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Designing Polymer Topology by Electrostatic Self-Assembly and Covalent Fixation

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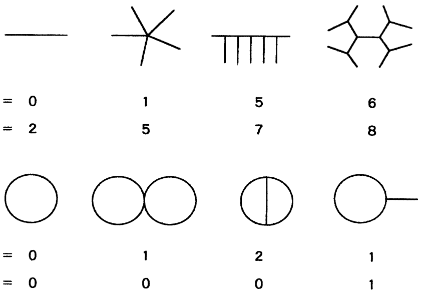
SUMMARY: A novel methodology (electrostatic self-assembly and covalent fixation) has been proposed for designing unusual polymer topologies such as star polymers, polymacromonomers, dumbbell-shaped polymers as well as model network polymers. Thus new telechelic polymers having moderately strained cyclic onium salt group as single or both end groups were prepared and subjected to an ion-exchange reaction to introduce multifunctional carboxylate anions as a counter-anion. The electrostatically self-assembled products were then subjected, either directly or after subsequent manipulation, to heat treatment to convert the ionic interaction into the covalent linkage by the ring-opening reaction to produce a variety of topologically unique polymer architectures in high yields.

Introduction

Topology of polymer molecules, in particular of non-linear ones, is characterized by their principal structural parameters, i.e., end group and junction (branch point) numbers as shown in Scheme 1, where some topologically unique polymers with the numbers are collected.

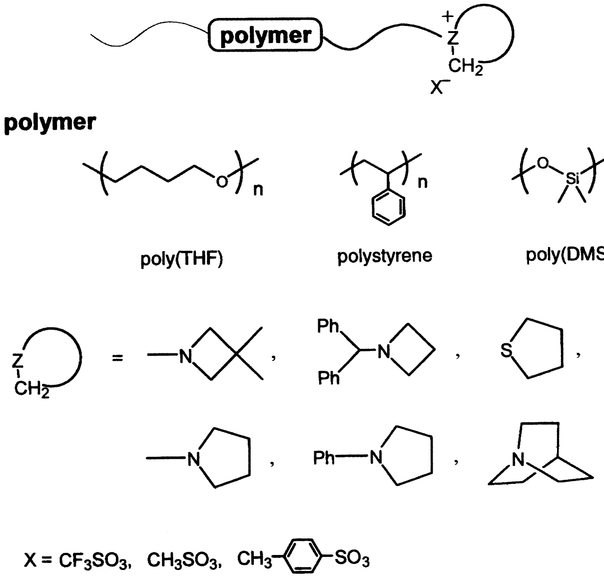


Scheme 1. Topology of polymer molecules with their junction (J) and terminus (T) numbers

Thus a novel means to precisely control these parameters is expected to create unprecedented properties and functions of advanced polymer materials as well as to realize molecular devices and molecular machines applicable in future nanotechnology systems.

We propose herein a novel methodology to produce various non-linear polymer topologies with exceptionally high efficiency by exploiting the self-assembly principle to preorganize linear polymer precursors and subsequently converting them into covalently linked permanent structures. Self-assembly of molecular components through non-covalent interactions plays critical roles in diverse biological events, typically in molecular recognition and molecular communication processes. Any forces weaker than covalent bonds, such as directional hydrogen bonds and metal-coordination bonds as well as non-directional van der Waals forces and Coulombic interactions, may be exploited to direct self-assembly. The self-assembly principle has drawn increasing attention both in basic and in applied fields of materials science since the self-assembly may provide a unique means to effectively preorganize (macro)molecular compounds and to subsequently convert them into permanent polymer, mesoscopic and macroscopic architectures otherwise difficult or impossible to make. We have thus utilized self-assembly through a Coulombic interaction of hydrophobic macromolecules having specific cationic end groups, namely moderately strained cyclic onium salt groups with multifunctional carboxylate groups introduced as counter-anions1).

