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Well-Defined Fullerene-Containing Homopolymers and Diblock Copolymers with High Fullerene Content and Their Use for Solution-Phase and Bulk Organization

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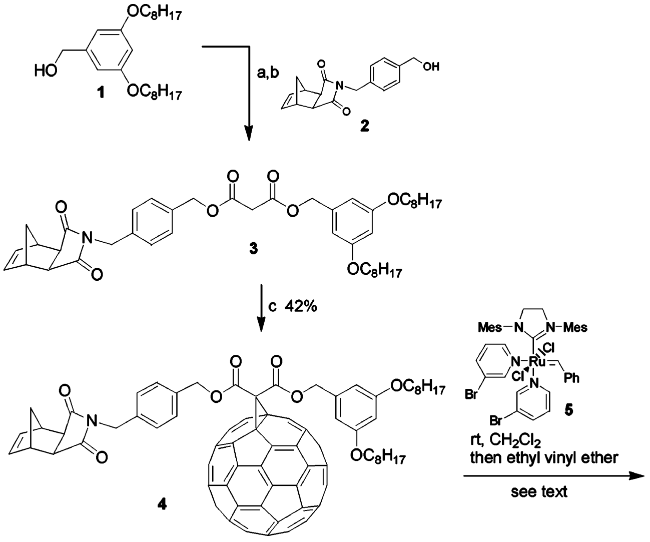
ABSTRACT: A fullerene-containing norbornene derivative is used for ring-opening metathesis polymerization to synthesize living polymers with high fullerene content. Incorporation of fullerene at every repeat of a small monomer allows high fullerene content and short inter-fullerene distances in a soluble polymer. The living nature of the polymerization also allows the synthesis of diblock copolymers, which exhibit micellar aggregation in solution and phase separation with interpenetrating C_{60}-domains in a thin film upon TEM imaging.

Among many applications, fullerenes serve as electron-transporting (n-type) semiconductors in applications such photovoltaics and field-effect transistors, as well as building blocks toward the development of functional nanoscale constructs.[1] Many groups have successfully pursued the direct functionalization of C_{60}, affording materials with useful properties and improved tractability.[2−4] More recently, oligomeric arrays of fullerenes have been created with an eye toward controlling several fullerenes as “nano-objects”. The organization of many fullerene structures is essential for their use as antennae or semiconducting nanowires. In addition, polyfullerenes could serve as a useful design principle for the bottom-up control of bulk film morphology crucial for the performance of organic electronics.[2]

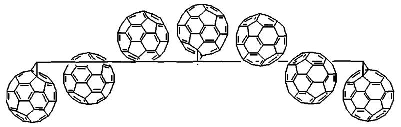
Some efforts have targeted monodisperse fullerene arrays, such as fullerene-containing dendrimers.[5] An alternative target molecule is a fullerene-containing polymer. Ideally, a soluble, linear C_{60}-polymer with a defined (small) inter-fullerene distance would be accessible with good control over polydispersity. The steric demands of fullerene structures, the limitations on potential chemistries in the presence of reactive fullerene groups, and the poor solubility of fullerene and its derivatives conspire to make the realization of this goal a challenge. Approaches to fullerene-containing polymers have appeared,[6] including graft-to methods with doped random copolymer,[7,8] the random copolymerization of a C_{60}-containing monomer,[4,9] and condensation polymerization[3,6,10,11] as well as supramolecular association.[12]

While these efforts have produced interesting polymers, high fullerene content is important for many applications. However, previously published work has produced polymers of rather low fullerene content. For example, a condensation polymerization approach affords material of 31 wt % fullerene[11] and a robust random copolymer approach produced at most polymers 29 wt % fullerene.[7] In addition, current methods generally do not allow chain-growth homopolymer synthesis from a C_{60}-containing monomer or allow control of chain ends important for many applications. We chose a ring-opening metathesis polymerization (ROMP) strategy using a C_{60}-containing norbornene-type monomer[13] as part of a program in our laboratories, demonstrating the unique ability of ruthenium ROMP catalysts for the synthesis of living polymers from sterically demanding monomers. Clear benefits of this approach include direct fullerene incorporation, rather than postpolymerization inclusion of fullerene, where complete coverage is often impossible to obtain. Additionally, ROMP defines a constant inter-fullerene distance controlled by monomer structure, unlike random copolymerization approaches (eq 1).

Scheme 1[a]



[a] Conditions: (a) Meldrum’s acid, neat, 120 °C; (b) DCC, DMAP, **2**; (c) C_{60}, CBr_4.



