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Dossier

Special Issue in Tribute to Yves Chauvin
Numéro spécial en hommage à Yves Chauvin

Synthesis and Ring-Opening Metathesis Polymerization of Second-Generation Dendronized Poly(ether) Monomers Initiated by Ruthenium Carbenes

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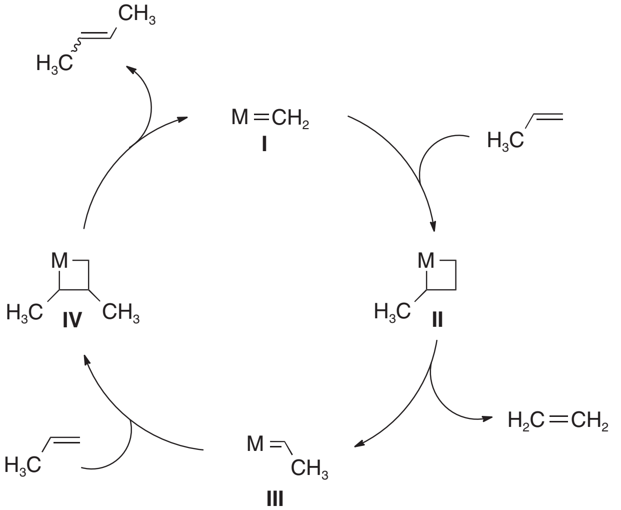
Abstract — *The Ring-Opening Metathesis Polymerization (ROMP) of second-generation dendronized monomers is described. Using the highly active and fast-initiating third-generation ruthenium complex* $[(H_2IMes)(pyr)_2Cl_2RuCHPh]$*, moderate to high molecular weight polymers (430-2230 kDa) are efficiently synthesized with low dispersities (Đ = 1.01-1.17). This study highlights the power of the metathesis approach toward polymer synthesis in a context where monomer structure can significantly impede polymerization.*

Résumé — La synthèse et la polymérisation par ouverture de cycle par métathèse des monomères poly(éther) de deuxième génération initié par le catalyseur de ruthénium de troisième génération — La polymérisation par ouverture de cycle par métathèse (ROMP, *Ring-Opening Metathesis Polymerization*) de monomers dendronisés de deuxième génération est décrite. En utilisant le complexe de ruthénium ayant une activité élevée et une initiation rapide de troisième génération $[(H_2IMes)(pyr)_2Cl_2RuCHPh]$, des polymères de masses moléculaires modérées à élevées (430 à 2230 kDa) sont synthétisés de manière efficace avec de basses polydispersités (Đ = 1,01 à 1,17). Cette étude met en évidence la puissance de l'approche de métathèse vers la synthèse de polymères dans un contexte où la structure de monomère peut empêcher de manière significative la polymérisation.

INTRODUCTION

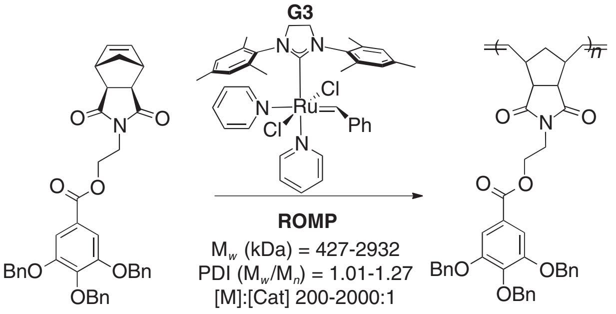
Since its discovery nearly six decades ago, olefin metathesis has evolved into a powerful method for the formation of C—C bonds, enabling the synthesis of simple to complex organic molecules [1]. Y. Chauvin proposed the commonly accepted mechanism for metathesis (Scheme 1), which illustrates the crucial involvement of a metal carbene and metallacyclobutane intermediate [2].