We describe first the synthesis of a variety of uniform-size polymers such as poly(tetrahydrofuran), polystyrene and poly(dimethylsiloxane), having a series of cyclic onium salt end groups, including four- and five-membered cyclic and six-membered bicyclic ammonium salt groups as well as five-membered cyclic sulfonium salt group2-5) (Scheme 2).

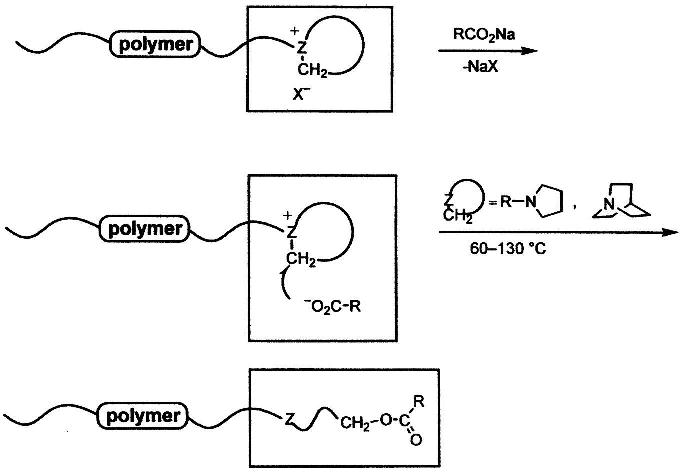


Scheme 2. Telechelics with cyclic onium salt groups

Second, we discuss the ring-opening reaction of cyclic onium salt groups located at the chain end of hydrophobic polymer segments. In particular, five-membered cyclic ammonium (pyrrolidinium) salt groups having either N-*methyl* or N-*phenyl* substituent are unique since they are stable with various carboxylates as a counter-anions under ambient conditions, but can undergo a selective ring-opening reaction at an appropriately elevated temperature to form covalent aminoester groups[6,7]. On the basis of this feature of the pyrrolidinium salt end groups, we have developed an efficient process to synthesize star polymers and poly(macromonomer)s from monofunctional telechelics, and dumbbell-shaped polymers and model network polymers from bifunctional telechelics through a simple ion exchange and subsequent heat treatment[7,8].

Telechelics with Moderately Strained Cyclic Onium Salt Groups

A series of poly(THF) having a variety of cyclic onium salt groups have been conveniently produced by a direct end-capping reaction of mono- and bifunctional living poly(THF)s. Thus we have introduced a series of ammonium salt groups of three-, four-, five-, and six-membered cyclic as well as of six-membered bicyclic structures. The three-membered cyclic ammonium salt end groups are highly reactive and undergo a spontaneous ring-opening reaction with the respective three-membered cyclic amine to produce a block copolymer in situ. The four-membered cyclic ammonium salt end groups, on the other hand, are incapable of causing the ring-opening reaction with four-membered cyclic amines at ambient temperature. Hence telechelic poly(THF) with four-membered cyclic onium salt groups can be isolated for the relevant spectroscopic and chromatographic characterization, and can be subsequently utilized as a reactive polymer precursor to produce a block copolymer by the reaction with three- and four-membered cyclic amines at an elevated temperature. Interestingly, the four-membered cyclic onium salt end groups can undergo the ion-exchange reaction from an original triflate to others like sulfonates or carboxylates through a simple precipitation of the telechelics solution into an aqueous solution containing desired anions as salts. Strong nucleophiles such as a carboxylate counter-anion can cause a quantitative ring-opening reaction of the four-membered cyclic ammonium salt groups at ambient temperature. Telechelic poly(THF)s having modestly strained five-membered cyclic as well as six-membered bicyclic ammonium salt groups can be isolated even with carboxylates as a counter-anion, but can undergo the ring-opening reaction at an elevated temperature, whereas the strain-free six-membered cyclic ammonium salt group fails to cause the ring-opening reaction. Thus telechelic poly(THF)s having the five-membered cyclic and the six-membered bicyclic ammonium salt groups are chosen as polymer precursors to be used for "electrostatic self-assembly" with appropriate carboxylate counter-anions, and are then subjected to "covalent fixation" to produce covalently linked permanent structures (Scheme 3).



