end-capping reaction with *N*-phenylpyrrolidine. Then, to an ice-cooled (<5 °C) aqueous solution containing a weighed amount of a sodium benzoate (10 equiv with respect to ionic groups) was added dropwise a THF solution of the obtained poly(THF) under vigorous stirring. After 1 h, the precipitated ion-exchange product (**1c**) was collected by filtration and dried in vacuo. This precipitation treatment was repeated three times to complete the reaction.

**1c:** $M_n$ (SEC) = 4600;[21] PDI = 1.28; $^1$H NMR $\delta$ = 1.40−1.80 (m, $CH_2CH_2O$), 2.04−2.20 (m, 2 H), 2.40−2.55 (m, 2 H), 3.20−3.60 (m, $CH_2CH_2O$), 4.00−4.12 (m, 4 H), 4.46 (s, 2 H), 4.48−4.62 (m, 2 H), 7.20−7.35 (m, 7 H), 7.35−7.70 (m, 5 H), 8.05−8.10 (d, $J$ = 7.5 Hz, 2 H).

**Preparation of Electrostatically Self-Assembled Polymer Precursors (2a, 2b, 4a and 4b).** To an ice-cooled (<5 °C) aqueous solution containing a weighed amount of a sodium terephthalate (10 equiv with respect to ionic groups) or poly(sodium acrylate) (1 equiv with respect to ionic groups) was added dropwise a THF solution of **1a** or **1b** under vigorous stirring. After 1 h, the precipitated ion-exchange product (electrostatically self-assembled polymer precursor) was col-

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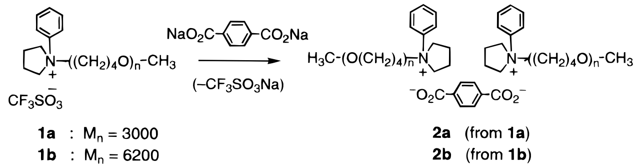
**Scheme 1**



lected by filtration and dried in vacuo. This precipitation treatment was repeated to complete the reaction. A portion of a series of precursors, **2a**, **2b**, **4a**, and **4b**, was subjected to the heat treatment at 100 °C for 5 h to give covalently linked products **3a**, **3b**, **5a**, and **5b**, respectively, in quantitative yields.

**Segment-Reshuffling Reaction between 2a and 2b and Subsequent Ring-Opening Reaction of Pyrrolidinium Salt End Groups.** A THF (1 mL) solution containing an equimolar amount of **2a** (14 mg) and **2b** (27 mg) was prepared and allowed to stand at 20 °C for 2 h. The electrostatically self-assembled polymer products **II** (41 mg), containing **2[a,b]** as well as **2a** and **2b**, were recovered by evaporating the solvent and were subjected to heat treatment at 100 °C for 5 h to give covalently linked products **III** quantitatively.

**Segment-Reshuffling Reaction between 4a and 1c and Subsequent Ring-Opening Reaction of Pyrrolidinium Salt End Groups.** A THF (1 mL) solution containing **4a** (52 mg) and **1c** (19 mg, 0.25 equiv with respect to **1a** in **4a**) was prepared and allowed to stand at 20 °C for 0.5 h. The electrostatically self-assembled products, containing **4[a,c]** (71 mg), were recovered by evaporating the solvent and were subjected to heat treatment at 100 °C for 5 h to give the covalently linked products quantitatively.

A purified polymacromonomer, **5[a,c]** (13 mg from 20 mg of the sample), was collected by means of the fractionation with an analytical SEC apparatus by repeating the experimental procedure 10 times.

**Segment-Reshuffling Reaction between 4a and 4b and Subsequent Ring-Opening Reaction of Pyrrolidinium Salt End Groups.** A THF (1 mL) solution containing an equimolar amount of polymacromonomer precursors **4a** (33 mg) and **4b** (16 mg) was prepared and allowed to stand at 20 °C for 0.5 h. The electrostatically self-assembled product **4[a,b]** (49 mg) was recovered by evaporating the solvent and was subjected to heat treatment at 100 °C for 5 h to give a covalently linked product, **5[a,b]**, quantitatively.

