Control in Both Backbone and Branch Segment Lengths of Poly(tetrahydrofuran) Polymacromonomers by Electrostatic Self-Assembly and Covalent Fixation

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Introduction

Polymacromonomers are a novel class of branched polymers, composed of a linear backbone segment with densely substituted side chains of either linear, flexible polymer segments or highly branched, dendritic segments (dendron-jacketed polymers). They are unique in forming anisotropic cylindrical three-dimensional structures, as observed directly by means of an AFM or SFM technique, where the otherwise flexible backbone segment is forced to adopt an extended rodlike form rather than its entropically favored random-coil form. In consequence, polymacromonomers can produce, through self-assembly, a variety of mesoscopically ordered structures. The precise control, therefore, over structural parameters in polymacromonomers such as the backbone segment length and the number of graft segments in addition to the graft segment length becomes an important prerequisite for the design and eventual modulation of the supramolecular structures achieved by them.

Polymacromonomers of high branch numbers have so far been prepared by a radical homopolymerization process under rigorously controlled conditions. While the control over the number of branch segments (the DP of the product) has been difficult to achieve. Very recently, a living radical polymerization process has been applied, and uniform size polymacromonomers have been synthesized using macromonomer molecular weights of a few thousand.

A macromolecular coupling reaction between a polyfunctional prepolymer and complemental end-functional polymer precursors, on the other hand, is an alternative means to produce a polymacromonomer with controlled structures, since both polymer precursors are, in principle, prepared by a living polymerization technique and fully characterized prior to the coupling reaction. In practice, however, polymer coupling processes by conventional reaction mechanisms have scarcely been applied because of the inefficiency by the low concentration of reactive groups located only at the chain end of a polymer precursor, as well as by the repulsive interaction and eventual macroscopic phase separation of two immiscible polymer precursors.

We have proposed an effective macromolecular coupling reaction process by addressing the above-mentioned drawbacks. Thus, a series of poly(THF) polymacromonomers were prepared in high yields by use of poly(THF) having an azetidinium salt, as well as a tetrahydrothiophenium salt, as a single end group. A highly efficient ion-exchange reaction of the poly(THF) precursor was observed to occur with poly(sodium acrylate), by precipitation of the former into aqueous solution of the latter. During this process an ionically self-assembled product is presumed to be formed, and this has been assumed a critical intermediate for the exceptionally efficient polymer coupling reaction. In this particular reaction, however, the ionically self-assembled precursor could not be isolated, since the azetidinium (four-membered ammonium) group and the tetrahydrothiophenium (five-membered sulfonium) group undergo a quantitative ring-opening reaction by carboxylate anions in poly(acrylate) at ambient condition to produce amino—ester and thio—ester (thus covalent bond) groups, respectively.

The isolation of the ionically self-assembled polymacromonomer precursor has subsequently been achieved by use of poly(THF) having a less strained N-phenylpyrroolidinium salt as a single end group. The relevant ion-exchange process with poly(sodium acrylate) could produce the ionically self-assembled and isolatable polymacromonomer precursor, and the subsequent heat treatment could convert the ion pair into covalent bond quantitatively to produce a polymacromonomer in high yield. In this relevance, a variety of noncovalently self-assembled, comb-shaped polymers and copolymers either by hydrogen bonds or by ionic interactions have also been reported to exhibit unique phase behaviors in bulk.

As a further extension of our “electrostatic self-assembly and covalent fixation” process, we report herein an efficient synthesis of a series of poly(THF) polymacromonomers with controlled backbone segment length as well as graft segment length. Thus, uniform size poly(THF) having an N-phenylpyrroolidinium salt group was subjected to the coupling reaction with poly(sodium acrylate) of defined DP values, prepared through the living polymerization of tert-butyl acrylate and subsequent saponification treatment.

Experimental Section

Materials. THF was dried over sodium benzophenone ketyl and distilled just before use. tert-Butyl acrylate was distilled from CaH2, n-Butyllithium (hexane solution) was titrated at 1.6 M. Unless otherwise noted, materials were obtained from commercial sources.