Ring-Opening Metathesis Polymerization (ROMP), an application of the metathesis reaction to polymer synthesis, has made a tremendous impact on synthetic polymer chemistry [3-8]. Well-defined and complex polymer architectures are readily synthesized through judicious identification of monomer and initiator. Norbornene and its functionalized derivatives have proven to be archetypical polymer precursors because of facile synthesis, affordability, and reactivity [9]. Moreover, the combination of inherent living characteristics



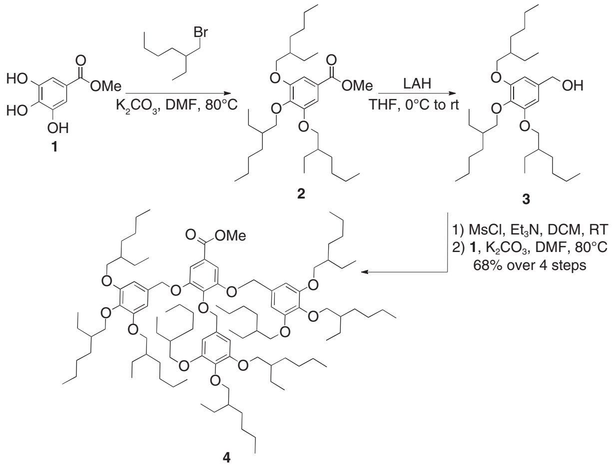
Scheme 1

The Chauvin mechanism of olefin metathesis.



Scheme 2

Polymerization of first-generation wedge-type monomers with **G3**.



Scheme 3

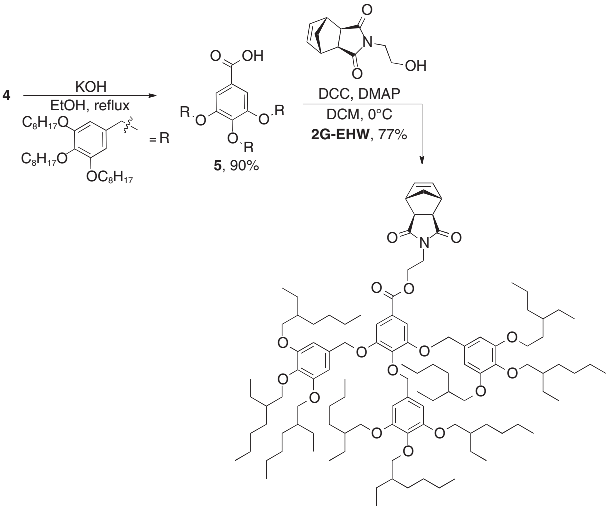
Synthesis of dendronized ester **4**.

and practicality associated with ROMP has made it a powerful tool among chemists and materials scientists [10].

Recently, our interest in ROMP has been directed towards the synthesis of molecular brush and dendronized block copolymers and their self-assembly to visible light reflecting one-Dimensional Photonic Crystals (1D PC) [11-19]. Photonic crystals are periodic nanostructured materials that possess a photonic band gap that inhibits select frequencies of light from propagating through the bulk material [15-19]. The access of periodicities large enough to interact with visible light is a challenge with block copolymers because of their inherent macromolecular chain-entanglement [20]. However, though the design and synthesis of polymer architectures that reduce chain-entanglement, we have demonstrated that such block copolymers can rapidly self-assemble to photonic crystals that reflect wavelengths of light across the visible spectrum and into the IR.

For instance, in the presence of the third-generation bis-pyridine initiator (**G3**), an efficient polymerization of discrete first-generation wedge-type monomers containing a functionalized *exo*-norbornene backbone tethered to a 1, 3, 4, 5-tetrasubstituted aromatic pendant/anchor group was achieved (Scheme 2) [21]. Ratios ([monomer]:[initiator]) ranging from 200-2000:1, provided a broad range of Molecular Weights (MW) (weight average MW (M_w) = 427 to 2932 kDa) along with low dispersities (*Đs*) (PDI = 1.01-1.27). The sequential copolymerization with an appropriate first-generation wedge-type monomer provided facile entry to block copolymers capable of self-assembling to 1D PC. However, at high MW (*e.g.* M_w = 1390-1940 kDa), self-assembly proved challenging, presumably due to chain entanglement. Thus, we hypothesized that an additional generation to the existing wedge-type system would increase polymer rigidity and decrease the propensity for chain entanglement.

Notably, previous studies have shown that if the linker length between the polymerizing *exo*-norbornene group and the pendant/anchor group is too short (<10 methylene units), similar second-generation dendronized monomers could not be efficiently polymerized to high MW polymers using similar carbene initiators [22]. In this manuscript, we challenge the ROMP method and showcase the ability of the highly active **G3** initiator to ring-open and polymerize sterically hindered dendronized MacroMonomers (MM) with short linker lengths to yield high MW homopolymers under ambient conditions. We envisioned that the incorporation of a highly reactive *exo*-norbornene carbodiimides polymerizable functionality (due to the excess ring strain) would



Scheme 4

Synthesis of dendronized monomer **2G-EHW**.

allow successful polymerization of second-generation wedge monomers with short linkers.