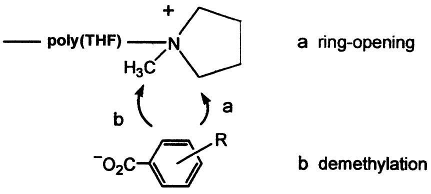
Scheme 3. Ion-exchange and ring-opening reactions

We have also prepared the relevant telechelic polystyrenes and poly(DMS)s having the five-membered cyclic and six-membered bicyclic ammonium salt groups through sequential end-group derivatizations of a living polystyrene and of a living poly(DMS) obtainable by anionic polymerization. Thus a direct end-capping reaction of mono- and bifunctional living polystyrene or poly(DMS) was performed with a chlorosilane derivative having a trimethylsilyl-protected hydroxy group. Subsequent deprotection followed by tosylation and quaternization with a five-membered cyclic amine (*N-methyl*pyrrolidine) or with a six-membered bicyclic amine (quinuclidine) was performed to produce telechelic polystyrenes and poly(DMS)s having moderately strained cyclic onium salt groups.

Ring-Opening Reactions of Five-membered Cyclic Ammonium Salt Groups

The ring-opening reactions of *N-methyl-* and of *N-phenyl*pyrrolidinium salt end groups with a variety of carboxylate counter-anions have been compared. A nucleophilic substitution reaction on the *N-methyl*pyrrolidinium salt group with carboxylate anions is often accompanied, besides by the ring-opening reaction, by a demethylation reaction through the nucleophilic attack at the N-*methyl* carbon. On the other hand, a Hofmann-type elimination is negligible under the usual ring-opening reaction conditions.

The reactivity of *N-methyl*pyrrolidinium groups has been thoroughly examined with a series of 4-substituted benzoate counter-anions with different pK_a values. An electron-donating 4-methoxybenzoate ($pK_a = 4.47$) produced the ring-opened product in a high yield and with high ring-opening selectivity at 100 °C, while an electron-withdrawing 4-nitrobenzoate (pK_a = 3.42) failed to cause any reaction even at 100 °C. It has also been shown that the higher the reaction temperature, the lower is the selectivity of the ring-opening reaction over the demethylation. (Scheme 4).



Scheme 4. Ring-opening versus demethylation reactions

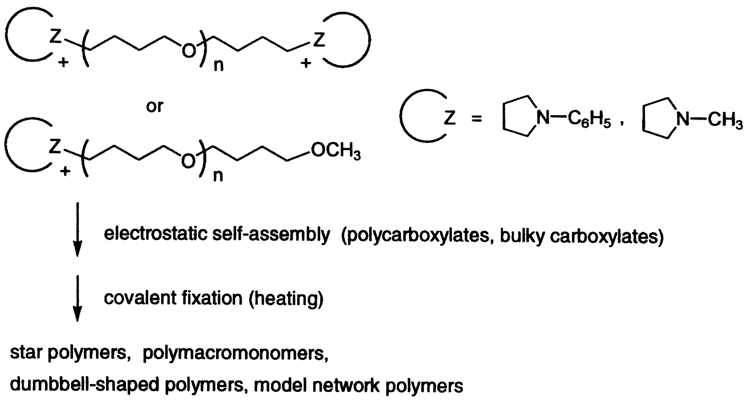
We have then synthesized an alternative polymer precursor, in which N-*methyl* group on a pyrrolidinium salt group is replaced by N-*phenyl* group. Since the nucleophilic substitution reaction on the phenyl group is strongly suppressed, the ring-opening reaction on aliphatic methylene groups is favored to occur. Furthermore, the ring-opening reaction will be promoted by introducing an aniline derivative group, which is a better leaving group than an alkylamino group in the nucleophilic substitution reaction. Indeed, the *N-phenyl*pyrrolidinium salt group caused a complete ring-opening reaction even at 80 °C with the 4-nitrobenzoate counter-anion at the endo-position of the five-membered pyrrolidinium ring exclusively, in contrast to the *N-methyl*pyrrolidinium salt end group under the relevant conditions. Moreover, unsubstituted benzoate and 4-methoxybenzoate counter-anions caused a quantitative and selective ring-opening reaction of the *N-phenyl*pyrrolidinium salt group without concurrent demethylation reaction, in contrast to the *N-methyl*pyrrolidinium salt groups.

