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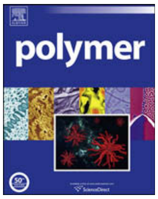

Synthesis, characterization and modification of azide-containing dendronized diblock copolymers

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ABSTRACT

A series of dendronized diblock copolymers having rigid backbone and reactive surface were synthesized by ring-opening metathesis polymerization (ROMP) from dendronized norbornene derivatives using the second generation Grubb's catalyst. The bromine-terminated block of those rigid nanostructures has been converted to more reactive azide groups in one straightforward step. The resulting polymers were then functionalized by post-polymerization reaction with fullerene C_{60} (electron acceptor) using thermal $[3+2]$ cycloaddition reaction or with porphyrin (electron donor) using copper-catalyzed "click chemistry", the ultimate goal being the preparation of efficient polymeric materials for photovoltaic applications. While fullerene addition was not complete (approximately 50%) because of cross-linking reactions and steric hindrance on the dendrimers surface, Zn-porphyrin introduction went to completion clearly demonstrating the usefulness of click chemistry for polymer functionalization.

1. Introduction

The recent efforts devoted to the development of efficient and straightforward methods to prepare dendronized polymers have led to the preparation of number of interesting polymer architectures with unique properties [1,2]. Compared to traditional linear or branched polymers, dendronized polymer chains adopt a more rigid conformation because of the greater steric hindrance [3]. This feature makes dendronized polymers very promising for the development of nano-architectures for different applications such as DNA complexation [4], optoelectronic properties [5], drug delivery systems [6] and catalyst support [7].

An interesting strategy to prepare functional dendronized polymers is to modify the polymers' surface via reactive groups (post-polymerization reaction). This strategy allows the preparation of several functional polymers from a single reactive pre-polymer, thus decreasing the overall number of synthetic steps. However, only few examples of post-polymerization reactions on dendronized polymers were reported in the recent literature. Among them, alkyne [8], ammonium [9], allyl [10] and alcohol [11] reactive groups were used to modify the dendrimers' surface in covalent or ionic fashion. The substitution rates are generally excellent even when introduction of very bulky substituents is performed [12].

One of the most efficient reactive groups to modify polymers' side chain is azide. It is very versatile since it can be involved in several types of coupling reactions, the most popular being the copper-catalyzed 1,3-dipolar cycloaddition with alkyne derivatives, often called "click chemistry" to form triazole derivatives [13–16]. Moreover, azide derivatives can react with different dienes to form triazoline and aziridine [17]. In materials science, cycloaddition reactions involving azide have been largely used to attach fullerenes on polymer scaffolds since it is one of the few reactions that keep the fullerene's π-electron system intact [18–21]. Thus, we hypothesized that dendronized diblock copolymers having azide groups in the surface could be a good template for the construction of many functional, rigid polymers for different applications. Herein we report the synthesis, characterization and modification of dendronized diblock copolymers having azide groups on surface. Because our ultimate goal is to develop a new series of electro- and photoactive polymers for energy conversion purposes, the polymers were functionalized with (1) fullerene (electron acceptor) using a thermal $[3+2]$ cycloaddition reaction and (2) porphyrin (electron donor and light harvesting unit) using click chemistry. Studies are underway to evaluate the performances of these two polymers as active layers in polymer photovoltaic cells. The diblock approach was used rather than the homopolymer one since it allows the tuning of the polymer properties (solubility, molecular

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weight, crystallinity, T_g, film forming ability, etc.). For the purpose of the present study, we used two different blocks; one having alkyl chains to enhance the polymer solubility, which is particularly useful in the case of C_{60}-based polymers, and another having azide groups allowing the introduction of the functional groups.

2. Experimental

2.1. Materials and characterization techniques

All solvents were dried and distilled under nitrogen over calcium hydride. All other reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out using silica gel (40–63 μm purchased from Silicycle). Thin layer chromatography (TLC) was carried out on a glass plate coated with silica gel F-254 purchased from Silicycle. Compound **2** was prepared using literature procedure [22].

^{1}H and ^{13}C NMR spectra were recorded on a Varian AS400 apparatus in $CDCl_3$ solution at 298 K (unless otherwise stated). Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane. IR spectra were obtained on a Bomem model MB-100 FTIR. High-resolution mass spectroscopy (HRMS) was performed on an Agilent model 62-10 MS-TOF. The size-exclusion chromatography (SEC) measurements were performed on a Waters 515 system using a series of two columns (Waters styragel linear/ Shodex KF804) with UV detector using polystyrene standards with THF as eluent. UV–vis absorption spectra were obtained on a Varian diode-array spectrophotometer (model Cary 500) using 1-cm path length quartz cells. Thermal gravimetric analysis (TGA) measurements were performed under nitrogen atmosphere at heating rate of 10 °C/min using TGA/SDTA851e Mettler system.

2.2. Monomer synthesis

*2.2.1. 5-Norbornene-2-methyl 3,4,5-triacetoxybenzoate (**3**)*

A round-bottomed flask equipped with a magnetic stir bar was charged with triacetylgallic acid (**2**) [22] (7.61 g, 25.7 mmol), thionyl chloride (5 mL) and benzene (50 mL). The mixture was heated to reflux under nitrogen for 1.5 h. The solvent was removed under reduced pressure and the crude product (acyl chloride) was dissolved in CH_2Cl_2 (90 mL) with 5-norbornene-2-methanol (2.2 mL, 18.2 mmol, mixture of *endo* and *exo* isomers) and Et_3N (2.5 mL). The mixture was stirred at room temperature overnight. The solution was poured in water and extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (silica gel, eluent 3:1 hexanes:ethyl acetate) to provide 3.05 g of the title product (**3**) as a colorless oil (30%). IR (NaCl): ν (cm^{-1}): 3061, 2970, 1785, 1721, 1162. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.78 (d, 2H, $J = 4.1$ Hz); 6.16–5.95 (m, 2H); 2.92–2.75 (m, 2H); 2.49–2.43 (m, 1H); 2.27 (s, 9H); 1.90–1.81 (m, 1H); 1.46–1.18 (m, 4H); 0.62–0.58 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 169.02, 167.97, 166.75, 164.69, 164.59, 143.63, 143.61, 139.50, 138.82, 138.76, 138.01, 137.94, 137.24, 136.45, 136.42, 132.41, 132.37, 128.98, 128.90, 122.46, 122.43, 122.18, 122.15, 69.92, 69.53, 69.24, 68.85, 49.65, 45.20, 44.16, 43.90, 43.88, 42.45, 41.85, 38.24, 38.03, 29.84, 29.17, 20.95, 20.83, 20.42. HRMS: Calculated for $C_{21}H_{22}O_8$: 420.1653 $[M + NH_4]^+$. Found: 420.1652.