1 RESULTS AND DISCUSSION

Our approach to second-generation dendronized macromonomers was realized through the execution of standard organic transformations. Ester **4** was synthesized in a 4-step sequence starting from methyl gallate **1** (Scheme 3). A three-fold O-alkylation with 2-ethylhexyl bromide provided compound **2**, which was reduced to its corresponding benzyl alcohol (**3**) with Lithium Aluminum Hydride (LAH). The treatment of **3** with mesyl chloride followed by nucleophilic displacement of the corresponding mesylate with **1** yielded the desired ester in 68% yield over four steps.

The exposure of **4** to alkaline conditions in boiling alcoholic solvent led to the formation of the corresponding carboxylic acid **5** which was isolated in 90% yield (Scheme 4). N, N'-dicyclohexylcarbodiimide (DCC) coupling with *N*-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2, 3, dicarboximide furnished the desired second-generation ethylhexyl wedge dendronized macromonomer (**2G-EHW**) in 77% yield.

The ROMP of **2G-EHW** led to the controlled synthesis of second-generation wedge-type polymers capable of being carried out over a broad range of [**2G-EHW**]:[**G3**] ratios. High conversions and remarkably low *Đ*s (entries 1-3) were achieved despite a short linker length (2 methylene units) and an extensive alkylether periphery (Tab. 1, Fig. 1).

TABLE 1

Results of the ROMP of **2G-EHW** mediated by **G3**[a]

Entry	[MM]/[G3]	Conv[b]	M_w (kDa)[c]	$Đ$ (M_w/M_n)[c]
1	200	100	4.29	1.01
2	400	99	1055	1.03
3	600	90	2086	1.17
4	800	65	2230	1.42
5	1000	0	-	-

[a] Polymerizations performed in 1 mL of THF over 2 hours at ambient temperature. [**2G-EHW**] = 90 mM.
[b] Determined by ^1H NMR.
[c] Determined by light scattering.

However, the reaction efficiency decreases or fails to polymerize at ratios greater than 800:1 [**2G-EHW**]:[**G3**] (Fig. 2) [23]. Nonetheless, the controlled synthesis of polymers with MW nearing 2100 kDa were efficiently achieved.

Detailed kinetic studies established a complete kinetic profile for monomer **2G-EHW**. A linear increase in MW with an increase in monomer conversion (Fig. 1a) and nearly constant *Đ* was observed during the course of polymerization; consistent with living polymerization characteristics (Fig. 3). Accordingly, for all the [**2G-EHW**]:[**G3**] ratios investigated a first-order dependence on [**2G-EHW**] was observed (Fig. 1b).

2 EXPERIMENTAL

2.1 General Considerations

$(H_2IMes)(PPh_3)_2(Cl)_2RuCHPh$ was received as a research gift from *Materia Inc.* and converted to **G3** via literature procedures [24]. All other chemicals were purchased from *Sigma Aldrich*. Solvents were purified by passage through solvent purification columns and further degassed with argon [25]. N-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3 dicarboximide was prepared according to literature procedure [26]. All reactions were carried out in flame-dried Schlenk-type glassware on a dual-manifold Schlenk line or in a nitrogen-filled glovebox. NMR spectra were recorded on a Varian *Inova* 500 MHz spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane. High resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility. Compound **2G-EHW** was analyzed by MALDI-TOF in reflector mode using a Voyager DE PRO time-of-flight mass spectrometer (*Applied Biosystems*). The MALDI matrix used was

