

Improved synthesis of fullerynes by Fisher esterification for modular and efficient construction of fullerene polymers with high fullerene functionality

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ABSTRACT

For the first time, the scope of Fisher esterification has been extended to fullerene derivatives to improve the synthesis of alkyne-functionalized fullerenes (fullerynes) using 1-chloronaphthalene as a solvent and a specially-designed, home-made reactor to promote high yield. The design allows for higher solubility of fullerene derivatives and a continuous azeotropic distillation for the removal of water to drive the reaction to completion with yields >90%. Both fullerynes (Fulleryne01 and Fulleryne02) were found to “click” to polymers, such as azide-functionalized poly(ϵ -caprolactone) (PCL-N₃), in high efficiency without the need for fractionation. As evidenced by ¹H NMR, ¹³C NMR, size exclusion chromatography, and matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry, the fullerene polymers thus obtained possess well-defined structure, narrow polydispersity (~ 1.01 by MALDI-TOF mass spectrometry; ~ 1.03 by size exclusion chromatography), and high fullerene functionality ($\sim 100\%$). They can serve as model compounds for the investigations of polymer structures and dynamics.

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1. Introduction

Fullerenes are fascinating carbon nanostructures with wide-ranging applications [1,2]. In order to improve pristine fullerene's compatibility with other functional materials, chemical modifications are often necessary, which has greatly expanded the scope of fullerene materials and their applications [3]. Problems in doing chemistry with fullerene usually involve, for example, the often unavoidable multiple addition and drastic reaction conditions [4,5], and result in a mixture of mono-addition product, multi-adducts, and unfunctionalized C₆₀. In small molecular fullerene derivatives, chromatographic methods are effective in the separation and purification of product. However, it can be a major concern for polymers, biological systems, and other heterogeneous systems where functional group reactivities are inherently low and purification is often difficult, if possible. Although there have been many reports on the synthesis of fullerene polymers of various architectures with sufficient control, it is still challenging to prepare

fullerene polymers with high degree of functionality ($\sim 100\%$), a variety of different compositions, and of complex architectures, in a modular and efficient way [2,6]. Such polymer-tethered C₆₀s are typical model compounds for shape amphiphiles. Shape amphiphiles usually refer to molecules possessing amphiphilic features based on differences in the shape of the molecular segments and are expected to show rich phase structure and self-assembling behavior in bulk and solution [7–9]. In addition, since polymers can often form supramolecular assemblies via self-assembly processes, such as crystallization [10–12] and micellization [13,14], it is also of great interest to study how the self-assembly of polymers can assist the ordered arrangement of C₆₀ units. Recently, we have shown a “click” chemistry approach to fullerene polymers by the model synthesis of well-defined C₆₀-end-capped polystyrene with high fullerene functionality in high yield [15]. The Cu-catalyzed Huisgen [3 + 2] cycloaddition reaction [16–18] between the alkyne-functionalized fullerene (thus named ‘fulleryne’) and azide-functionalized materials proceeded efficiently at room temperature without side reactions between azide and C₆₀ core (Scheme 1). This approach has also been reported by other researchers in the synthesis of a variety of fullerene materials, such as porphyrin-C₆₀ conjugate [19], fullerene sugar ball [20], C₆₀-