*2.2.2. 5-Norbornene-2-methyl 3,4,5-trihydroxybenzoate (**4**)*

A round-bottomed flask equipped with a magnetic stir bar was charged with **3** (2.49 g, 6.19 mmol), methanol (30 mL) and water (10 mL). The mixture was stirred for 10 min at 0 °C and K_2CO_3 (2.20 g, 15.9 mmol) was added. The solution was stirred at 0 °C for 30 min and then acidified with HCl until it reached pH 2. The mixture was poured in water and extracted twice with ethyl acetate. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to provide 1.68 g of the title product (**4**) as a yellow oil (98%) that was used for the next step without further purification. IR (NaCl): ν (cm^{-1}): 3363, 3060, 2967, 2869, 1687, 1330, 1239. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.18 (d, 2H, $J = 3.0$ Hz); 6.15–5.92 (m, 2H); 3.74–3.24 (m, 1H); 2.91–2.73 (m, 2H); 2.37–2.25 (m, 1H); 1.83–1.76 (m, 1H); 1.43–1.20 (m, 4H); 0.52–0.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 144.06, 137.91, 137.78, 137.20, 137.05, 136.64, 136.46, 132.39, 132.31, 110.14, 67.86, 66.86, 49.77, 49.62, 45.22, 45.19, 42.44, 42.42, 41.77, 41.74, 29.14, 28.99. HRMS: Calculated for $C_{15}H_{16}O_5$: 277.1071 $[M + H]^+$. Found: 277.1071.

*2.2.3. 5-Norbornene-2-methyl 3,4,5-tri(10-bromodecyloxy)-benzoate (**5**)*

A round-bottomed flask equipped with a magnetic stir bar was charged with **4** (1.28 g, 4.63 mmol), dibromodecane (11.2 g, 37.7 mmol), 18-crown-6 (0.123 g, 0.460 mmol), K_2CO_3 (6.40 g, 46.31 mmol) and acetone (25 mL). The mixture was heated to reflux for 48 h. The solvent was removed under reduced pressure and the crude material was poured in water and extracted twice with CH_2Cl_2. The combined organic layers were washed with brine followed by water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting yellow oil was purified by column chromatography (silica gel, hexanes followed by hexanes/ethyl acetate 20:1) to provide 2.92 g of the title product (**5**) as a colorless oil (67%, mixture of *endo* and *exo* isomers). IR (NaCl): ν (cm^{-1}): 3059, 2928, 2855, 1744, 1715, 1430, 1333, 1215. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.25 (d, 2H, $J = 3.2$ Hz); 6.17–5.99 (m, 2H); 4.36–3.87 (m, 8H); 3.39 (t, 6H, $J = 6.8$ Hz); 2.94–2.51 (m, 2H); 1.88–1.63 (m, 12H); 1.50–1.28 (m, 40H); 0.65–0.62 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 166.65, 166.55, 155.64, 153.01, 152.99, 142.58, 142.52, 137.90, 137.85, 137.22, 136.47, 132.47, 125.27, 108.30, 108.25, 73.65, 69.37, 69.35, 69.21, 68.53, 68.20, 49.66, 49.63, 45.29, 44.25, 43.98, 42.46, 41.87, 38.40, 38.17, 34.22, 33.08, 33.06, 33.04, 30.54, 29.85, 29.82, 29.73, 29.71, 29.63, 29.58, 29.57, 29.53, 29.39, 29.21, 29.06, 29.01, 28.95, 28.90, 28.43, 28.41, 28.37, 26.29, 26.27, 25.92. HRMS: Calculated for $C_{45}H_{73}Br_3O_5$: 931.3081 $[M + H]^+$. Found: 931.3074.

*2.2.4. Methyl 3,4,5-trihexyloxybenzoate (**7**)*

A round-bottomed flask equipped with a magnetic stir bar was charged with **6** (4.00 g, 21.72 mmol), bromohexane (18.3 mL, 0.130 mol), 18-crown-6 (0.574 g, 2.17 mmol), K_2CO_3 (30.0 g, 0.217 mol) and acetone (25 mL). The mixture was heated to reflux overnight and the solvent was removed under reduced pressure. Water was added to the crude material and the resulting mixture was extracted twice with CH_2Cl_2. The combined organic layers were washed with NaOH 10% (aq.) followed by water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was purified by column chromatography (silica gel, hexanes/ethyl acetate 20:1) to provide 8.65 g of the title product (**7**) as a colorless oil (91%). IR (NaCl): ν (cm^{-1}): 2954, 2932, 2871, 2860, 1722, 1433, 1336, 1218, 1112, 766. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.25 (s, 2H); 4.04–4.00 (m, 6H); 3.88 (s, 3H); 1.83–1.72(m, 6H); 1.50–1.46 (m, 6H); 1.34–1.32 (m, 12H); 0.90 (t, 9H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 167.17, 153.05, 142.55, 124.89, 108.16, 73.70, 69.36, 52.32, 31.78, 29.49, 25.98, 22.91, 14.31. HRMS: Calculated for $C_{26}H_{44}O_5$: 437.3262 $[M + H]^+$. Found: 437.3261.

*2.2.5. 3,4,5-Trihexyloxybenzoic acid (**8**)*

A round-bottomed flask equipped with a magnetic stir bar was charged with **7** (8.63 g, 19.8 mmol), methanol (100 mL) and water

(100 mL). KOH (11.10 g, 0.20 mol) was added and the mixture was heated to reflux overnight. The mixture was slightly acidified to pH 6 with HCl 3 N. The solvent was removed under reduced pressure and the mixture was poured in water and extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give 8.35 g of the title product (**8**) as a white solid in a quantitative yield. M.p. = 41–43 °C. IR (NaCl): ν (cm^{-1}): 3075, 2953, 2931, 2869, 2859, 1687, 1587, 1433, 1226, 1128, 1114. ^1H NMR (400 MHz, $CDCl_3$, ppm): 11.87 (s, 1H); 7.34 (s, 2H); 4.07–4.01 (m, 6H); 1.86–1.72 (m, 6H); 1.51–1.46 (m, 6H); 1.36–1.33 (m, 12H); 0.93–0.90 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 172.48, 153.08, 143.36, 123.98, 108.75, 73.78, 69.39, 31.80, 29.47, 25.99, 22.86, 14.26. HRMS: Calculated for $C_{25}H_{42}O_5$: 423.3105 $[M+H]^+$. Found: 423.3111.