**Measurements.** SEC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020, a UV detector model UV 8020 at 254 nm, and a conductivity detector model CM 8010. Column sets of either 2 × TSK G3000HXL, 1 × TSK G5000HXL, or 2 × TSK G5000HXL were employed with THF as an eluent at a flow rate of 1.0 mL/min. IR spectra were recorded on a JASCO FT/IR-410 infrared spectrometer by casting the sample from the chloroform solution on a NaCl plate. $^1$H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in $CDCl_3$ at 40 °C. The proton chemical shifts (ppm) were referenced from the signal of tetramethylsilane.

## Results and Discussion

**1. Reshuffling in Electrostatically Self-Assembled Precursors by Poly(THF)s Having an *N*-Phenylpyrrolidinium Salt End Group with a Terephthalate Counteranion.** Reshuffling of poly(THF)s having an *N*-phenylpyrrolidinium salt end group (**1**) within an electrostatically self-assembled precursor has been carried out first in a simple model system. Thus, the two electrostatically self-assembled polymer precursors **2a** and **2b** were prepared separately from the two units of poly(THF), either **1a** or **1b** with MW values of 3000 or 6200, respectively, and a sodium terephthalate (Scheme 1).

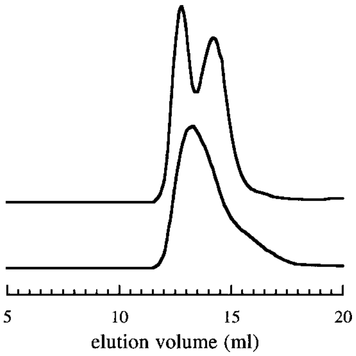


**Figure 1.** SEC (RI) traces of the mixture of **3a** and **3b** (top) and of the reaction product obtained by mixing **2a** and **2b** and subsequent heat treatment (bottom). (Column: 2 × TSK G3000HXL. Eluent: THF, 1 mL/min.)

**Table 1. Synthesis of Polymacromonomers through Reshuffling in Electrostatic Self-Assembly and Subsequent Covalent Fixation**[a]

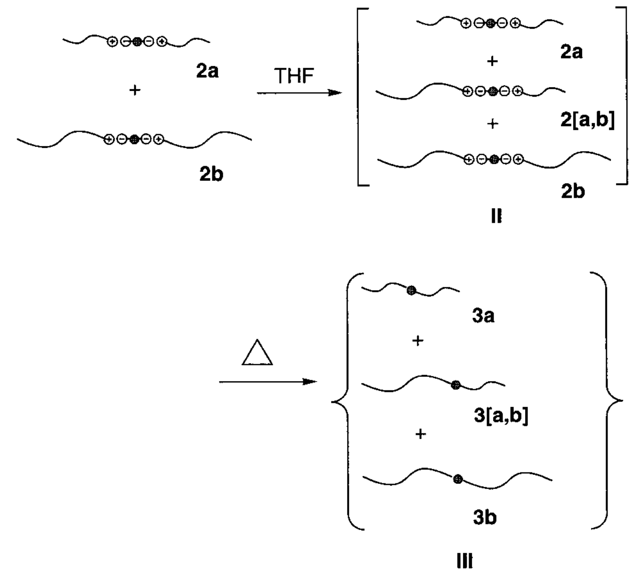
| run | starting precursor[c] | feed molar ratio of branch segments | self-assembled precursor | covalently linked product[d] | $M_p$(SEC)[e] |
|---|---|---|---|---|---|
| 1 | **2a/2b** | 1/1 | **II** | **III** | 9500 |
| 2[b] | **2a/2b** | 1/1 | | **3a**, **3b** | 13000, 7100 |
| 3 | **4a/1c** | 4/1 | **4[a,c]** | **5[a,c]** | 50000 |
| 4 | **4a** | | | **5a** | 47000 |
| 5 | **4b** | | | **5b** | 75000 |
| 6 | **4a/4b** | 1/1 | **4[a,b]** | **5[a,b]** | 62000 |
| 7[b] | **4a/4b** | 1/1 | | **5a**, **5b** | 70000 |