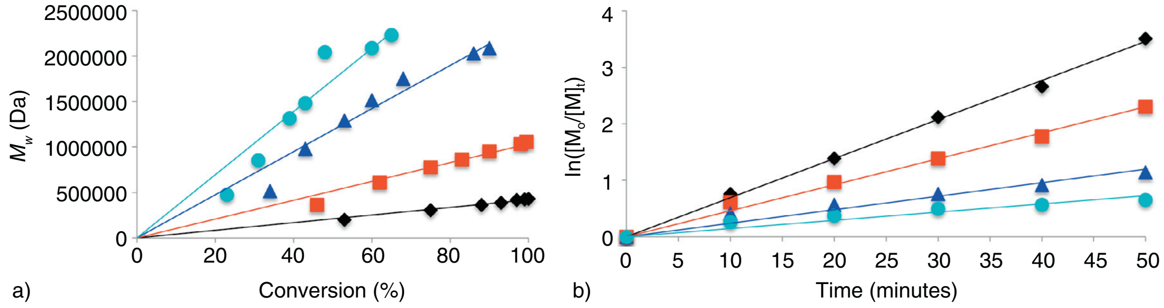


Figure 1

a) Plot of M_w as a function of **2G-EHW** conversion ([**2G-EHW**]:[**G3**] = 200 (◆), 400 (🟥), 600 (▲), 1000 (●). b) Semilogarithmic plots of ln([**2G-EHW**$_o$]/[**2G-EHW**$_t$]) as a function of time for the ROMP of **2G-EHW** by **G3**. Conditions: [**2G-EHW**] = 90 mM; [**G3**] = 450 µM (◆), 220 µM (🟥), 150 µM (▲), 110 µM (●). Polymerizations were performed in anhydrous/degassed THF at ambient temperature.

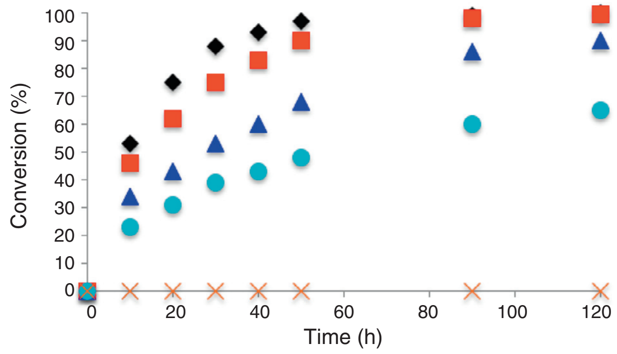


Figure 2

Kinetic data comparing the polymerization of **2G-EHW**. [**2G-EHW**]:[**G3**] ratio 200:1 (◆), 400:1 (🟥), 600:1 (▲), 800:1 (●), 1000:1 (×).

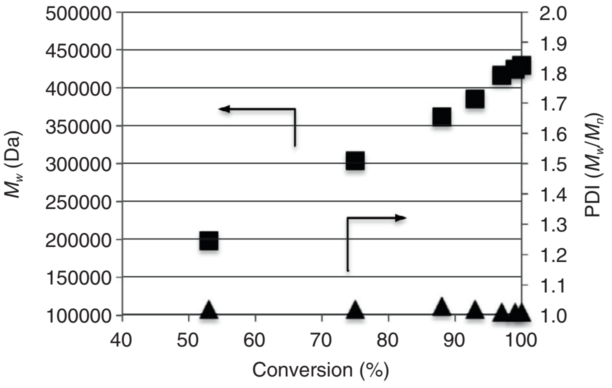


Figure 3

Plot of M_w (left) and $Đ$ (right) as a function of **2G-EHW** conversion ([**2G-EHW**]:[**G3**] = 200:1).

dithranol prepared at 10 mg/mL in THF. The instrument was externally calibrated with the manufacturer Sequazyme^{TM} Kit. Polymer MW were determined utilizing THF as the eluent by MultiAngle Light-Scattering (MALS) Gel Permeation Chromatography (GPC) using a miniDAWN TREOS light-scattering detector, a Viscostar viscometer, and an OptilabRex refractive index detector, all from *Wyatt Technology*. An *Agilent* 1200 UV−Vis detector was also present in the detector stack. Absolute MW were determined using *dn*/*dc* values calculated by assuming 100% mass recovery of the polymer sample injected into the GPC.

2.2 Procedures

To a flame dried 500 mL round-bottom flask equipped with a magnetic stir bar was added K_2CO_3 (55.0 g, 398 mmol, 8.00 eq), anhydrous DMF (260 mL), methyl gallate (9.15 g, 49.7 mmol, 1.00 eq) and 2-ethylhexyl bromide (53.0 mL, 298 mmol, 6.00 eq). The reaction was fitted with a water-cooled condenser, placed under an inert atmosphere of argon and heated to 80°C for 14 h. The reaction was stopped by the addition of H_2O (500 mL). The mixture was transferred to a separation funnel and the aqueous layer was washed with Et_2O (3 × 300 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, vacuum filtered and concentrated under reduced pressure. The material was used crude and subjected to reduction conditions.