2.2.6. *5-Norbornene-2-methyl 3,4,5-trihexyloxybenzoate (**9**)*

A round-bottomed flask equipped with a magnetic stir bar was charged with **8** (4.20 g, 9.94 mmol), 5-norbornene-2-methanol (3.0 mL, 24.8 mmol, mixture of *endo* and *exo*), *N,N*-dicyclohexylcarbodiimide (2.25 g, 10.9 mmol), 4-(dimethylamino)pyridine (0.60 g, 4.91 mmol) and CH_2Cl_2 (35 mL). The mixture was stirred for 16 h at room temperature. The solution was poured in water and extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (silica gel, hexanes/ethyl acetate 10:1) to provide 3.57 g of a mixture of *endo* and *exo* product (**9**) as a colorless oil (68%). IR (NaCl): ν (cm^{-1}): 2955, 2933, 2871, 2861, 1716, 1430, 1334, 1214, 1111. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.27 (d, 2H, $J = 3.1$ Hz); 6.21–6.00 (m, 2H); 4.39–4.18 (m, 1H); 4.03 (t, 6H, $J = 6.4$ Hz); 3.91–3.86 (m, 1H); 2.96–2.79 (m, 2H); 2.57–2.50 (m, 1H); 1.91–1.27 (m, 27H); 0.93–0.89 (t, 9H, $J = 6.6$ Hz); 0.68–0.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 166.72, 166.61, 153.05, 153.04, 137.85, 132.48, 125.34, 125.26, 108.33, 108.28, 73.73, 69.43, 69.41, 68.54, 49.65, 44.26, 43.98, 42.47, 41.87, 38.40, 38.18, 31.97, 31.81, 29.51, 29.21, 26.00, 25.94, 22.92, 22.86, 14.32, 14.26. HRMS: Calculated for $C_{33}H_{52}O_5$: 529.3888 $[M+H]^+$. Found: 529.3895.

2.3. *Polymer synthesis*

2.3.1. *General ROMP procedure for the preparation of diblock copolymers*

All the polymerizations were performed under nitrogen atmosphere. The monomer **5** and CH_2Cl_2 (0.017 M) were placed together in a round-bottomed flask with a magnetic stir bar. The ruthenium carbene **10** (1.0 mol%) and CH_2Cl_2 (8.0×10^{-4} M) were placed together in a 5 mL round-bottomed flask equipped with a magnetic stir bar. These flasks were evacuated and back-filled with N_2 three times, which is enough to ensure that most of the residual oxygen was removed from the flasks. The catalyst solution was then introduced via syringe with the monomer **5** and the solution was stirred for 3 h at room temperature. A CH_2Cl_2 (0.1 M) solution of monomer **9** was then introduced via syringe. The solution was stirred for 16 h at room temperature. The mixture was then diluted with CH_2Cl_2 and ethyl vinyl ether (ca. 1 mL) was added and the mixture was stirred for 15 min. The polymer was precipitated twice in methanol and dried under vacuum to provide **P1Br** and **P2Br** as soft rubbery white solids. IR (NaCl): ν (cm^{-1}): 2953, 2931, 2870, 2859, 1716, 1430, 1332, 1214, 1112. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.22 (br); 5.32 (br); 4.20 (br); 3.98 (br); 3.39 (br); 2.50 (br); 1.77 (br); 1.41 (br); 0.89 (br).

2.3.2. *Polymer **P1Br***

Following the general procedure described above, **P1Br** was prepared using the following quantity: monomer **5** (50.0 mg, 53.6 μmol) and monomer **9** (538 mg, 1.02 mmol). Yield: 0.41 g (70%).

2.3.3. *Polymer **P2Br***

Following the general procedure described above, **P2Br** was prepared using the following quantity: monomer **5** (80 mg, 85.7 μmol) and monomer **9** (408 mg, 0.77 mmol). Yield: 0.30 g (62%).

2.3.4. *Polymer **P1N₃***

A round-bottomed flask equipped with a magnetic stir bar was charged with **P1Br** (0.379 g, 0.70 mmol), sodium azide (15.0 mg, 0.23 mmol), sodium iodide (0.2 mg, 1.3 μmol), DMF (10 mL) and THF (1 mL). The solution was stirred at 80 °C for 22 h. The solvent was removed under reduced pressure and the resulting product was washed four times with water and then twice with acetone. The polymer was dried under vacuum to provide 0.376 g (98%) of the desired product as a soft rubbery white solid. IR (NaCl): ν (cm^{-1}): 2930, 2859, 2095, 1715, 1429, 1213, 1111. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.22 (br); 5.33 (br); 4.20 (br); 3.98 (br); 3.24 (br); 2.49 (br); 1.75 (br); 1.46 (br); 1.31 (br); 0.88 (br).

2.3.5. *Polymer **P2N₃***

The polymer was prepared using the same procedure described above for the preparation of **P1N₃**. **P2Br** (0.245 g, 0.44 mmol), sodium azide (20.0 mg, 0.31 mmol) and sodium iodide (0.2 mg, 1.30 μmol) were used to provide 0.241 g (99%) of the desired product as a soft rubbery white solid.

2.3.6. *Polymer **P1C₆₀***

The thermal [3 + 2] cycloaddition reactions were performed under nitrogen atmosphere in the dark. A round-bottomed flask equipped with a magnetic stir bar was charged with **P1N₃** (0.353 g, 0.66 mmol), C_{60} (54.3 mg, 75.4 μmol) and toluene (25 mL). The solution was heated to reflux for 27 h. The solvent was removed under reduced pressure and THF was added to the resulting product. The brown mixture was filtered and this procedure was repeated three times (or until no trace of C_{60} appears on thin layer chromatography plate) and the THF solutions were combined. The solvent was removed under reduced pressure to provide 0.310 g (78%) of the desired product as a brown rubbery solid. IR (NaCl): ν (cm^{-1}): 2930, 2859, 2095, 1715, 1429, 1213, 1111. ^1H NMR (400 MHz, $CDCl_3$, ppm): 7.22 (br); 5.31 (br); 4.21 (br); 3.98 (br); 2.52 (br); 1.74 (br); 1.56 (br); 1.46 (br); 1.31 (br); 0.88 (br).

2.3.7. *Polymer **P2C₆₀***

The polymer was prepared using the same procedure described above for the preparation of **P1C₆₀**. **P2N₃** (0.218 g, 0.40 mmol), C_{60} (67.0 mg, 93.0 μmol) and toluene (25 mL) were used to provide 0.241 g (88%) of the desired product as a brown rubbery solid.

2.3.8. *Polymer **P1P***

A 10 mL round-bottomed flask equipped with a magnetic stir bar was charged with **P1N₃** (100 mg, 0.19 mmol), porphyrin **12** (27.6 mg, 1.2 eq. per azide), $CuBr(PPh_3)_3$ (2.6 mg, 2.79 μmol), diisopropylethylamine (10.0 μL, 0.57 mmol) and THF (2 mL). The resulting mixture was stirred at room temperature for 24 h in the dark under nitrogen. Then, CuI (1.0 mg) was added and the resulting mixture was stirred for an additional five days. The polymer solution was then added to cold methanol (100 mL) and the purple precipitate was collected by filtration and rinsed thoroughly with methanol. **P1P** was dried under vacuum for 24 h to provide 0.112 g (97%) of the desired product as a purple rubbery solid. IR (NaCl): ν (cm^{-1}): 2929, 2858, 1716, 1430 1211, 1110, 997. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.81 (br); 8.13 (br); 7.96 (br); 7.53

(br); 7.22 (br); 5.29 (br); 4.21 (br); 3.97 (br); 2.42 (br); 1.84 (br); 1.72 (br); 1.43 (br); 1.31 (br).