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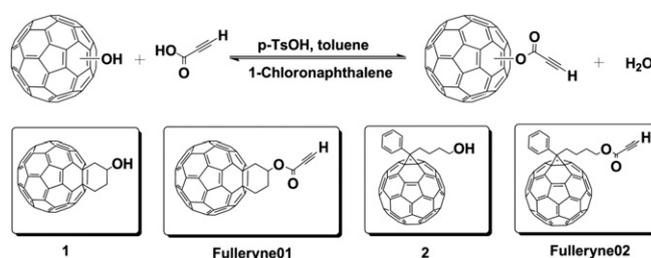
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poly(*N*-isopropyl acryl amide) (PNIPAM) [21], C₆₀-viral nanoparticle conjugates [22], and others [23–25]. No complicated purification procedures, such as fractionation, were necessary in these cases. Considering its modularity and efficiency, this approach is quite advantageous in the construction of fullerene materials for a variety of applications. In order for this approach to be viable for practical applications, it is essential and critical to find fullerynes that are readily available from C₆₀ (synthetic facility), very reactive (chemical reactivity), and potentially multifunctional (material function). Fulleryne01 (Scheme 2), a C₆₀ propiolate, has been shown to possess “click” reactivity in reactions with azide-functionalized polymer in our previous reports [15,26]. Its practical usage was hindered by its poor availability since the yield of the final esterification step was only 17% when it was first reported. In this article, we report an improved synthesis of Fulleryne01 with up to 92% yield by Fisher esterification using 1-chloronaphthalene as the solvent and a specially-designed, home-made reactor to promote efficiency (Scheme 2). To the best of our knowledge, this is the first example in doing Fisher esterification with fullerene derivatives. This method was also applied with high yield to the synthesis of Fulleryne02 (Scheme 2), a derivative of phenyl-C₆₁-butyric methyl ester (PCBM). With improved accessibility of fullerynes, the “click” chemistry approach to fullerene materials can be viable as a general, efficient method, and these fullerynes can serve as versatile building blocks in the modular and efficient construction of advanced fullerene materials. Specifically as an example, in the present work, C₆₀-end-capped poly(ϵ -caprolactone)s (PCL-C₆₀) were synthesized with controlled molecular weight, narrow polydispersity, and high fullerene functionality (~100%) by sequential ring opening polymerization, nucleophilic substitution, and “click” coupling with both Fulleryne01 and Fulleryne02 (Scheme 3). Being a typical shape amphiphile with a semi-crystalline polymer tail, PCL-C₆₀s are expected to show interesting self-assembling behaviors based on the interplay between the crystallization of PCL and aggregation of C₆₀.

2. Results and discussions

2.1. Synthesis of fullerynes by Fisher esterification

It has been shown by both the mechanistic study and experiment that the Huisgen cycloaddition reaction can proceed in high efficiency under mild conditions when electron-deficient alkynes are used [27–29]. Therefore, the terminal alkynes with an adjacent carbonyl group, such as fullerene propiolates, are good candidates for fullerynes with high reactivity. The preparation of propiolates has been thoroughly studied in the literature, such as DCC/DMAP mediated esterification of propiolic acid [30], the acyl chloride method [31], and mixed anhydride route [32]. None of these methods were effective in the preparation of fullerene propiolates in our attempts. The addition of propynoyl chloride resulted in the immediate formation of a resinous precipitate without detectable

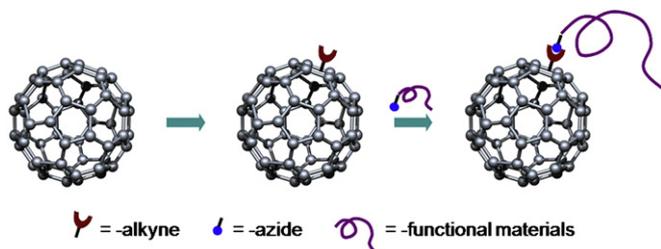


Scheme 2. Synthesis of Fulleryne01 and Fulleryne02 by Fisher esterification.

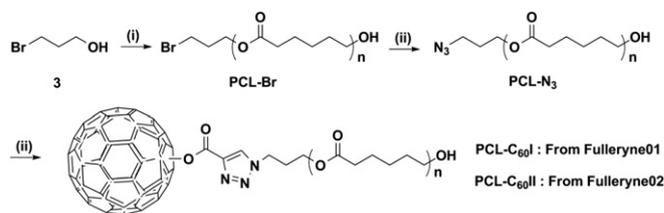
amount of product [31]. In the mixed anhydride route, the low solubility of fullerene carbonochloridate in THF prevented its effective reaction with sodium prop-2-ynoate [32]. The problems are mostly associated with either the poor solubility of the fullerene derivative in polar solvents or with side reactions, such as Michael addition, that are promoted by the adjacent carbonyl group [32].

