# Synthesis of Rod-Like Dendronized Polymers Containing G4 and G5 Ester Dendrons via Macromonomer Approach by Living ROMP

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Ⓢ Supporting Information

ABSTRACT: High generation dendronized polymers with high molecular weight were synthesized by ROMP via macromonomer approach. The polymerization was achieved in living manner and the macromolecules exhibited rod-like conformation. Correlation between the monomer structures and the conformation of the final polymers was investigated in detail. The rigid rod conformation in solution was confirmed by both light scattering and viscometric analysis and the single polymer chains were visualized by AFM.
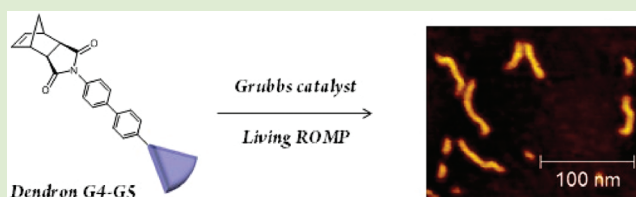
Dendronized polymers are unique macromolecules that are composed of dendrons attached to polymer backbones.[1] These polymers have many advantages because one can design a polymer with a precisely controlled molecular architecture and desired properties by tuning the polymer backbone and the dendritic wedge independently. Also, several dendronized polymers exhibit an extended conformation owing to the steric repulsion between the repeating units. Hence, dendronized polymers are considered as new materials for a wide range of applications in fields of biomaterials,[2] drug delivery,[3] electronics,[4] and energy storage.[5]

Despite the great potential of dendronized polymers, their synthesis still proves to be challenging; hence, a more general method for both synthesis and controlling molecular weight and polydispersity of such polymers is desired. The synthesis of dendronized polymers by macromonomer approach[6] has following advantages over alternative methods such as graft-to approach[7] and graft-from approach.[8] First, dendronized polymers prepared from purified macromonomers are defect-free structures, whereas dendronized polymers prepared by the alternative methods inevitably contain defects, because the complete coverage of dendrons, especially for the high-generation ones is synthetically challenging. Moreover, the macromonomer approach enables the direct synthesis of block copolymers by the sequential addition of the monomers.[9] However, a prominent drawback of this approach is that the polymerization of macromonomers having high-generation (higher than G3) dendrons with high degree of polymerization is difficult because of their bulky side chains that hinder propagation.[6e,10] Moreover, the living polymerization of the macromonomers is extremely challenging because unfavorable reactions such as chain termination and chain transfer outcompete the chain propagation. For instance, dendronized polymers up to G2 were synthesized by living radical polymerization such as atom transfer radical polymerization (ATRP) and reversible addition–fragmentation transfer (RAFT) polymerization. However, from the macromonomers

beyond G2, only low molecular weight polymers with broad polydispersity index (PDI) were obtained.[6a,11] Recently, ring-opening metathesis polymerization (ROMP)[12] has been considered as one of the most efficient methods for synthesizing dendronized polymers[13] and graft polymers (bottle-brush)[14] because typical monomers, norbornene derivatives, are very reactive due to the large ring strain and highly active catalysts have been developed.[15,16] For this reason, the polymers having G3 dendrons[9] were prepared by living ROMP using third generation Grubbs catalyst.[15] Herein, we report the first example of the synthesis of high generation dendronized polymers with dendrons up to fifth generation (G5) by living ROMP using the Grubbs catalysts.[16] This provided polymers having molecular weight exceeding one million daltons and low (1.05 for G4) to moderate (>1.40 for G5) PDIs. Furthermore, the extended conformation of these polymers, both in solution and solid states, was verified.

The synthesis of macromonomers having G3 to G5 dendrons and polymers is summarized in Scheme 1. The macro-monomers were prepared by imidization of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride with various amino alcohols. To synthesize monomers containing biphenyl linker, 4-bromoaniline was introduced to norbornene and was then coupled with 4-hydroxyphenylboronic acid by Suzuki reaction to generate a biphenyl moiety. From these alcohols, the ester dendron units were grown from the focal point by an efficient divergent growth method developed by Fréchet and Hult.[9,10a] Each macromonomer was purified by flash column chromatography and characterized by NMR spectroscopy, matrix-assisted laser desorption/ionization mass-spectrometry (MALDI-MS) and elemental analysis (see Supporting Information). ROMP of these macromonomers was carried out using Grubbs catalyst I