2.3.9. *Polymer **P2P***

The polymer was prepared using the same procedure described above for the preparation of **P1P**. **P2N$_3$** (100 mg, 0.19 mmol), porphyrin **12** (55.2 mg), CuBr(PPh$_3$)$_3$ (5.2 mg, 5.58 µmol), diisopropylethylamine (20.0 µL, 1.14 mmol) and THF (2 mL) were used to provide 0.121 g (92%) of the desired product as a purple rubbery solid.

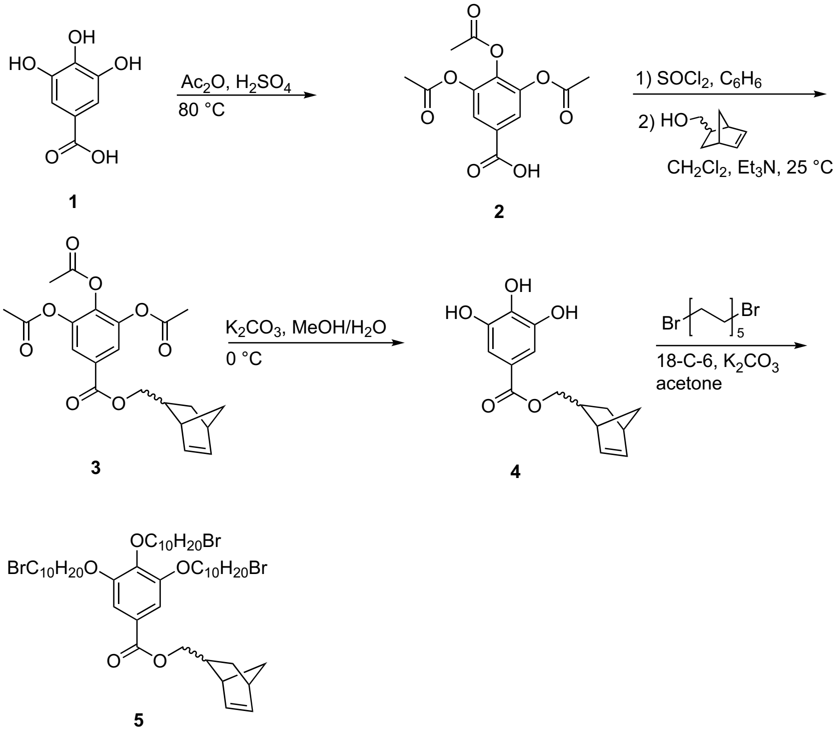
3. Results and discussion

3.1. *Synthesis of monomers and polymers*

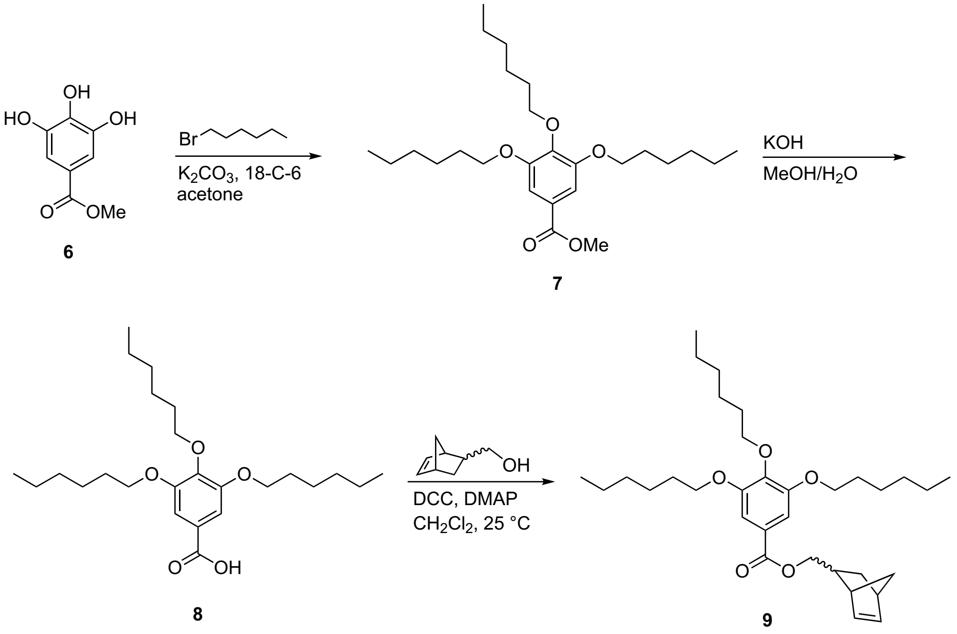
The synthesis of monomers **5** and **9** is depicted in Schemes 1 and 2. The synthesis of functional monomer **5** was achieved in four steps from gallic acid. First, the phenol groups were protected with acetyl following a known procedure to give **2** in good yield [22]. It is noteworthy that attempts to react gallic acid directly with 5-norbornene-2-methanol using Steglich esterification reaction failed (no reaction observed). This can be attributed to the increased electron-donating ability of phenol compared to its acetylated form, thus reducing the electrophilicity of carboxylic acid group. Compound **2** was then treated with thionyl chloride followed by 5-norbornene-2-methanol (mixture of *endo* and *exo*) in CH$_2$Cl$_2$ and NEt$_3$ to provide compound **3** in 30% yield. The phenol groups were deprotected under alkaline conditions and reacted with 1,10-dibromodecane using K$_2$CO$_3$ as base in acetone to give the final monomer **5** in moderate yield.

Monomer **9** was synthesized using similar reactions in a different order. Compound **6** was treated with 1-bromohexane in the same conditions used previously for the synthesis of monomer **5** to give the trialkylated compound **7**. Then, the methyl ester was hydrolyzed in alkaline aqueous conditions to give compound **8** in quantitative yield. Steglich esterification reaction between 5-norbornene-2-methanol (mixture of *endo* and *exo* isomers) and compound **8** using *N*,*N*-dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) in CH$_2$Cl$_2$ afforded the final monomer **9**.