Electrostatic Self-Assembly and Covalent Fixation of Novel Telechelics

We describe here a novel efficient process to produce star polymers and poly(macromonomer)s as well as dumbbell-shaped polymers and model-network polymers of poly(THF) through the electrostatic self-assembly and covalent fixation strategy (Scheme 5).

Star polymers and poly(macromonomer)s

An efficient ion-exchange reaction of a monofunctional poly(THF) having an *N-phenyl*pyrrolidinium salt end group with a multicarboxylate (such as sodium benzene-1,3,5-tricarboxylate) occurred by the repeated precipitation into aqueous solution containing an excess amount of a multicarboxylate salt.



Scheme 5. Electrostatic self-assembly and covalent fixation

Subsequent heat treatment of the ionically assembled polymer precursor caused the selective ring-opening reaction to give a covalently linked star polymer with three arms in a high yield. The telechelic poly(THF) was then utilized in the macromolecular ion-exchange reaction with poly(sodium acrylate) through the repeated precipitation. The ion-exchange reaction of triflate for carboxylate proceeded quantitatively, and no sign of the ring-opening reaction was detected for the isolated ion-exchanged product, i.e., the electrostatically assembled poly(macromonomer) precursor. The subsequent heat treatment again caused the selective ring-opening reaction to give a covalently linked poly(macromonomer) in a high yield. Furthermore, by using a uniform size poly(sodium acrylate), prepared by living polymerization of *tert*-butyl acrylate, a well-defined poly(THF) poly(macromonomer) with controlled backbone segment length having both predetermined branch segment numbers and branch segment length was obtained9). The isolation of the electrostatically self-assembled precursor can provide a further opportunity for the structural manipulation of star polymers and poly(macromonomer)s, and a star copolymer and a copoly(macromonomer) having different types of graft chain segments were produced10).

On the other hand, the reaction of monofunctional poly(THF) having either a four-membered cyclic ammonium or a five-membered cyclic sulfonium (tetrahydrothiophenium) salt end group with sodium benzene-1,3,5-tricarboxylate or poly(sodium acrylate) led to a spontaneous ring-opening reaction under ambient conditions, and the ionically assembled polymer precursor could not be isolated as an intermediate11,12). Another attempt to prepare the relevant poly(macromonomer) using telechelic poly(THF) and poly(dimethylsiloxane) having an *N-methyl*pyrrolidinium salt end group, on the other hand, was circumvented due to the extensive demethylation caused by carboxylate anions in poly(acrylate) component.

Dumbbell-shaped polymers

The electrostatic self-assembly and covalent fixation process have also been applied to the synthesis of dumbbell-shaped polymers. Thus telechelic poly(THF)s having cyclic onium salt groups were prepared with a series of bulky carboxylates as counter-anions. Subsequent heating of these telechelic polymer precursors in the absence or presence of macrocycles has been performed to cause the ring-opening reaction of cyclic onium salt groups converting the preformed ionic assembly into the covalently linked permanent structures, aimed at producing efficiently macromolecular rotaxan structures.