Scheme 1. Synthesis of Monomers and Polymers
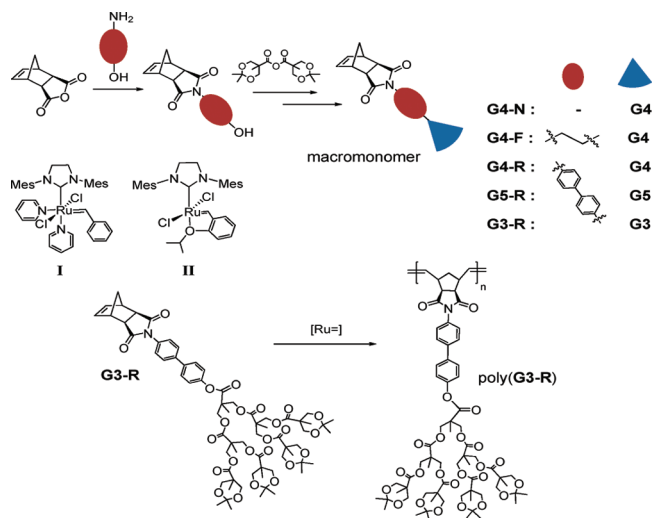
or **II** in THF at various temperatures, and complete conversion of the macromonomers occurred within three hours.

First, we examined the ROMP of the macromonomer **G4-N**, whose G2 and G3 analogs had undergone the living ROMP in a previous study.[9] As the dendrons were highly bulky and congested, the ROMP at room temperature was sluggish. Although the complete conversion of **G4-N** occurred at 50 °C (Table 1, entry 1), a moderate PDI of 1.35 was measured for

Table 1. ROMP of Various Macromonomers[a]

entry	monomer	T (°C)	[M]/[I]	M_n (conv)[b]	PDI[b]	M_n (theo)[c]	M_n (MALLS)[d]
1	**G4-N**	50	300	129k	1.35	659k	602k
2	**G4-F**	40	300	150k	1.07	680k	566k
3	**G4-R**	r.t.	50	23k	1.04	120k	153k
4	**G4-R**	r.t.	100	41k	1.06	239k	233k
5	**G4-R**	r.t.	200	86k	1.08	478k	399k
6	**G4-R**	r.t.	300	125k	1.09	718k	661k
7	**G4-R**	r.t.	500	205k	1.05	1196k	1128k
8	**G3-R**	r.t.	300	80k	1.08	391k	312k

[a]The polymerization was performed by **I** in THF at various temperatures. [b]The numbers were determined by THF-SEC calibrated by PS standards. [c]Theoretical molecular weight. [d]The molecular weight was determined by MALLS-VIS-RI detector.

poly(**G4-N**) even with the ultrafast-initiating catalyst **I**. This PDI, broader than expected, was presumably because of the slow propagation caused by the steric hindrance between the propagating carbene and the bulky monomers. To enhance the ROMP process, new monomers containing following linkers between norbornene and the G4 ester dendrons were prepared: a flexible ethylene linker unit and a rigid but linear biphenyl linker unit as in macromonomers **G4-F** and **G4-R**, respectively (Scheme 1). The ROMP of **G4-F** still required elevated temperature for the catalyst activation and the complete conversion of the macromonomer was observed at 40 °C, but without broadening of the PDI this time (1.07, Table 1, entry 2). This result suggested that the macromonomer **G4-F** became more reactive to ROMP (due to the higher k_p/k_t) by the introduction of the linker so that the PDI was significantly lower than that of **G4-N**. Further lengthening the linker by increasing the number of the carbon chain would make the side

chain too flexible and such dendronized polymer would not exhibit rod-like conformation.[11c,13d] Therefore, we decided to incorporate long but rigid biphenyl group as a new linker. Following this idea, we studied the ROMP of **G4-R** containing the biphenyl linker, and observed very efficient ROMP even at room temperature (Table 1, entries 3−7). Moreover, we observed the characteristics of living polymerization, such as narrow PDIs (<1.10) and excellent molecular weight control over a wide range of degree of polymerization (DP) from 50 to 500 (Figure 1a). The absolute molecular weight was
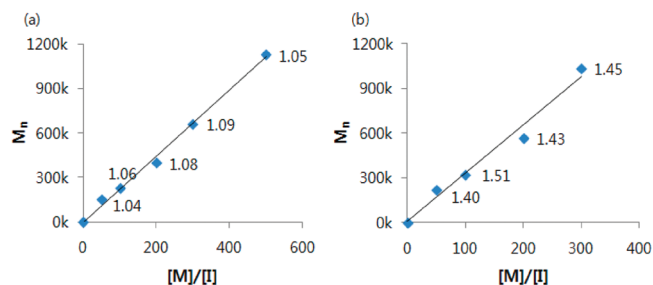