Fisher esterification is a classic reaction and has been widely used to synthesize propiolates commonly in a high yield [33,34]. It is known to be an equilibrium reaction between an alcohol and an acid to give the desired ester and water under the catalysis of acidic species (Scheme 2). Based on Le Chatelier's Principle, with higher concentrations of the starting materials, more products will form at equilibrium. Moreover, if the side products, such as water, can be continuously removed from the system, the equilibrium can be pushed forward to the product side. Generally, Fisher esterification works well with large scale preparations where a significant amount of water is generated and removed. The Dean–Stark trap is often used in the laboratory to remove water by azeotropic distillation with toluene or benzene [35]. The reaction usually involves grams of sample and the aqueous and organic components forms phase-separated layers in the trap, facilitating removal of water. Alternatively, the Soxhlet extractor can also be used in combination with activated molecular sieves for the effective removal of small quantities of water [35].

At first, the Fisher esterification did not seem to work well for fullerene derivatives since they usually have low solubility in terms of its molar concentration in toluene and benzene, which would make the reaction very inefficient. For example, the solubility of C₆₀ is only 2.1×10^{-4} mol/L (1.7 mg/mL) in benzene and 4.0×10^{-4} mol/L (2.8 mg/mL) in toluene [3]. Furthermore, considering the relatively high molecular weight of fullerene derivatives (e.g., 792 Da for fullerene alcohol **1**), the water generated in this case is only at the milligram scale if the reaction is carried out with a sample of several hundreds of milligrams, which cannot be phase-separated from toluene to be removed. For example, the water generated from the reaction between 0.2 g of **1** and propiolic acid is 4.5 mg, assuming 100% yield. If the solubility of **1** is similar to C₆₀ in toluene (2.8 mg/mL), the saturated toluene solution will have a volume of 71 mL, corresponding to a weight of 61.4 g (density of toluene is 0.86 g/mL). The concentration of water in toluene will be 0.0073 wt



Scheme 1. A general functionalization methodology to fullerene materials via “Click” chemistry.



Scheme 3. Synthesis of C₆₀-end-capped poly(ϵ -caprolactone)s^a: (i) Sn(Oct)₂, ϵ -caprolactone, toluene, 60 °C, 55%; (ii) NaN₃, DMF, 60 °C, 94%; (iii) Fulleryne01 (or Fulleryne02), CuBr, PMDETA, toluene, 85% (or 87% for Fulleryne02).

%, far below the solubility limit of water in toluene (0.033 wt%) [36]. As a result, the reaction will be extremely sensitive to any residual moisture in the system. Indeed, in a trial run of the reaction in toluene using a Dean–Stark apparatus overnight or using a Soxhlet extractor with activated 4 Å molecular sieves, only trace amount of product formation were observed (Table 1, Entry I). These issues might account for the fact that there has not been any report on the application of Fisher esterification to the synthesis of fullerene derivatives. Nevertheless, by manipulating the reaction conditions, it is still possible to improve the yield of Fisher esterification because, after all, it is an equilibrium reaction.

The first approach was to increase the solubility of fullerene derivatives in the system by using an uncommon solvent, 1-chloronaphthalene, as the reaction medium. Being a chlorinated aromatic solvent with high boiling point (259 °C/760 mmHg) and inert under most reaction conditions, 1-chloronaphthalene is known to be a relatively good solvent for fullerenes. Its solubility for C₆₀ is as high as 51 mg/mL (97×10^{-4} mol/L) [3]. Toluene was used as a co-solvent to remove water azeotropically from the system. By doing so, it has been shown that the reaction efficiency was greatly improved. In the case of **1**, the yield increased to 34% and 38% using a Dean–Starks apparatus and a Soxhlet extractor, respectively (Table 1, Entry II and III). For fullerene alcohol **2**, which was obtained by reduction of PCBM using DIBAL-H (in 93% yield, see Supporting Information), the esterification was very efficient with yields of 84% and 85%, respectively (Table 1, Entry II and III). Fulleryne02 was then fully characterized by ¹H NMR, ¹³C NMR, FT-IR, and MALDI-TOF to confirm the chemical structure and purity (see Supporting Information for characterization data and discussions). An additional advantage of using 1-chloronaphthalene in Fischer esterification is that, after the reaction is complete and toluene is removed, the reaction mixture can be directly applied to the top of a silica gel column for the recovery of 1-chloronaphthalene using hexanes, the purification of the product using toluene, and the recovery of unreacted alcohols by further eluting with toluene/ethyl acetate (v/v = 95/5), which increases the overall efficiency of the process. The better yields obtained for **2** than **1** are probably due to the higher solubility of **2** in the mixed solvent of 1-chloronaphthalene/toluene. This process works sufficiently well for the preparation of Fulleryne02, but more efforts are required to optimize the preparation conditions of Fulleryne01.