The triphenylacetate anion, whose trityl group is reported to be bulky enough to prevent dethreading macrocyclic compounds such as 30-crown-10 and cyclodextrins, was introduced as a counter-anion of the *N-methyl*pyrrolidinium salt end groups of poly(THF). Subsequent heat treatment, however, caused the decarboxylation reaction of the triphenylacetate anion to produce a triphenylmethane, instead of the desired ring-opening reaction. Therefore, two commercially available bulky carboxylates, sodium 3,3,3-triphenyl- and 3,3,3-tris(4-chlorophenyl)propanoates as well as two newly prepared bulky carboxylates, a dendritic carboxylate and another having an alkyl spacer, i.e., 4-(7,7,7-triphenylheptyloxy)benzoate, were then employed as potential blocking reagents.

The ion-exchange reaction with these bulky carboxylates was performed by precipitation into water from a THF solution of a mixture of the polymer precursor and the carboxylate salt with an equimolar amount of ionic groups. The nucleophilic attack of the carboxylate anion took place during subsequent heat treatment, predominantly at the ring methylene position on the *N-methyl*pyrrolidinium group, though with the concurrent reaction at N-*methyl* position. Nevertheless, a series of dumbbell-shaped poly(THF)s having bulky end groups was isolated in pure form by preparative thin layer chromatography.

Further attempts to entrap macrocyclic compounds, such as 30-crown-10 or cyclodextrins have been performed, but with only limited success, presumably due to surmounted entropic repulsion preventing the threading of macrocyclic compounds on a linear polymer molecule by its chain ends at low concentration.

Model network polymers

The bifunctional poly(THF) having *N-phenyl*pyrrolidinium salt end groups has also been utilized to undergo the ion exchange and subsequent covalent fixation reaction with tri-, tetra- and hexacarboxylates by a simple precipitation procedure as described in the previous sections. The pseudo-network products were thus obtained, in which poly(THF) segments are combined through Coulombic interaction between *N-phenyl*pyrrolidinium cations and carboxylate anions. All pseudo-network products were soluble in common organic solvents, permitting full characterization by solution NMR spectroscopy. The complete ion-exchange reaction was thus confirmed to occur.

A series of ionic pseudonetworks were then subjected to heat treatment in the bulk in order to convert the ionic into covalent linkage. All products became insoluble but swollen in common organic solvents. The gel content was nearly quantitative in all cases. The selective ring-opening reaction was confirmed to occur by the IR spectroscopy. Thus, the obtained network products are considered model networks, in which both the number of the segments at the junction points and the length of the segments between the junction points are precisely defined. The former corresponds to the functionality of the carboxylate used, and the latter to the molecular weight of the starting telechelic poly(THF). Indeed, the higher the molecular weight of the prepolymer, the higher the swelling degree of the network product. Moreover, the network product with a hexacarboxylate showed significantly lower swelling degree compared with those with tri- and tetracarboxylates.

The model-network synthesis with poly(dimethylsiloxane) having *N-methyl*pyrrolidinium salt end groups by the electrostatic self-assembly and covalent fixation has also been achieved. However, an attempt to prepare the relevant poly(THF) model networks using telechelic poly(THF) with *N-methyl*pyrrolidinium salt groups failed to produce gel products (network) in high yields. This is apparently due to the concurrent demethylation.

Further Perspectives

We are currently developing, as an extension of these studies, a novel methodology for the preparation of well-defined monocyclic and multicyclic polymers based again on an electrostatic self-assembly of polymer precursors having moderately strained five-membered cyclic ammonium salt groups with multicarboxylate counter-anions. Upon diluting with an appropriate organic medium to a few grams per liter, the polymer precursor and the carboxylate units form a self-assembled product with the smallest numbers of polymer components to retain the stoichiometry between counter-ion pairs. Subsequent covalent fixation through the ring-opening reaction of cyclic ammonium salt groups by carboxylate counter-anions provides an efficient means for topologically unique polymer architectures containing cyclic polymer units.

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