(1)

Our target monomer (**4**) was synthesized with a late-stage incorporation of the C_{60} unit to minimize synthetic difficulties, especially on scale-up (Scheme 1). In a single pot, coupling of solubilizing group **1**, norbornenyl derivative **2**, and Meldrum’s acid produced malonate **3**. Incorporation of C_{60} then produced the monomer **4**. Polymerization of monomer **4** was carried out

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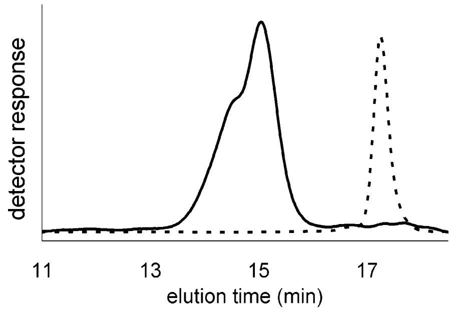
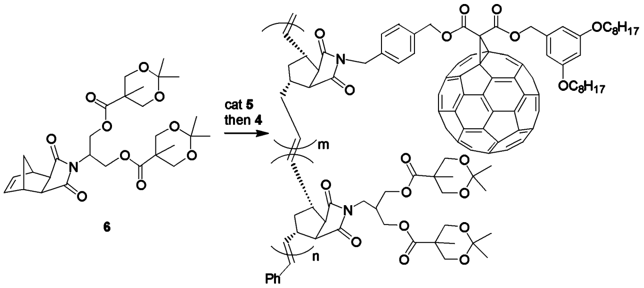


Figure 1. Size-exclusion chromatography analysis of poly(**4**) (solid line) and monomer **4** (dotted line). Solvent, chloroform; flow rate, 1.0 mL/min; detector, refractive index.

Scheme 2



in the presence of the ruthenium pyridine complex **5**[14] at room temperature in either CH_2Cl_2 or chlorobenzene to afford a dark brown polymer after treatment with ethyl vinyl ether to remove ruthenium from the polymer and precipitation into ether. Complete consumption of the monomer and formation of a poly(norbornene) derivative could be confirmed by ^1H NMR and size exclusion chromatography (SEC). Solubility is a concern with all fullerene compounds, and the solubility of poly(**4**), which is 50 wt % C_{60}, is strongly dependent on the degree of polymerization. For example, at a 50:1 monomer:catalyst ratio, an essentially insoluble polymer was formed, while at a 25:1 ratio, the polymer formed, poly(**4**)$_{25}$, was readily soluble (>15 mg/mL) in chloroform or chlorobenzene.

Analysis of poly(**4**)$_{25}$ by SEC revealed a sharp peak with a tail at high molecular weights (see Figure 1), resulting in a calculated polydispersity of 1.48 and M_n of 20.3K based on polystyrene standards (theoretical value: 35.9K). Similar unexplained tailing at high molecular weights in SEC has been observed for unrelated graft-to polymers upon incorporation of C_{60}.[7] In light of diblock experiments (vide infra) we believe that this feature is an artifact potentially resulting from aggregation and that the actual polydispersity is considerably lower, in line with that obtained with other ROMP polymers. Size determination of poly(**4**) by dynamic light scattering (DLS) revealed a sharp, monotonic size distribution.

A major advantage of the living polymerization approach described here is the possibility to prepare diblock or end-functionalized polymers useful as amphiphilic materials or for surface immobilization, respectively. To establish the feasibility of such processes, copolymerization of monomer **4** with a sterically demanding second-generation dendronized monomer was carried out (Scheme 2). Block copolymerization proceeded smoothly with a variety of monomer ratios, and the resulting polymers display considerably increased solubilities when compared to poly(**4**). Again, complete consumption of both monomers was observed by crude NMR in all polymerizations. As a result of aggregation and interactions with the column, analysis of the diblock copolymers by SEC leads to multimodal peaks at very high molecular weights. However, comparison to independently synthesized poly(**6**) is useful to confirm the absence of chain-terminated homopolymer (see Supporting Information). The aggregation of amphiphilic fullerene-containing materials in SEC is well documented; the effect is robust enough to allow for purification by preparative SEC.[15]

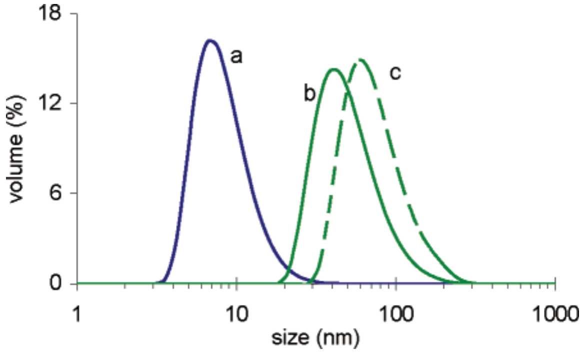


Figure 2. Dynamic light scatting size analysis of polymers. Measurements taken in chloroform solution (1 mg/mL) at 20 °C. (a) poly(**6**)$_{100}$; (b) poly(**6**)$_{35}$-*block*-poly(**4**)$_{100}$; (c) poly(**6**)$_{35}$-*block*-poly(**4**)$_{70}$.