The diblock copolymerization reactions were carried out using a mixture of monomers **5** and **9** in different ratios; 5:95 for **P1Br** and 10:90 for **P2Br**. Higher ratio of monomer **5** could be used with success but for the purpose of this study and due to the low solubility expected for the C$_{60}$-containing polymers, we decided to keep the amount of functional monomers below 10%. The synthesis of polymers **P1** and **P2** is depicted in Scheme 3. First, monomer **5** was treated with 1 mol% of Grubb's second generation catalyst in CH$_2$Cl$_2$ at room temperature under inert atmosphere for 3 h. The choice of the very active second generation Grubb's catalyst was motivated by the poor results obtained by Fréchet et al. in their attempts to polymerize bulky *endo*-norbornene derivatives using the third generation Grubb's catalyst which is considered the best for block copolymer synthesis from norbornene monomer [23]. Also, Sanda and Masuda recently showed that the second generation catalyst is very efficient for block copolymer synthesis even though it is less common [24]. Then, a solution containing monomer **9** in CH$_2$Cl$_2$ was quickly added to the active polymeric solution and the resulting viscous solution was stirred for an additional 16 h at room temperature. After treatment with an excess of ethyl vinyl ether to remove the ruthenium species from the polymer, the solution was poured in methanol providing **P1Br** and **P2Br** as white soft rubbery materials. The disappearance of ^{1}H NMR signals associated to the norbornene unit (5.99–6.17 ppm) in both crude (see SI1, Supporting information) and purified materials (Fig. 1) along with the appearance of broad signals between 5.12 and 5.51 ppm confirms the complete consumption of monomers **5** and **9** and the conversion to polymeric materials. The resulting polymers are readily soluble in common organic solvents such as THF, chloroform and toluene. Using ^{1}H NMR analysis, we measured a molar ratio (**5**:**9**) of



Scheme 1. Synthetic route for monomer **5**.

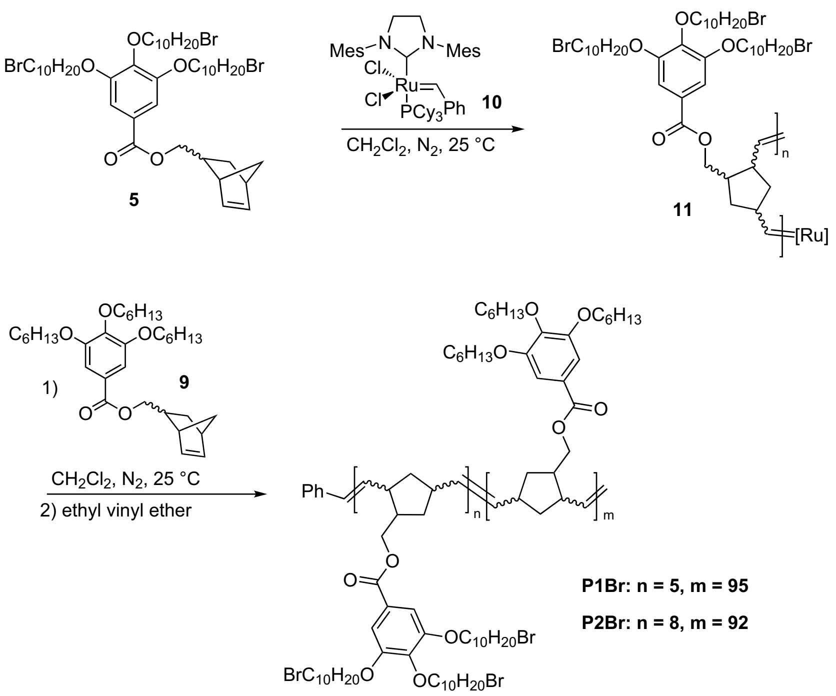


Scheme 2. Synthetic route for monomer **9**.

5:95 and 8:92 in **P1Br** and **P2Br**, respectively, which is equal or close to the initial feed ratio.

In order to modify the dendronized diblock copolymers with functional groups, bromine atoms were replaced by azide groups by reacting **P1Br** and **P2Br** with an excess of sodium azide and a catalytic amount of sodium iodide in DMF at 80 °C for 24 h to give **P1N$_3$** and **P2N$_3$**, respectively. The appearance of a new band at 2095 cm^{-1} in the IR spectra (see Figure SI2, Supporting information) along with the disappearance of the $\underline{CH_2}$–Br signal (3.39 ppm) and appearance of the $\underline{CH_2}$–N_3 signal (3.24 ppm) in the ^{1}H NMR spectra confirms the introduction of azide groups along the polymer side chains in quantitative yield.

The introduction of C_{60} onto the diblock copolymer side chain was achieved using a modified protocol developed by Hawker [18]. **P1N$_3$** and **P2N$_3$** were heated (~110 °C) with C_{60} (1.1 eq. per azide group) in toluene for 24 h under nitrogen in the dark. The reactions were conducted in dilute conditions (3×10^{-3} M of C_{60}) with a slight excess of C_{60} to minimize intra- and interchain cross-linking reactions [19]. The resulting C_{60}-containing polymers (**P1C$_{60}$** and **P2C$_{60}$**) were purified by iterative precipitations in THF to remove



Scheme 3. Synthetic route for the dendronized diblock copolymers **P1Br** and **P2Br**.