To a 500 mL round-bottom flask containing crude ester **2** (49.7 mmol, 1.00 eq) was added anhydrous THF (155 mL). The solution was cooled to 0°C. Once cool, LAH (3.77 g, 99.4 mmol, 2.00 eq) was carefully added. The reaction placed under an inert atmosphere of argon and allowed to stir and gradually warm to room temperature overnight. The reaction was cooled to 0°C. Once cool, the reaction was

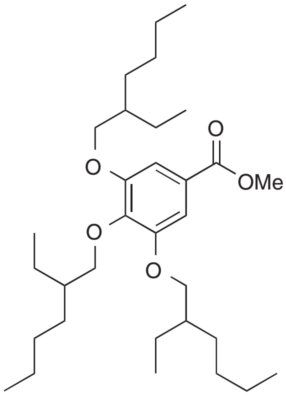


Figure 4

Methyl 3,4,5-tris((2-ethylhexyl)oxy)benzoate (2).

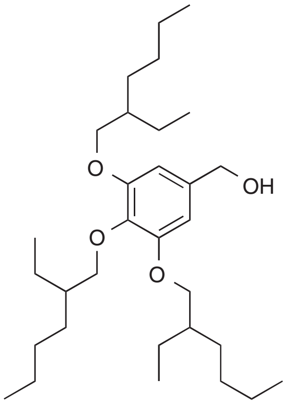


Figure 5

(3,4,5-tris((2-ethylhexyl)oxy)phenyl)methanol (3).

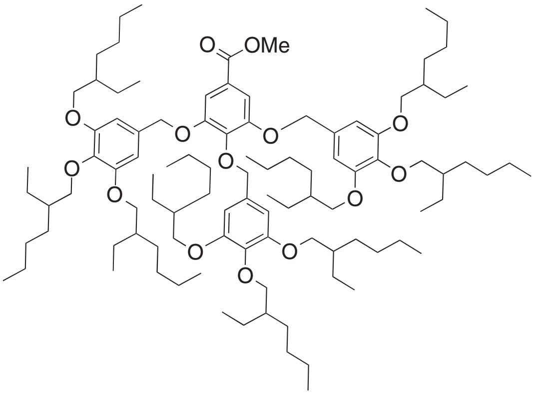


Figure 6

Methyl 3,4,5-tris((3,4,5-tris((2-ethylhexyl)oxy)benzyl)oxy) benzoate (4).

stopped by the addition of H_2O (20 mL) and diluted with Et_2O. A saturated aqueous solution of Rochelle's salt was added and the mixture was aggressively stirred for one hour. The two layers were separated and the aqueous layer was washed with Et_2O (3 × 300 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, vacuum filtered and concentrated under reduced pressure. The material was used crude for the next step.

To a 500 mL round-bottom flask containing crude alcohol **3** (49.7 mmol, 1.00 eq) was added anhydrous DCM (165 mL). The solution was cooled to 0°C. Once cool, distilled Et_3N (10.3 mL, 74.6 mmol, 1.50 eq) was added. MsCl (4.61 g, 59.6 mmol, 1.20 eq) was carefully added dropwise over two minutes. The reaction was placed under an inert atmosphere of argon and allowed to stir and gradually warm to room temperature overnight. The reaction was stopped by the addition of H_2O (150 mL). The two layers were separated and the aqueous layer was washed with Et_2O (3 × 200 mL). The organic layers were combined, washed with a saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, vacuum filtered and concentrated under reduced pressure. To a separate 1 L round bottom flask was added methyl gallate (2.41 g, 13.1 mmol, 1.00 eq), K_2CO_3 (14.3 g, 104 mmol, 8.00 eq) and anhydrous DMF (300 mL). The crude mesylate (49.7 mmol, 1.00 eq) was dissolved in DMF (50 mL) and added to the reaction flask by cannula transfer. The reaction flask was equipped with a reflux condenser and heated to 80°C for 12 h then cooled to room temperature and stirred for an additional 12 h. The reaction was stopped by the addition of H_2O (300 mL) and EtOAc (300 mL). The mixture was transferred to a separation funnel and the aqueous layer was washed with Et_2O (3 × 400 mL). The organic layers were combined, washed copious amounts of H_2O, brine, dried over $MgSO_4$, vacuum filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography (95:5 pentane:Et_2O then 80:20 pentane:Et_2O) on silica gel to provide the desired product as a light yellow oil (14.37 g, 68% yield over 4 steps) $R_f = 0.57$ (80:20 hexanes/Et_2O). ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.36 (s, 2H), 6.67 (s, 2H), 6.65 (s, 4H), 5.14 (s, 2H), 5.07 (s, 4H), 3.86 (s, 3H), 3.84-3.76 (m, 14H), 3.72-3.66 (m, 4H), 1.75-1.25 (m, 81H), 0.96-0.85 (m, 54H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 153.5, 152.4, 142.5, 137.6, 137.5, 132.3, 131.7, 125, 109.7, 105.6, 104.8, 75.8, 75.7, 75.3, 71.6, 71.1, 70.9, 52.1, 40.6, 39.4, 30.4, 29.3, 29, 23.8, 23.7, 23.1, 23, 14.2, 14.1, 11.2, 11.1; IR (neat): 2958, 2928, 2873, 2859, 1721, 1591; HRMS-(FAB+)-m/z 1607.262 $[(M+H)^+$ requires 1607.259].