Synthesis of Poly(THF)s Having an N-Phenylpyrroloidinium Salt End Group (1). Poly(THF)s of different molecular weights (Mn = 2100, 3000, 5600, and 6200) having an N-phenylpyrroloidinium salt end group (1) were prepared by the termination of a living poly(THF), initiated by methyl trifluoromethanesulfonate (methyl triflate), with N-phenylpyrroloidine. The number (Mn) and weight-average (Mw) molecular weight as well as polydispersity index (PDI = 1.16–1.21) of 1 were estimated by means of SEC after the conversion from an ionic pyrroloidinium salt end group into a covalent amino—ester group by the reaction with sodium benzoate (Scheme 1), since 1 itself caused an elution delay and a peak tailing due to the interaction between the ionic end group of 1 and polystyrene gel of SEC column.

Synthesis of Uniform Size Poly(sodium acrylate)s (2). A living anionic polymerization of tert-butyl acrylate was
Fractionation of Polymacromonomer. The precipitation treatment was carried out in the THF-methanol system at −15 °C in order to isolate the polymacromonomer fraction. Thus, 0.15 g of pure polymacromonomer was obtained from 0.35 g of the crude mixture after the second fractionation treatment (entry 5 in Table 1).

Measurements. IR spectra were recorded on a J ASCO FT/IR-410 infrared spectrometer by casting the sample from the chloroform or a KBr pellet. 1H NMR spectra were recorded with a J EOL J NM-AL300 apparatus in CDCl3 or in D2O at 40 °C. The proton chemical shifts (ppm) were referenced from the signal of tetramethylsilane. SEC measurements were performed using a Tosoh model CCPG 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. A column of either TSK G3000HXL, TSK G4000HXL, or TSK G5000HXL was employed with THF as an eluent at a flow rate of 1.0 mL/min.

Results and Discussion

The macromolecular ion-exchange reaction between a series of uniform size polymer precursors, i.e., poly(TTHF)s having an N-phenylpyrrolidinium salt group (1) and poly(sodium acrylate)s (2), was performed as in the previous study (Scheme 3).25 Simple precipitation of 1 into an aqueous solution containing 2 was thus carried out repeatedly. The progress of the ion-exchange reaction was monitored by IR spectroscopic analysis of the recovered products, and the precipitation treatment was repeated until absorptions at 1030 and 639 cm⁻¹ due to the initial counteranion of 1, i.e., triflate, totally disappeared. The supplementary precipitation treatment was required for the reaction of 1 with 2 having higher molecular weights. Thus, twice was enough for the complete reaction of 1 of the MW of 2K with 2 of the DP of 24 (entry 1 in Table 1), while as many as six times was required for that of 1 of the MW of 5K and 2 of the DP of 52, resulting in a low yield of final product (entry 5 in Table 1).

The subsequent heating treatment was performed at 100 °C for 5 h. 1H NMR as well as IR spectroscopic analysis indicated that the ionically self-assembled product was converted into the covalently linked polymacromonomer through a selective and quantitative ring-opening reaction of pyrrolidinium salt groups in 1 by carboxylate anions in 2 to produce amino-ester groups.18 Figure 1 shows, for example, 1H NMR spectra of the ionically self-assembled product (top) and of the isolated covalently linked polymacromonomer after the heat treatment (bottom, entry 5 in Table 1). In the spectrum of the polymacromonomer, the signals due to an N-phenylpyrrolidinium salt group visible in the spectrum, demonstrating the covalently linked polymacromonomer was successfully obtained with high efficiency.

SEC analysis was performed for a series of polymacromonomer products of different combination of precursors 1 and 2. As has been commonly observed in star polymers and polymacromonomers, the apparent MWs of a series of polymacromonomers by SEC were substantially smaller than those calculated from multiplying the MW of 1 by the DP of 2 (Table 1). It is also shown in Figure 2 that the SEC profiles for the products obtained from 1 of the MW of 2K and 2 of either the DP

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*References and notes are not provided in the natural text format.*

Performing procedures of the macromolecular ion-exchange reaction between 1 and 2 and Ring-Opening Reaction of Pyrrolidinium Salt End Group. A THF solution of 1 (10–20 wt %) was added dropwise into a cold water containing a weighed amount of 2 (ca. 1 equiv with respect to ionic groups) under vigorous stirring. After stirring for 1 h, the precipitated ion-exchange product was collected by filtration and dried in vacuo for 2 h. This precipitation treatment was repeated to complete the ion-exchange reaction. The recovered ionically self-assembled products 3 were then subjected to a heat treatment at 100 °C for 5 h.
Table 1. Ion-Coupling Reaction between Poly(THF) Having an N-Phenylpyrrolidinium Salt End Group (1) and Poly(sodium acrylate) (2)