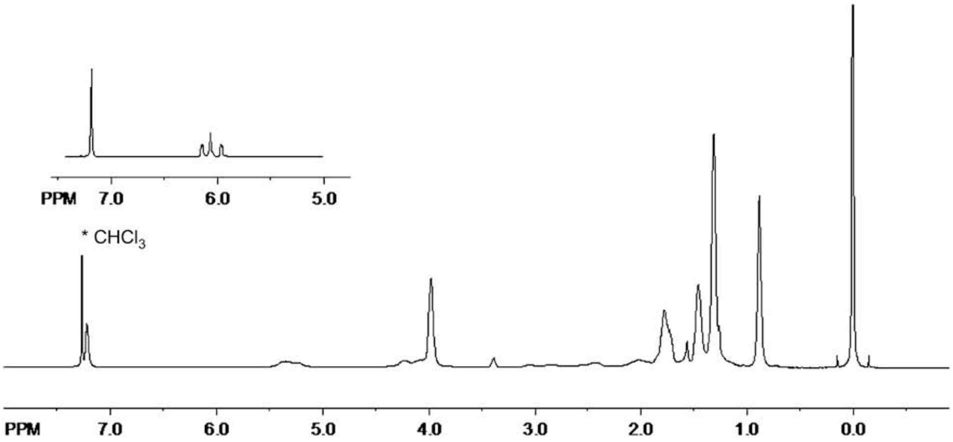
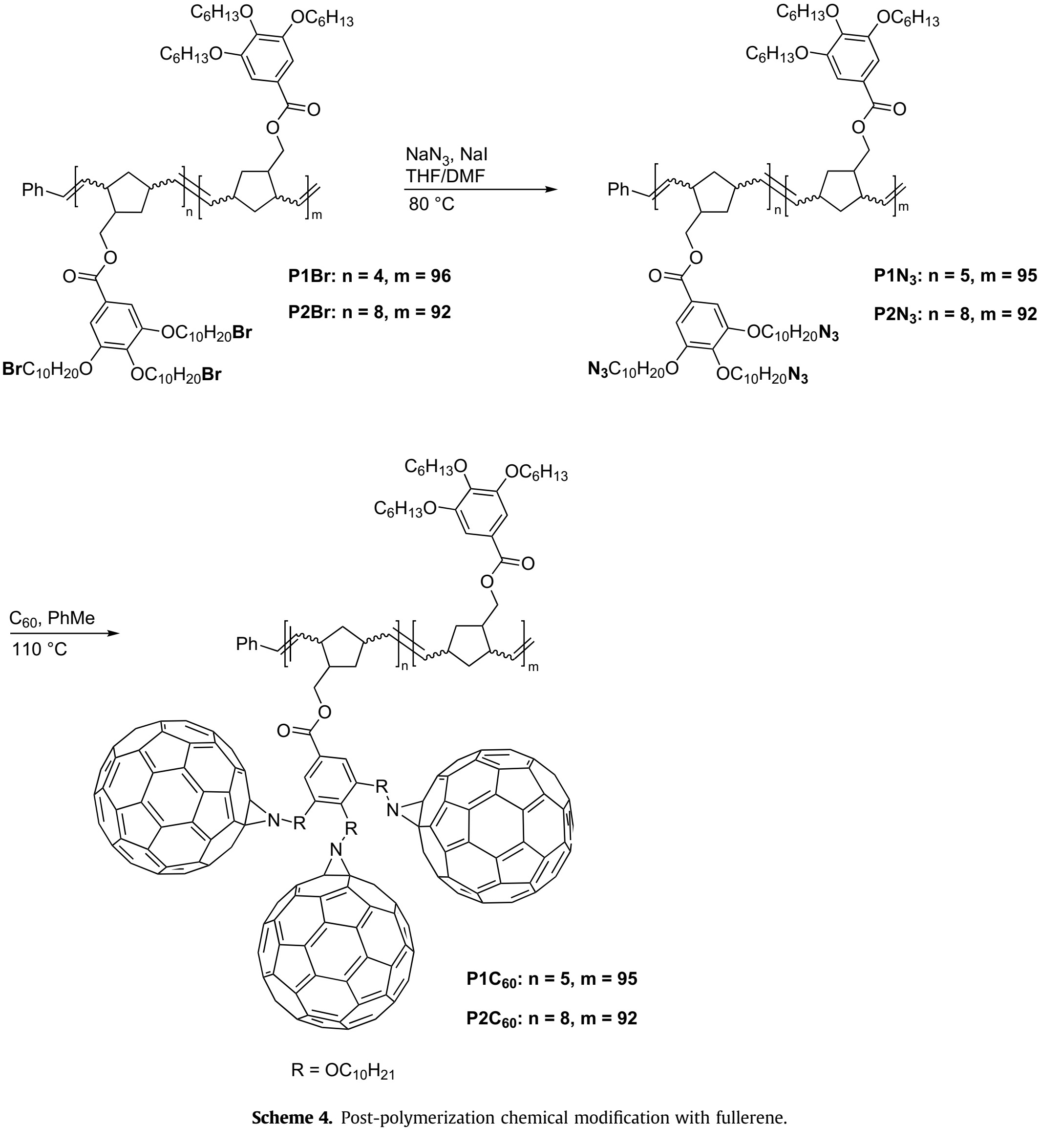


Fig. 1. 400 MHz ^{1}H NMR spectrum of **P1Br** in $CDCl_3$ at 25 °C. Inset: ^{1}H NMR spectrum of monomer **5** in the norbornene region.



Scheme 4. Post-polymerization chemical modification with fullerene.

Table 1
Characterization of polymers.

Monomer/polymer	Yield (%)	SEC[a]		
		$\overline{M}_n$ ($\times 10^{-3}$ kDa)	$\overline{M}_w$ ($\times 10^{-3}$ kDa)	$\overline{M}_w/\overline{M}_n$
P1Br	62	118	401	3.4
P1N$_3$	98	243	561	2.3
P1C$_{60}$	88	206	503	2.4
P2Br	70	130	482	3.7
P2N$_3$	99	156	393	2.5
P2C$_{60}$	78	131	340	2.6

[a] Referred to polystyrene standards in THF at 25 °C.

unreacted C_{60} to give brown soft rubbery materials readily soluble in aromatic solvents and CS_2. It is worth mentioning that **P1C$_{60}$** and **P2C$_{60}$** are much less soluble once they have been dried. This behavior has been previously observed for C_{60}-containing polymers but the causes are still uncertain [20] (Scheme 4).

3.2. Polymer characterization

3.2.1. Size-exclusion chromatography

Molecular weight values of diblock copolymers are summarized in Table 1. SEC analysis of **P1Br** and **P2Br** showed broad peaks resulting in $\overline{M}_n$ of 118.1 and 129.8 kDa and polydispersity index (PDI) of 3.4 and 3.7, respectively. It is noteworthy that no sign of homopolymer contamination was observed in the SEC traces. The large PDI values can be attributed to the different relative rates of initiation and propagation of *endo* and *exo* isomers, the former being less reactive due to higher steric hindrance nearby the alkene [25]. This behavior has been observed several times in ROMP polymerization when a mixture of *endo* and *exo* norbornene is used [26]. Fréchet et al. recently showed that the difference of reactivity between these two isomers is particularly critical when bulky groups such as dendrimers are attached to the norbornene unit [25]. Another explanation for the high PDI values is the higher rate of propagation than initiation with the Grubb's second generation catalyst [27]. Since large PDI values are not a drawback for the purpose of our study, no optimization of the reaction conditions was conducted.