Analysis by DLS indicated that the diblock copolymers ($m = 35$, $n = 70$ or 105) form well-controlled aggregates in chloroform, THF, or toluene solution.[16] The observed diblock copolymer distributions (Figure 2b) indicate the complete lack of free polymer chains, and the observed size (ca. 80 nm) is consistent with a single-layer micelle, presumably with C_{60} occupying the interior. The diblock material (trace b) is monotonic without any features below 10 nm corresponding to chain-terminated homopolymer, which does not aggregate (trace a, synthesized independently). Aggregates of C_{60} are reported to have improved light-harvesting properties,[17] and the polymers reported here afford well-defined and potentially site-isolated large aggregates of C_{60}. In contrast to the diblock copolymers analyzed in Figure 2, DLS analysis of diblock copolymers with very large dendron domains ($m = 35$, $n = 200$) showed incomplete aggregation in solution, as expected where one block begins to dominate the structure and the material begins to behave as a homopolymer (see Supporting Information).

Given the importance of thin-film morphology for a variety of polymer electronics applications, we explored by transmission electron microscopy (TEM) the morphology of diblock copolymers using thin films formed by a drop-cast method. The films displayed well-defined phase segregation (Figure 2) of random orientation. The film morphology is consistent with that observed for other norbornene ROMP-based diblock copolymers.[18] The length scale of the features (see red scale bar) are consistent with fully extended conformation of entire individual polymer chains of about 40 nm, reflecting the steric bulk about the backbone rather than a random coil. Importantly, diblock copolymer composition can be used to control the nanoscale morphology of the thin films. While poly(**6**)$_{70}$-*block*-poly(**4**)$_{35}$ (Figure 3) exhibited a continuous network of fullerene-rich regions, a diblock copolymer with larger dendron domains, poly(**6**)$_{200}$-*block*-poly(**4**)$_{35}$, exhibited only isolated regions of fullerene density. The disordered nature of the morphology observed is quite different from the very ordered alignment obtainable with random coil block copolymers and may reflect unique features of rod−rod copolymers enforced in this case by steric bulk about the backbone.

We have described a living polymerization that affords polymers with 50 wt % C_{60} and a defined spacing between fullerenes controlled by five carbon−carbon bonds along the polymer backbone. The living nature of our ROMP polymer-

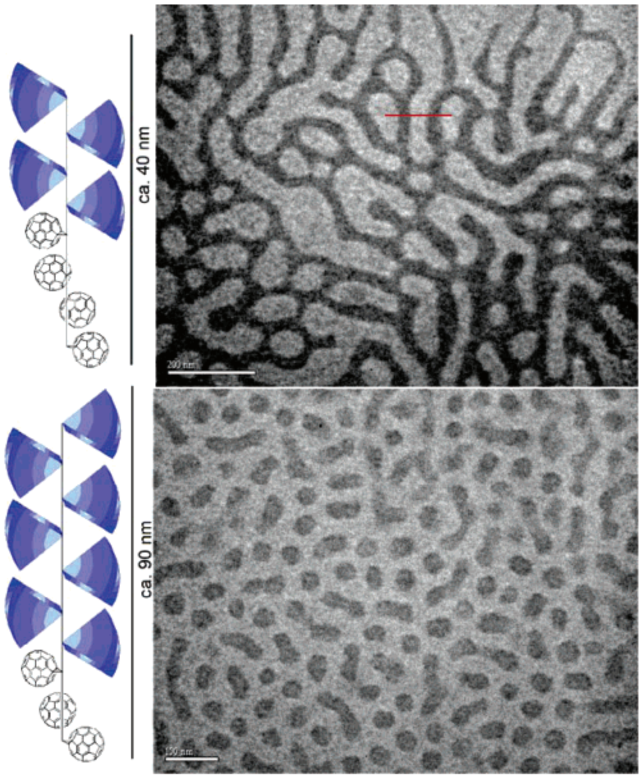


Figure 3. Transmission electron microscopy image of a thin film of poly(**6**)$_{70}$-*block*-poly(**4**)$_{35}$ (above) and poly(**6**)$_{200}$-*block*-poly(**4**)$_{35}$ (below) on a carbon-supported copper grid with representation of the block copolymer (left). Red bar = 153 nm. The image was taken without stain; dark areas indicate fullerene-rich regions.

ization allows the synthesis of diblock copolymers that display unique aggregation behavior in solution. Thin films of fullerene-rich diblock polymers form a continuous C_{60} network applicable to charge transport in electronic applications. This morphology can be tuned to isolate the C_{60} domains by altering block size.

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Supporting Information Available: Synthetic details and characterization data for the synthesis of monomers, detailed polymerization procedures, and additional characterization data for polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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