<table>
<thead>
<tr>
<th>entry</th>
<th>1&lt;sup&gt;a&lt;/sup&gt; M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>2&lt;sup&gt;a&lt;/sup&gt; DP</th>
<th>repetition times of precipitation</th>
<th>recovered yield (%)</th>
<th>polymacromonomer yield (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (SEC) (PDI)&lt;sup&gt;d&lt;/sup&gt; [×10&lt;sup&gt;-4&lt;/sup&gt;]</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (calc)&lt;sup&gt;e&lt;/sup&gt; [×10&lt;sup&gt;-4&lt;/sup&gt;]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2100</td>
<td>24</td>
<td>2</td>
<td>86</td>
<td>89</td>
<td>1.6 (1.20)</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>5600</td>
<td>24</td>
<td>4</td>
<td>50</td>
<td>84</td>
<td>5.6 (1.18)</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>2100</td>
<td>52</td>
<td>3</td>
<td>49</td>
<td>90</td>
<td>2.7 (1.23)</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>3000</td>
<td>52</td>
<td>3</td>
<td>71</td>
<td>88</td>
<td>4.7 (1.48)</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>5600</td>
<td>52</td>
<td>6</td>
<td>64</td>
<td>68</td>
<td>5.9 (1.43)</td>
<td>29</td>
</tr>
<tr>
<td>6</td>
<td>6200</td>
<td>52</td>
<td>5</td>
<td>64</td>
<td>84</td>
<td>7.8 (1.65)</td>
<td>32</td>
</tr>
</tbody>
</table>

<sup>a</sup> See also Scheme 1.  
<sup>b</sup> See also Scheme 2.  
<sup>c</sup> Estimated from SEC peak area ratio.  
<sup>d</sup> Determined by SEC with a calibration using linear polystyrene standards by a conversion factor of 0.556.  
<sup>e</sup> Calculated from the length and the number of branch segments.

Scheme 3

Figure 1. The 300 MHz <sup>1</sup>H NMR spectra of ionically assembled precursor 3 (top) and covalently linked polymacromonomer 4 after the fractionation treatment (bottom) (sample: entry 5 in Table 1, CDCl<sub>3</sub>, 40 °C, * = satellite signal, x = impurity).

Notes

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As for the SEC measurement of polymacromonomers and “dendron-jacketed” polymers of cylindrical structures, an elution anomaly has been often reported in contrast to those of the flexible, random-coil shaped polymers. In our experiments with a series of polymacromonomers, the products listed in Figure 2 consistently showed symmetrical, uniform size distributions in a reproducible manner. On the other hand, the product of largest size, as shown in Figure 3, showed noticeable broadening before and after the fractionation treatment in comparison to its smaller size analogues. Since all polymacromonomers prepared in the present study are thought to be consistently uniform in their structures with both defined backbone and graft segment lengths, this anomaly may well be regarded as a characteristic feature of polymacromonomers in solution.

In conclusion, we have demonstrated that the “electrostatic self-assembly and covalent fixation” process has been successfully applied for the synthesis of a series of polymacromonomers having both controlled backbone and graft segment lengths. The isolation of ionically self-assembled precursors is a critical step of this effective methodology, and it may provide a unique opportunity to perform a subsequent manipulation of this ionically self-assembled precursors. Thus, further attempts to construct novel polymacromonomers, including a polymacromonomer having mixed graft segments, are currently in progress in our laboratory.

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References and Notes

(1) Tsukahara, Y. Macromolecular Design: Concept and Practice Polymer Frontiers International Inc.: New York, 1994; Chapter 5, p 161.
(22) To determine the molecular weight of the given poly(THF)s by SEC, the calibration by polystyrene standards may not be automatically applied, since the hydrodynamic volumes of the different polymers are not identical. A conversion factor of 0.556 is therefore used to obtain an accurate molecular weight. See: Burgess, F. J.; Cunliffe, A. V.; Dawkins, J. V.; Richards, D. H. Polymer 1977, 18, 733–740.
(25) Teyssié et al. reported that the molecular weight of poly-(tert-butyl acrylate), as measured by SEC on the basis of a polystyrene calibration, was in very close agreement with the absolute molecular weight, at least in the range smaller than 30,000. See: Wang, J.-S.; Bayard, Ph.; Jérôme, R.; Varshney, S. K.; Teyssié, Ph. Macromolecules 1994, 27, 4890–4895.