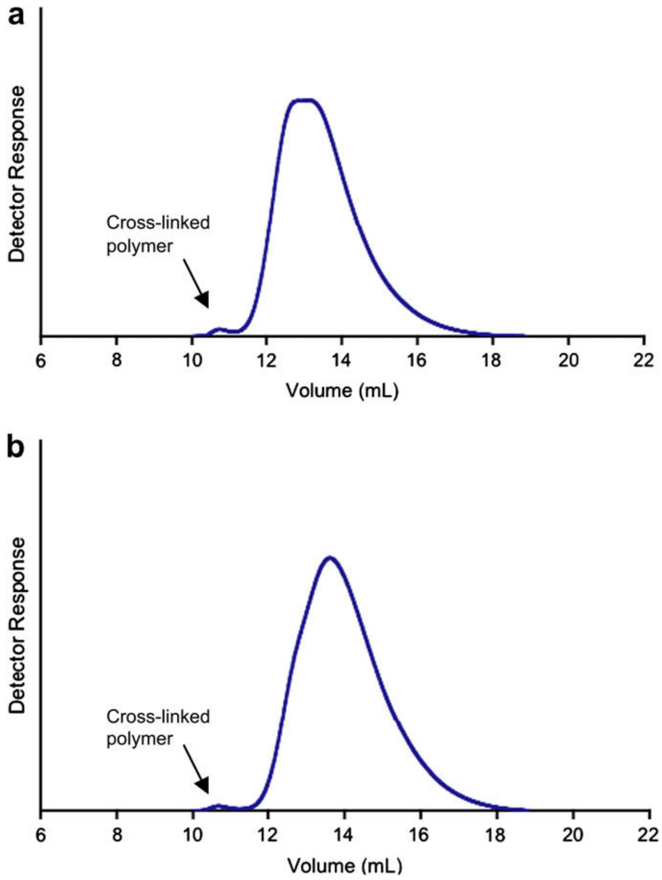


Fig. 2. Size-exclusion chromatography traces of (a) **P1C$_{60}$** and (b) **P2C$_{60}$**.

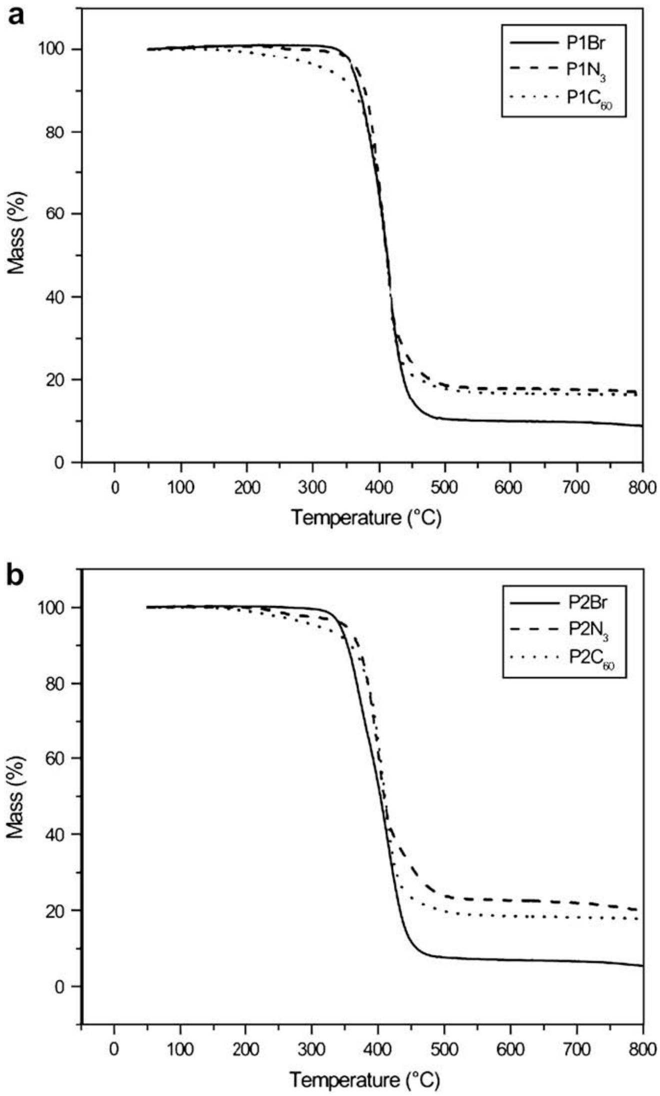


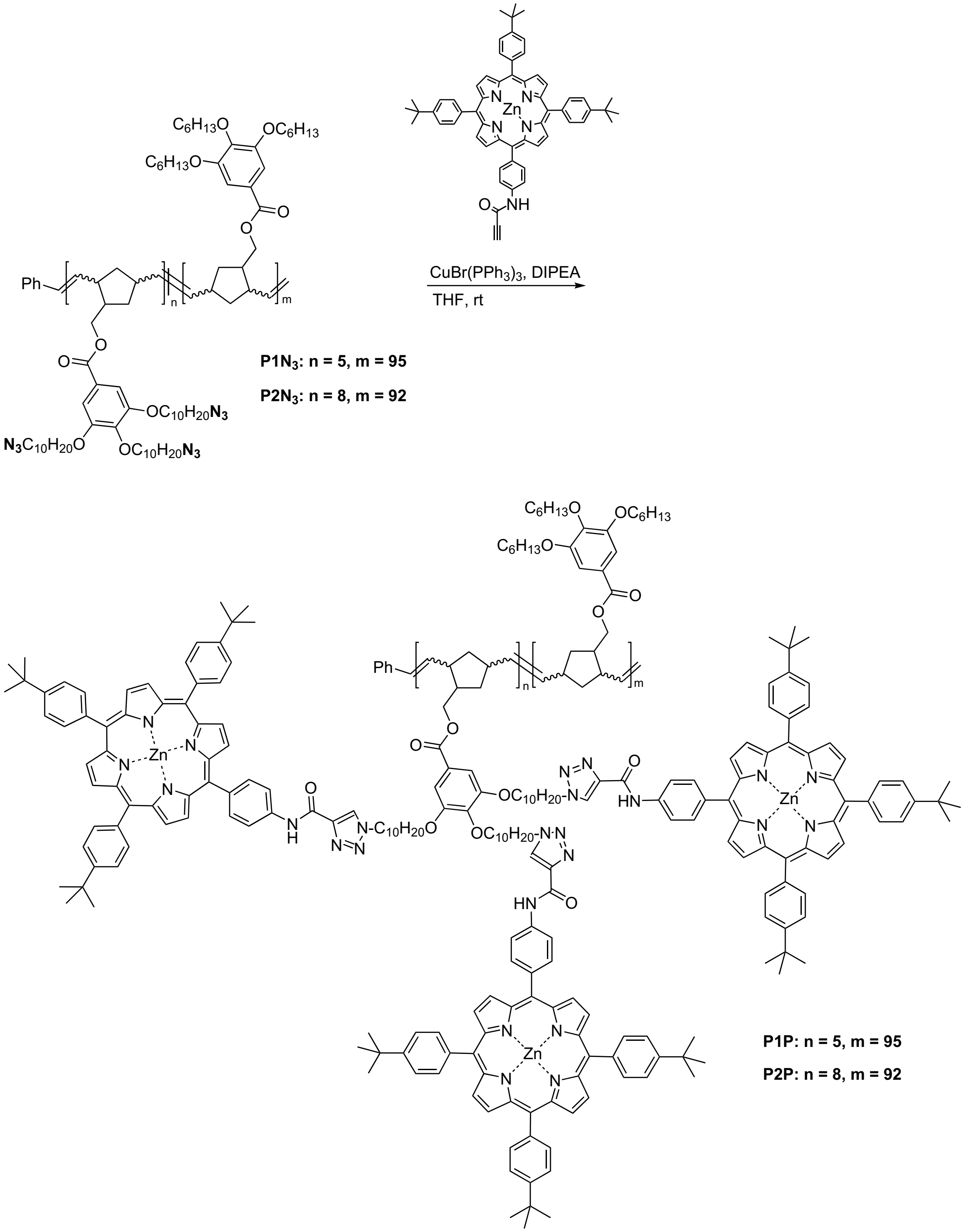
Fig. 3. TGA traces of diblock copolymers recorded under N_2 at a heating rate of 10 °C/min. The fullerene percentages were calculated at 575 °C.