Figure 1. The plots for measured M_n vs [M]/[I] to show the controlled polymerization (a) for poly(**G4-R**) and (b) for poly(**G5-R**). The values on the graph are PDI.

determined by multiangle laser light scattering (MALLS) detector and the observed M_n in all cases matched relatively well with the theoretical values within experimental error. The M_n obtained from the MALLS technique was five times higher than that determined by the conventional method using polystyrene (PS) calibration. This implies that the hydrodynamic radius (R_h) of the G4 polymers was greatly underestimated with regard to that of PS standards.[1c,8d,10a] This experiment presents the first example of direct synthesis of G4 dendronized polymers by living polymerization.

Based on the results above, the ROMP of G5 macromonomers was attempted. Initially, the macromonomers with and without the ethylene linker were tested for ROMP. However, these attempts did not afford any desired polymers even at high temperature conditions. On the other hand, ROMP of the G5 macromonomer with the biphenyl linker, **G5-R**, resulted in the complete conversion of the monomer using second generation Grubbs catalyst or Hoveyda-Grubbs catalyst **II** at 50 °C (Table 2). Poly(**G5-R**) synthesized using the

Table 2. Synthesis of G5 Polymers[a]

[M]/[I]	M_n(MALLS)[b]	M_n (theo)[c]	PDI[b]
50	222k	228k	1.40
100	320k	457k	1.51
200	568k	914k	1.43
300	1036k	1371k	1.45

[a]The polymerization was performed by **II** in THF at 50 °C. [b]The molecular weight was determined by THF-SEC with MALLS-VIS-RI detector. [c]Theoretical molecular weight.

second generation Grubbs catalyst showed a relatively high PDI of 1.7, because of the low initiation rate constant (k_i), whereas the PDI decreased to 1.4 when a faster initiating **II** was used.[16] However, the ultrafast initiating catalyst **I**, which should have resulted in considerably narrower PDI, did not promote an efficient ROMP of **G5-R** because of lower stability of the catalyst. Although the PDI of poly(**G5-R**) was moderate only

because of the unsatisfactory k_i/k_p, the molecular weight was remarkably controlled in a linear fashion according to the [M]/[I] ratio (Figure 1b) because the bulky dendrons did not allow a chain transfer reaction. In short, ROMP of **G5-R** containing the novel biphenyl linker afforded the largest G5 dendronized polymer obtained by macromonomer approach thus far, with high molecular weight exceeding one million daltons. Again, the molecular weights of poly(**G5-R**) determined by the conventional method were ten times smaller than those obtained by the MALLS detector. This indicates that the R_h of poly(**G5-R**) was underestimated even more than the previous case of poly(**G4-R**).

Although many dendronized polymers have been prepared, the relationship between their chemical structure and polymer conformation is rarely investigated in systematic manner.[17] Hence, we conducted a detailed investigation of the conformational analysis of various dendronized polymers in THF solution at 35 °C by SEC equipped with MALLS-viscometry (VIS) detectors. From these analysis, shape parameters α and Flory exponent ν were calculated from the slopes of the Mark−Houwink−Sakurada plot (log IV vs log M_w) and the conformation plot (log R_g vs log M_w), respectively; these parameters indicate the conformation of the polymer chain in solution. The polymer with a large α and ν resembles more rod-like conformation (for a sphere, $\alpha = 0$, $\nu < 0.3$; for a random coil, $\alpha < 0.8$, $0.3 < \nu < 0.6$; for a rod-like structure, $0.8 < \alpha < 2.0$, $0.6 < \nu < 1.0$ and for a perfect rod $\alpha = 2.0$, $\nu = 1.0$).[18] The values measured for the polymers are summarized in Table 3; these values showed a definite dependence of the various

Table 3. Shape Parameter Data in Solution

polymer	poly(**G4-N**)	poly(**G4-F**)	poly(**G4-R**)	poly(**G5-R**)	poly(**G3-R**)
ν^a	0.78	0.76	0.77	0.87	0.60
α^b	1.08	0.85	1.04	1.20	0.78

^{a}Calculated from conformation plot determined by MALLS. ^{b}Calculated form Mark−Houwink plot obtained by VIS detector.

dendronized polymers on the type of the linkers and the size of the dendrons (see SI for the details). We examined the shape parameters for poly(**G4-N**)−(**G4-R**), all of which contained the same G4 dendron but different linker units. Among these three polymers, poly(**G4-N**), which did not contain a linker, showed the largest α and ν values because its dendrons were closest to the polymer backbone and this congestion caused maximum repulsion that stretched the polymer chains further apart. In contrast, poly(**G4-F**) containing the flexible ethylene linker showed the smallest α and ν values because the randomly rotating dendrons had higher degree of freedom, thus imposing less stress on the polymer conformation. On the other hand, poly(**G4-R**), which contained the rigid and linear biphenyl linker, showed α and ν values comparable to those of poly(**G4-N**) because the degree of freedom for the dendrons was limited by the rigid biphenyl linker. As a result, the polymer chain with the restricted motion could retain its rod-like conformation in solution.