[a] Reshuffling was performed in THF solution for 0.5−2.0 h at 20 °C. Ring-opening reaction of *N*-phenylpyrrolidinium salt end groups was performed at 100 °C for 5 h under nitrogen. [b] Polymacromonomers were mixed after the heat treatment. [c] Precursors **2a** and **2b** and **4a** and **4b** were prepared by the reaction of **1a** ($M_n$ = 3000) and **1b** ($M_n$ = 6200) with a sodium terephthalate and with a poly(sodium acrylate) (DP = 52), respectively. **1c**: $M_n$ = 4600. [d] All products were recovered quantitatively. [e] Peak molecular weight determined by SEC with the calibration using polystyrene standards by a conversion factor of 0.556.[21]

The polymer precursors **2a** and **2b** were then heated separately at 100 °C for 5 h under a nitrogen atmosphere to give "coupled" poly(THF)s **3a** and **3b** with narrow molecular weight distributions ($M_w/M_n$ = 1.18 and 1.15, respectively). The observed MW values of **3a** and of **3b** were 7100 and 13000, respectively, and was nearly twice of that of the original **1a** and **1b**, respectively. Thus, the SEC profile of the mixture of **3a** and **3b** was observed to be bimodal as shown in Figure 1 (top) (run 2 in Table 1).

An equimolar amount of the electrostatically self-assembled polymer precursors **2a** and **2b** were then mixed together in THF at 20 °C and allowed to stand for 2 h to cause reshuffling of the two different poly(THF) segments in **2a** and **2b**. After evaporating the solvent, the newly formed electrostatically self-assembled polymer precursor **II** was heated at 100 °C for 2 h (Scheme 2, run 1 in Table 1). As was found in the previous studies,[14] IR and NMR spectroscopic analysis indicated the quantitative ring-opening reaction of pyrrolidinium salt groups. The observed SEC profile of the covalently linked polymer **III** was, in contrast to that for the mixture of **3a** and **3b**, unimodal but broader in the MW region just between the MWs of **3a** and **3b** (Figure 1, bottom). And the polydispersity index for **III** (PDI = 1.25) was very close to that for the mixture of **3a** and **3b** (PDI = 1.24), indicating that the reshuffling process is a random one.

**Scheme 2**



These results clearly demonstrates that reshuffling of poly(THF) segments took place between **2a** and **2b**, and the subsequent covalent fixation could produce a "coupled" polymer of different segment lengths, **3[a,b]**, in addition to those of the identical branch length, **3a** and **3b**, by "self-reshuffling". And the present SEC measurement apparently failed to resolve the three poly(THF) components, **3a**, **3b** and **3[a,b]**, of different molecular weights.

**2. Synthesis of *Co*polymacromonomers through Reshuffling in Electrostatic Self-Assembly and Subsequent Covalent Fixation. 2.1. Reshuffling between an Electrostatically Self-Assembled Polymacromonomer Precursor (4a) and α-Benzyloxy-*ω*-(*N*-phenylpyrrolidinium) poly(THF) (1c).** Reshuffling of poly(THF) segments in the electrostatically self-assembled polymacromonomer precursor **4a**, prepared from **1a** ($M_n$ = 3000) and poly(sodium acrylate) (DP = 52), was performed with another relevant poly(THF) precursor, **1c**, having a longer segment ($M_n$ = 4600) and having a benzoate counteranion of the *N*-phenylpyrrolidinium salt end group. In **1c**, moreover, a benzyloxy group was introduced at the opposite end of the poly(THF) segment so as to use it as an NMR spectroscopic "marker" to monitor the reshuffling process.

Thus, a mixture of **4a** and **1c** (0.25 equiv with respect to **1a** in **4a**) was prepared in THF at 20 °C and allowed to stand for 0.5 h. After the solvent was evaporated off, the recovered product was subjected to heat treatment at 100 °C for 5 h (Scheme 3, run 3 in Table 1). The SEC profile of the product was bimodal (middle in Figure 2), corresponding to one for the polymacromonomer fraction and another for the poly(THF) precursor fraction (starred peak).[15] The latter was formed through the ring-opening reaction of a pyrrolidinium salt group in **1a** and/or **1c** by a benzoate counteranion. On the other hand, the former showed a peak shape similar to that of the relevant polymacromonomer **5a** prepared from **4a** (top in Figure 2), but with a noticeable peak shift toward the higher molecular weight region. The pure polymacromonomer portion was then isolated by means of fractionation with an analytical SEC apparatus (bottom in Figure 2) and was analyzed by $^1$H NMR (Figure 3).