To a round-bottom flask containing **4** (9.90 g, 6.15 mmol, 1.00 eq) was added EtOH (30 mL) and KOH (3.45 g,

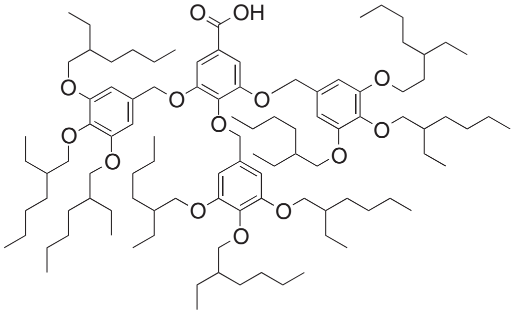


Figure 7

3-((3-((3-ethylheptyl)oxy)-4,5-bis((2-ethylhexyl)oxy)benzyl)oxy)-4,5-bis((3,4,5-tris((2-ethylhexyl)oxy)benzyl)oxy)benzoic acid (5).

61.5 mmol, 10.0 eq). The flask was equipped with a water-cooled reflux condenser and heated to 80°C for 5 h. The reaction was allowed to cool to room temperature and stirred for an additional 12 h then cooled to 0°C. Once cool, conc. HCl was added until a neutral pH was achieved. The mixture was concentrated under reduced pressure then diluted with EtOAc and brine. The solution was transferred to a separation funnel and the two layers were separated. The aqueous layer was washed with EtOAc (3 × 150 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, vacuum filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography (90:10 pentane:EtOAc) on silica gel to provide the desired product as a light yellow oil (8.78 g, 90% yield) R_f = 0.15 (80:20 pentane/EtOAc). ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.43 (s, 2H), 6.66 (s, 2H), 6.65 (s, 4H), 5.15 (s, 2H), 5.07 (s, 4H), 3.85-3.74 (m, 14H), 3.69-3.65 (m, 4H), 1.73-1.26 (m, 81H), 0.94-0.84 (m, 54H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 153.7, 152.7, 143.5, 137.7, 132.4, 131.6, 124.1, 110.4, 105.7, 105.1, 75.98, 75.94, 75.5, 71.9, 71.3, 71.1, 40.8, 39.7, 30.7, 30.6, 29.5, 29.3, 29.2, 23.9, 23.8, 23.3, 23.2, 14.3, 14.2, 11.4, 11.3; IR (neat): 2958, 2928, 2873, 1686, 1591; HRMS-[(FAB+) m/z 1594.247 requires 1594.251)].