Next, we studied how the generation size of the dendrons influenced the solution conformation of the dendronized polymers containing the same biphenyl linker. As anticipated, large α and ν values were obtained for higher generation dendronized polymers (Table 3, poly(**G3-R**)−(**G5-R**)). The increase in α ($0.78 < 1.04 < 1.20$) and ν ($0.60 < 0.77 < 0.87$)

from G3 to G5 dendronized polymers verifies that the stiffness of the polymer chain increases with the dendron generation, reaching its maximum value for the G5 polymer. Based on the solution conformation analysis, we successfully conducted systematic studies to investigate the influence of the dendron generation and the structure of linkers on the overall conformation of polymers in solution.

The conformational information can be visually interpreted using atomic force microscopy (AFM) technique because single polymer chains could be clearly observed for all the polymers deposited on a mica surface by spin coating process (Figure 2).
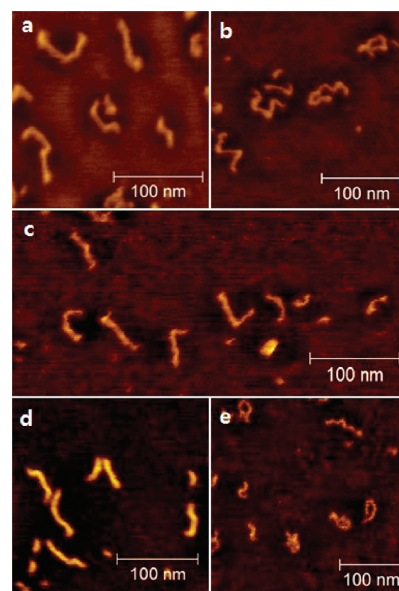

Figure 2. AFM images of dendronized polymers on mica surface: (a) poly(**G4-N**), (b) poly(**G4-F**), (c) poly(**G4-R**), (d) poly(**G5-R**), (e) poly(**G3-R**).

The G4 polymers witout a linker and with the biphenyl linker, that is, poly(**G4-N**) and poly(**G4-R**), respectively, showed a similar extended conformation (Figure 2a,c), while poly(**G4-F**), with the flexible ethylene linker, exhibited much more entangled conformation (Figure 2b). The largest G5 dendronized polymer, poly(**G5-R**), also showed the extended rod-like conformation, whereas poly(**G3-R**) having the smallest G3 dendron showed the most entangled conformation (Figure 2d,e). This was predicted from the lowest shape parameter values for poly(**G3-R**) ($\alpha = 0.78$ and $\nu = 0.60$). It is important to note that these images of rigid-rods are not caused by surface because the surface of mica does not show template effect, whereas graphite does.[13b,c] In short, our systematic analysis demonstrated that the rigidity of the polymers observed from AFM images correlated well with that suggested by the shape parameter values obtained by the light scattering and viscometry analysis in solution. From the conformation information for both the solution and solid states, we concluded that the structure of the linker had profound effect on the polymer conformation and introducing the biphenyl linker to the monomers was the excellent strategy to increase the ROMP activity by decreasing the steric hindrance without compromising the rigidity of the polymer chains.

In conclusion, we synthesized various dendronized polynorbornenes containing high generation dendrons up to G5 by living ROMP. By using the biphenyl linker, we were able to

polymerize G4 and G5 macromonomers under mild conditions to afford rod-like polymers with controlled molecular weight and narrow to moderate PDIs. The synthesis of the G4 and G5 dendronized polymers having high molecular weight exceeding one million daltons demonstrates the power of the highly active Grubbs catalysts when combined with monomers with a suitable design. We also investigated the effect of the structures of linkers and the generation of dendrons on the conformation of polymer chains which changed from random coil to rigid-rod structure. This systematic investigation led to the conclusion that the analysis for the dendronized polymers in solution state agreed well with the solid state imaging analysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, NMR data, mass data, elemental analysis for monomers, polymerization procedure, MALLS-VIS-RI analysis, and NMR data of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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