All signals, except for those due to a stabilizer (2,6-di-*tert*-butyl-4-methylphenol) in the THF eluent of SEC (marked with an × in Figure 3), were reasonably assigned to those due to a polymacromonomer having mixed branch segments **5[a,c]**. Thus, a singlet signal at 4.50 ppm due to benzyloxy methylene protons as well as signals at around 7.32 ppm due to benzyloxy phenyl protons, originated from **1c**, are visible in addition to that at 3.32 ppm due to methoxy protons originated from **1a**. These results shows that reshuffling of poly(THF) segments took place between **4a** and **1c**, and the subsequent covalent fixation could produce a polymacromonomer having mixed branch segments **5[a,c]**. The relative content of the longer branch segment form **1c** in the obtained **5[a,c]** was calculated to be 8 in the total 52 branch segments by comparing the signal intensity of benzyl protons with that of *N*-phenyl protons (marked with b in Figure 3). This value is close agreement with

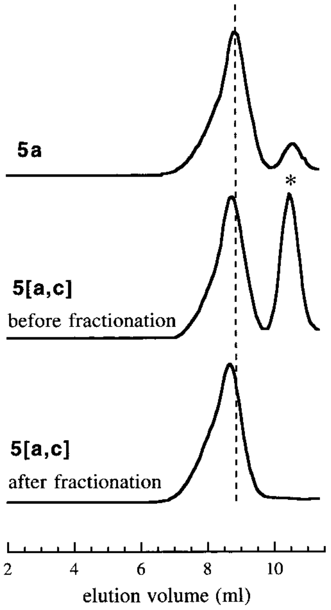
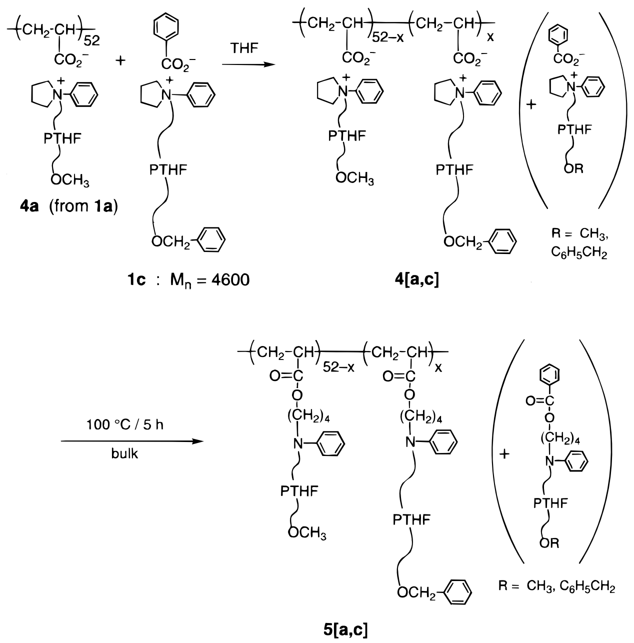


**Figure 2.** SEC (RI) traces of **5a** (top) and of the reaction product obtained by mixing **4a** and **1c** and subsequent heat treatment before (middle) and after (bottom) the fractionation treatment. (Column: TSK G5000HXL. Eluent: THF, 1 mL/min. * = benzoate-terminated poly(THF).)