To a round-bottom flask containing **5** (8.78 g, 5.50 mmol, 1.00 eq) was added anhydrous DCM (150 mL) and cooled to 0°C. Once cool, N-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3 dicarboximide (1.60 g, 6.06 mmol, 1.10 eq), DMAP (335 mg, 2.75 mmol, 0.500 eq) and N, N'-dicyclohexylcarbodiimide (1.25 g, 6.06 mmol, 1.10 eq) were added. The reaction was allowed to stir and gradually warm to room temperature for 12 h. The reaction was stopped by concentration under reduced pressure. The crude material was purified by flash chromatography (85:15 hexanes:EtOAc) on silica gel to provide the desired product as a light yellow oil (7.80 g, 77% yield) R_f = 0.37 (80:20 hexanes/EtOAc). ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.33 (s, 2H), 6.67 (s, 6H), 6.24 (t, J = 2 Hz, 2H), 5.11 (s, 2H), 5.09 (s, 4H), 4.37 (t, J = 4.5 Hz, 2H), 3.89 (t, J = 5 Hz, 2H), 3.82-3.74 (m, 14H), 3.67 (dd, J = 2.5, 5.0 Hz, 4H), 3.20 (t, J = 1.5 Hz, 2H), 2.67 (d, J = 1 Hz. 2H), 1.71-1.20 (m, 81H), 0.94-0.83 (m, 56H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 165.7, 153.4, 152.6, 142.8, 137.8, 137.6, 132.5, 131.8, 124.6, 109.6, 105.5, 105, 76, 75.9, 75.5, 71.5, 71.2, 71.1, 61.9, 47.9, 45.4, 42.7, 40.7, 39.7, 37.5, 30.7, 30.6, 29.5, 29.2, 23.9, 23.8, 23.3, 23.2, 14.3, 14.2, 11.3, 11.2; HRMS: the detected mass corresponds to a radical cation with m/z 1804.3023 corresponding to $[M+Na-H]^+$ requires 1804.3043.

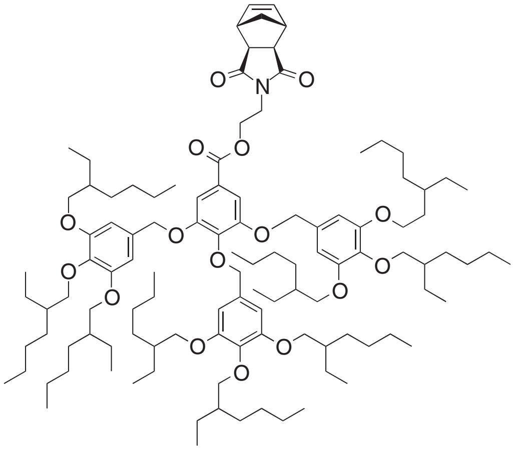


Figure 8

2-((3aR,4R,7S,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)ethyl 3-((3-((3-ethylheptyl)oxy)-4,5-bis((2-ethylhexyl)oxy)benzyl)oxy)-4,5-bis((3,4,5-tris((2-ethylhexyl)oxy)benzyl)oxy)benzoate (2G-EHW).

2.3 Synthesis of Second Generation Dendronized Homopolymer

To a 4 dram vial was added **2G-EHW** (160 mg, 0.0900 mmol, 200 eq). To the vial was added a magnetic stir bar and taken into a nitrogen filled glovebox. To the vial was added THF (1 mL). With rapid stirring, 49 μL of an appropriate concentration of **G3** in THF was quickly added *via* syringe. For kinetic analysis, a 0.05 mL aliquot of the reaction solution was taken at predetermined time intervals and injected into a 1 mL septum sealed vial containing a solution of 25 μL of ethyl vinyl ether in 0.7 mL of THF. The aliquot was analyzed by GPC to determine the MW of the polymer. After the solvent was allowed to evaporate from the vials, the polymer residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy to determine the percent of monomer conversion by comparing the peaks corresponding to the wedge polymer and the unreacted monomer. The polymerization was stopped by the addition of ethyl vinyl ether (0.2 mL) and addition of methanol (25 mL). The mixture was allowed to stir for 1 h. The polymer was isolated by vacuum filtration and dried under vacuum at ambient temperature to a constant weight.

2G-EHW Homopolymer: ^{1}H NMR (500 MHz, CDCl$_3$, 25°C): δ 7.37-7.33 (m), 6.67-6.61 (m), 5.11-5.04 (m), 3.79-3.73 (m), 3.61 (bs), 1.70-1.56 (m), 1.49-1.24 (m), 0.94-0.80 (m). *dn*/*dc* value = 0.1082.

CONCLUSION

The synthesis of wedge-type dendronized polymers was achieved *via* the ruthenium-mediated ROMP of second-generation functionalized *exo*-norborene poly(ether) monomers. These substantially hindered monomers were efficiently polymerized using the highly active **G3** ruthenium carbene initiator. Well-defined (*Đ* = 1.01-1.17) high molecular weight (2100 kDa) polymers are accessible. Furthermore, we have demonstrated that a relatively short two carbon linker length is well tolerated in the ring-opening event. This investigation has provided the foundation necessary to explore the synthesis of rigid block copolymer systems with potential for infrared reflecting photonic properties and will be disseminated in due course.

ACKNOWLEDGMENTS

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