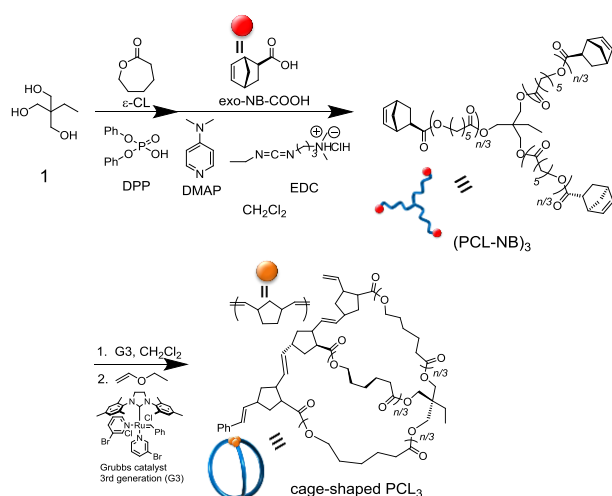


Novel Synthetic Strategy for Multicyclic Polymers

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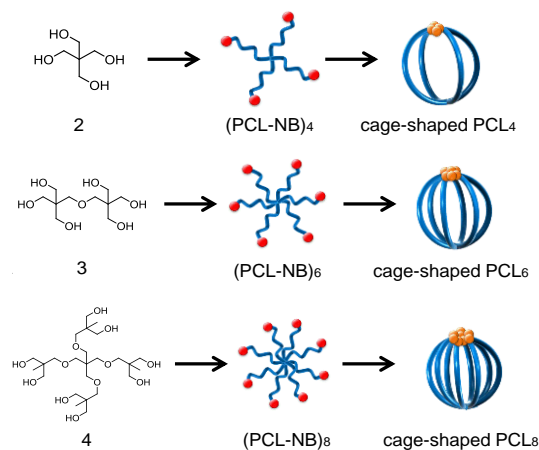
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Constructing various macromolecular architectures, such as cyclic, star, and brush polymers, has been one of the central subjects in the polymer chemistry field over the past few decades. Among the various macromolecular architectures, macromolecules possessing cyclic architectures are of great interest because of their intriguing properties such as lower viscosity and higher glass transition temperature, which are not found in their traditional linear or branched counterparts due to the nature of the endless structure. Therefore, multicyclic polymers, such as trefoil-shaped and figure-eight-shaped polymers, have been synthesized to investigate their specific properties. However, the synthesis of multicyclic polymers still remains challenging due to the inherent synthetic difficulties. Here, we propose a novel synthetic strategy to multicyclic polymers, which involves the intramolecular consecutive cyclization of linear or star-shaped polymers having polymerizable groups. In this study, we attempted the synthesis of cage-shaped poly(ϵ -caprolactone)s (cage-shaped PCL_{*x*}s) as well as 8-, trefoil-, and quatrefoil-shaped poly(ϵ -caprolactone)s by the intramolecular consecutive cyclization via ring-opening metathesis oligomerization (ROMO) of linear or star-shaped poly(ϵ -caprolactone)s with norbornenyl groups at ω -chain ends or chain center, as shown in Schemes 1–3.

Scheme 1. Synthetic pathway for cage-shaped PCL₃

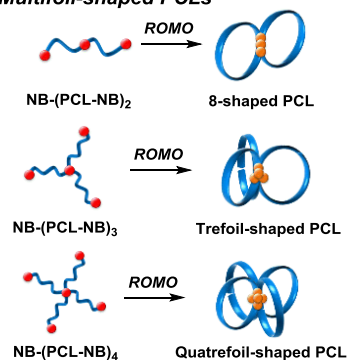
The star-shaped PCL with norbornenyl groups at ω -chain ends ((PCL-NB)₃; $M_{n,NMR} = 5,890 \text{ g mol}^{-1}$, $M_{n,SEC} = 9,440 \text{ g mol}^{-1}$, $D = 1.07$) was synthesized by the ring-opening polymerization of ϵ -caprolactone using trimethylolpropane, followed by the condensation reaction with *exo*-5-norbornene-2-carboxylic acid (NB-COOH). The intramolecular consecutive ROMO of (PCL-NB)₃ was carried out using the Grubbs catalyst 3rd generation (G3) in CH₂Cl₂ to lead cage-shaped PCL₃. The NMR and MALDI-TOF MS measurement revealed that the fully proceeding of cyclization reaction and the formation of desired product, respectively. Furthermore, the SEC trace of the obtained product shifted to lower molecular weight region ($M_{n,SEC} = 6,770 \text{ g mol}^{-1}$, $D = 1.09$), indicating the formation of the cyclic product with smaller

hydrodynamic volume as compared to (PCL-NB)₃. Thus, these results confirmed that desired cage-shaped PCL₃ was obtained by the intramolecular consecutive ROMO. In an analogous manner, varied arm-numbered cage-shaped PCLs and multifoil-shaped PCLs, were successfully synthesized using corresponding polymer precursors. Each multicyclic polymers could be prepared with controlled molecular weight.

Scheme 2. Synthesis of cage-shaped PCL₄, 6, and 8S

Furthermore, we tried the synthesis of other multicyclic polymers such as 8-, trefoil-, and quatrefoil-shaped polymers by intramolecular consecutive cyclization via ROMO. A linear PCL with norbornenyl groups at the ω -chain ends and chain center (NB-(PCL-NB)₂; $M_{n,NMR} = 6,200 \text{ g mol}^{-1}$, $M_w/M_n = 1.05$) was synthesized by the ROP of ϵ -CL and the condensation reaction with NB-COOH. The synthesis of 8-shaped PCL ($M_{n,NMR} = 6,530 \text{ g mol}^{-1}$, $M_w/M_n = 1.07$) was achieved by the intramolecular consecutive cyclization via ROMO of NB-(PCL-NB)₂ under the same conditions as cage-shaped PCL_{*x*}s. In a similar manner, the synthesis of trefoil- and quatrefoil-shaped PCLs was achieved by the intramolecular consecutive cyclization via ROMO of corresponding NB-(PCL-NB)_{*y*}s ($y = 3$ and 4).

Multifoil-shaped PCLs



Scheme 3. Synthesis of 8-, trefoil-, and quatrefoil-shaped PCLs