**Scheme 3**



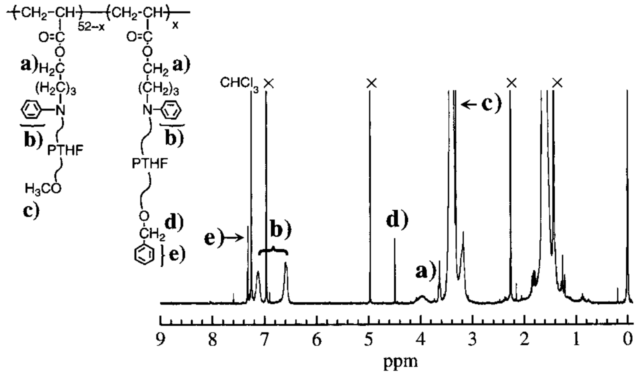
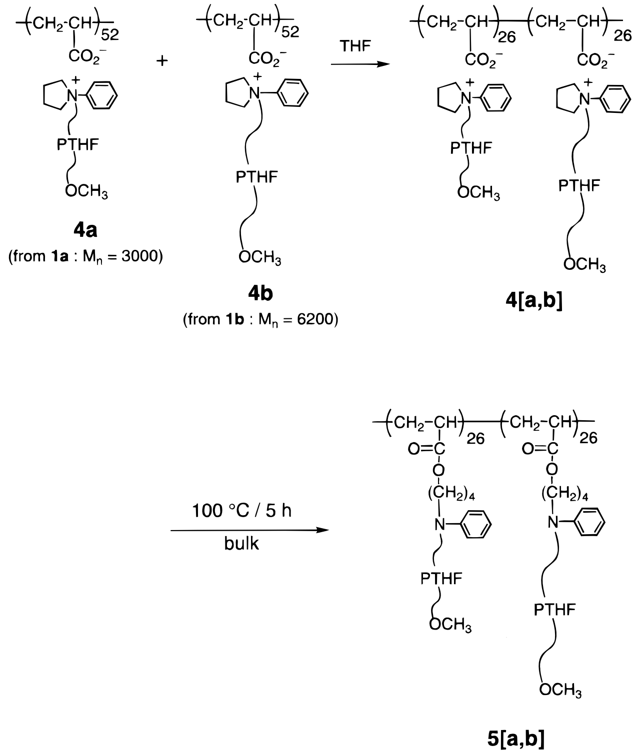


**Figure 3.** 300 MHz $^1$H NMR spectrum of poly(THF) polymacromonomer with two different branch segment lengths **5[a,c]**. ($CDCl_3$, 40 °C; × = stabilizer in THF, 2,6-di-*tert*-butyl-4-methylphenol.)

**Scheme 4**



the estimated one (10) by the feed ratio of **1a** and **1c** (4:1) within the limit of experimental error, showing that the reshuffling process, in this system, proceeds rapidly and irrespectively of the branch segment length to produce a product of a nearly equilibrated segment content.

**2.2. Reshuffling in Electrostatically Self-Assembled Polymacromonomer Precursors 4a and 4b.** On the basis of above-described results, reshuffling of different poly(THF) segments in electrostatically self-assembled polymacromonomer precursors **4a** and **4b** was performed to produce a polymacromonomer having mixed branch segments (Scheme 4, run 6 in Table 1). Thus, an equimolar amount of **4a** and **4b** was mixed in THF, and a new polymacromonomer precursor, **4[a,b]** was recovered by evaporating the solvent. The subsequent heat treatment was carried out to produce the covalently linked *co*polymacromonomer **5[a,b]**. The SEC profile of **5[a,b]** is compared with the relevant polymacromonomers **5a** and **5b** obtained separately from **4a** and **4b**, respectively (run 7 in Table 1).[15] As shown in Figure 4, an equimolar mixture of the polymacromonomers **5a** and **5b** gives an UV trace composed of the two fractions with equal peak areas (dashed line, top), since both **5a** and **5b** contain equal number of UV-detectable aromatic rings (*N*-phenyl groups) located at each branch segments. The branch segment length is, on the other hand, longer in **5b** than in **5a**, and hence, a RI trace is composed of the larger fraction in **5b** than in **5a** (dashed line, bottom). In consequence, the UV profile of the equimolar mixture of **5a** and **5b** is dissimilar to the corresponding RI profile. By contrast, the UV profile of **5[a,b]** was nearly identical to the RI profile. These results indicate again that a rapid reshuffling between the poly(THF) segments in **4a** and **4b** took place to produce **4[a,b]**, and the subsequent heat treatment could convert the electrostatically self-assembled product into a covalently linked polymacromonomer **5[a,b]** having mixed branch segments in an equilibrated segment content. And it can be assumed that the two different poly(THF) segments in **5[a,b]** are randomly distributed along the backbone segment in the obtained polymacromonomer, since the reshuffling process in the ion-exchange reaction can scarcely be affected by the segment length of poly(THF) precursors used in this study.