Interestingly, SEC analysis of **P1N$_3$** and **P2N$_3$** showed different behaviors than those of their precursors. The $\overline{M}_n$ values of **P1N$_3$** and **P2N$_3$** are significantly higher than those of **P1Br** and **P2Br** but the PDI values are lower (2.3 and 2.5, respectively). Although these differences are not well understood, they can be ascribed to a significant conformational change in solution because of the introduction of more polar substituents (azide groups) on a small part of the polymer surface. These polar groups might provide an amphiphilic nature to the polymer chain leading to partial aggregation or micellization in THF solution [28]. The smaller PDI values for **P1N$_3$** and **P2N$_3$** can be attributed to the extra purification step (precipitation) performed after the reaction of **P1Br** and **P2Br** with sodium azide.

The $\overline{M}_n$ and PDI values of **P1C$_{60}$** and **P2C$_{60}$** are similar to those observed for their azide precursors. The small decrease in the $\overline{M}_n$ values can be attributed to a change in the polymer conformation in solution or to the reduction in the hydrodynamic radius of the C_{60}-containing block owing to the insolubility of C_{60} in THF [21]. The decrease is more pronounced for **P2C$_{60}$** since it has a longer C_{60}-containing block. It is noteworthy that a small higher molecular weight shoulder appears in both **P1C$_{60}$** and **P2C$_{60}$** SEC analyses (Fig. 2). Small amount of cross-linked materials (less than 1%) formed during the reaction of **P1N$_3$** and **P2N$_3$** with C_{60} (reaction of azide groups of two different polymer chains with one C_{60} moiety) is likely responsible for this shoulder. Attempts to conduct the C_{60} addition reaction at higher reagent concentration were unsuccessful since only insoluble materials which are attributed to highly cross-linked polymers were obtained. Because of the negligible amount of cross-linked material, no extra step was carried out to remove it.

3.2.2. Thermogravimetric analysis

The TGA analyses were conducted on all polymers and the results are summarized in Fig. 3. Despite the presence of thermally sensitive ester groups, all the polymers have relatively high



Scheme 5. Post-polymerization chemical modification with Zn-porphyrin **12**.

temperature of decomposition (above 300 °C). For **P1N$_3$** and **P2N$_3$**, a small weight loss (N_2 formation) attributed to the decomposition of azide into reactive nitrene species was observed between 200 and 300 °C (Fig. 3).

TGA analyses were conducted on **P1C$_{60}$** and **P2C$_{60}$** to determine the weight fraction of C_{60} in the polymers. These values were determined by calculating the residue difference at 575 °C between C_{60}-containing polymers and their bromine-containing (**P1Br** and **P2Br**) derivatives. Considering a substitution rate of 100%, **P1C$_{60}$** and **P2C$_{60}$** can contain a maximum amount of 17 wt% and 24 wt%, respectively (considering the calculated ratio of **5** and **9** from the ^{1}H NMR analysis of **P1Br** and **P2Br**). However, the experimental values are much lower as shown in Fig. 3. In fact, the percentages of C_{60} in **P1C$_{60}$** and **P2C$_{60}$** are 7 wt% and 12 wt%, respectively, indicating that only ca. 50% of the theoretical amount was incorporated in both cases. Although it would have been surprising to convert all the azide into the C_{60} adduct, the substitution rates are rather low compared to other C_{60}-based polymers prepared from azide derivatives [18,20]. The steric congestion on the polymer chain surface can be responsible to some extent for the low substitution yield observed. This suggests that the dendronized polymer approach shows some limitations for the introduction of large functional groups, especially fullerene, using the post-polymerization strategy. Because the azide signals have disappeared in both **P1C$_{60}$** and **P2C$_{60}$** IR spectra (see Figure SI3, Supporting information), we suggest that significant amount of C_{60} undergoes more than one azide addition. This substitution pattern can be attributed to the spatial proximity of the azide groups on the polymer surface. The proximity effect is known to be an efficient method to prepare C_{60}-containing cyclic compounds from multi-azide derivatives [29].

To better understand the steric factor upon functional group introduction on the dendronized polymer surface and to show the generality of our method, we attempted to attach a bulky porphyrin unit [30] on the azide-containing block using a 1,3-dipolar cycloaddition (click chemistry) reaction. For solubility reason, the reactions on **P1N$_3$** and **P2N$_3$** were performed in THF using $CuBr(PPh_3)_3$ as catalyst in the presence of diisopropylethylamine (DIPEA) as base (Scheme 5) [31].

After precipitation in methanol, **P1P** and **P2P** were obtained in pure form as purple soft rubbery fiber. The disappearance of the signals at 3.24 ppm in the ^{1}H NMR spectra and 2095 cm^{-1} in the IR spectra (Figures SI4 and SI5, Supporting information) suggests that all the azide groups had reacted in both **P1N$_3$** and **P2N$_3$** meaning that one monomer unit can accommodate three porphyrin units despite their relatively large dimensions. Complete substitution provides densely packed porphyrin units along the polymer backbone, regardless to the ratio of the azide-functionalized block. The better substitution rate for functionalization with porphyrin compared to fullerene can be attributed to the better efficiency of the click chemistry reaction, the smaller volume occupied by the porphyrin unit compared to fullerene and to the multiple addition of azide groups on the C_{60}.

4. Conclusions

In this study, we successfully synthesized soluble dendronized diblock copolymers with different ratios of functionalized norbornene monomers using ROMP in non-optimized conditions. The high-molecular weight polymers were then chemically modified with the versatile azide group to allow the introduction of fullerene and porphyrin units, two important building blocks for the construction of photovoltaic materials. The substitution rate for thermal [3 + 2] cycloaddition with fullerene was moderate because of the steric hindrance and the nature of the reaction involved while the porphyrin units were incorporated quantitatively via the click chemistry reaction. All the polymers remain soluble in common organic solvents meaning that copolymers having higher ratio of the functional block could be synthesized. The synthesis of new dendronized diblock copolymers with more space between the azide groups to decrease the steric hindrance and the occurrence of multiple azides addition on C_{60} is underway.

Acknowledgments

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.01.053.

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