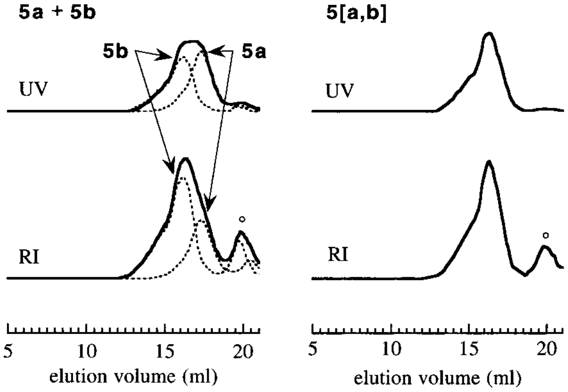


**Figure 4.** SEC traces (RI, refractive index; UV, ultraviolet) of the mixture of **5a** and **5b** (left), and of the reaction product **5[a,b]** obtained by mixing **4a** and **4b** and subsequent heat treatment (right). (Column: 2 × TSK G5000HXL. Eluent: THF, 1 mL/min. ° = hydroxyl-terminated poly(THF) concurrently formed in the reaction.[14])

Assuming that reshuffling of poly(THF) segments in electrostatically self-assembled precursors is a purely random process, the compositional distributions of the two branch units in the obtained polymacromonomer, i.e., the sequence distribution and the compositional distribution, can be estimated by the statistical method. According to the literature,[22] the mean sequence length, $N(\mathbf{1a})$, of **1a** in polymacromonomer **5[a,c]** and in **5[a,b]** and the most probable sequence length, $\langle N(\mathbf{1a})\rangle$, are given by

$$\mathrm{N}(\mathbf{1a}) = \left(\mathrm{Fx} - \frac{\mathrm{Fx}^2}{4}\right)^{-1} \tag{1}$$

$$\langle N(\mathbf{1a})\rangle = -\left[\ln\left(1 - \frac{\mathrm{Fx}}{2}\right)\right]^{-1} \tag{2}$$

where Fx is the molar fraction of segment X (X = **1c** for **5[a,c]**, Fc = $^1/_5$; X = **1b** for **5[a,b]**, Fb = $^1/_2$) in the polymacromonomer. Also the mean square standard deviation of the segment X composition in the polymac-

**Table 2. Compositional Polydispersity of Polymacromonomers[a]**

| entry | polymacromonomer | Fx[b] | $N(\mathbf{1a})$[c] | $\langle N(\mathbf{1a})\rangle$[d] | $\sigma^2$ ($\times 10^3$)[e] |
|---|---|---|---|---|---|
| 1 | **5[a,c]** | 0.2 | 5.3 | 4.7 | 3.1 |
| 2 | **5[a,b]** | 0.5 | 2.3 | 1.7 | 4.8 |

[a] See ref 22. [b] Fx is the molar ratio of segment X (X = **1c** for **5[a,c]**; X = **1b** for **5[a,b]**) in the polymacromonomer. [c] N(**1a**) is the mean sequence length (units) of **1a** in the polymacromonomer. [d] $\langle N(\mathbf{1a})\rangle$ is the most probable sequence length (units) of **1a** in the polymacromonomer. [e] $\sigma^2$ is the mean square standard-deviation of X composition in the polymacromonomer (i.e., Fx).

romonomer, $\sigma^2$, is given by

$$\sigma^2 = \frac{\mathrm{Fx} - \mathrm{Fx}^2}{\mathrm{DP}} \tag{3}$$

Compositional polydispersity parameters of the two copolymacromonomer thus estimated are collected in Table 2.

In conclusion, novel poly(THF) polymacromonomers having mixed branch segments with different chain lengths have been produced through reshuffling of poly(THF) segments in electrostatically self-assembled precursors and subsequent covalent fixation. The reshuffling process utilizing poly(THF)s having an *N*-phenylpyrrolidinium salt end group occurred rapidly, and an electrostatically self-assembled polymacromonomer precursor of an equilibrated segment component was obtained, prior to the quantitative conversion into a covalently linked *co*polymacromonomer. Thus, the composition in the produced *co*polymacromonomer will be controlled by the feed ratio of the starting self-assembled polymacromonomer precursors. Further studies in progress in our laboratory include an atomic force microscopic analysis of polymacromonomers, and the synthesis of polymacromonomer having incompatible branch segments through the reshuffling in electrostatic self-assembled precursors.

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