The next attempt was made to completely exclude the moisture from the system and to drive the reaction equilibrium to the product side. Similar to anionic polymerization where the most stringent reaction conditions are required, it is possible to reduce the water content down to parts per million (ppm) levels with glass-blowing and high vacuum line techniques [37,38]. To this end, a special reactor was designed based on our understanding of the reaction mechanism and made by glass-blowing techniques (Fig. 1 and Fig. S1). Fig. 1 shows a schematic drawing of this reactor and Fig. S1 (see Supporting Information) is a photograph of a real reactor. It consists of three flasks: reaction flask (A), water-removal

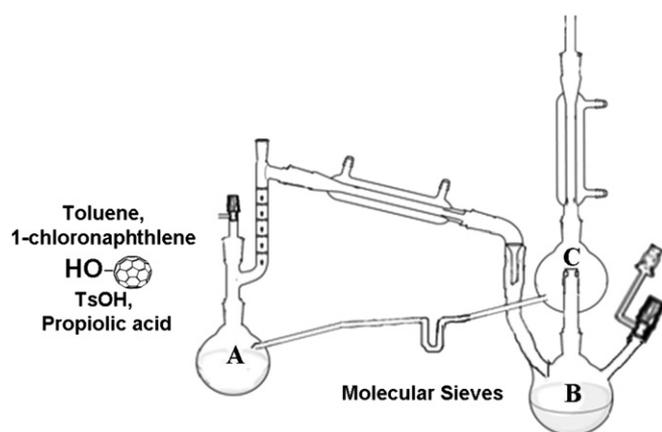


Fig. 1. Schematic drawing of the reactor design for Fisher esterification of fullerene derivatives.

flask (B), and toluene reservoir (C). All the reactants and solvents were carefully purified and thoroughly dried before reaction. The reactor was attached to a vacuum line and flame dried three times before use. The reactants and 1-chloronaphthalene were placed in flask A and the activated 4 Å molecular sieves were placed in flask B. Being inert and efficient, molecular sieves were a perfect choice for this purpose. Toluene was then transferred into flasks A and B by vacuum distillation. After refilling the system with extra-dry nitrogen, the flasks (A and B) were placed in two oil baths of preset temperature (~120 °C). Then a unidirectional circulating system of toluene was formed from the reaction flask (A) to the water-removal flask (B) to the toluene reservoir (C) and then back to the reaction flask (A). The redistillation of toluene seemed essential in the complete removal of water from the system, as reflected by the results. The cycle went continuously to push the reaction to completion. In this case, both Fulleryne01 and Fulleryne02 were obtained in over 90% yields (Table 1, Entry IV), which can be considered remarkable when compared to the trace amount of product in the first trial. Both the syntheses of Fulleryne01 and Fulleryne02 have been scaled up to several grams of product in our laboratory using this method. We are trying to scale it up to even larger quantities to make it commercially viable. With the ready accessibility of fullerenes, the “click” approach to fullerene materials can be viewed as a modular and efficient one. As an example, a series of C₆₀-end-capped PCLs (PCL-C₆₀) was synthesized using both Fulleryne01 and Fulleryne02, which will be discussed in the following section.

2.2. Modular functionalization of PCL with fullerenes (synthesis of PCL-C₆₀)

The synthesis of fullerene poly(ε-caprolactone) conjugates has been reported by several groups in the past, using either a “grafting-from” approach or a “grafting-to” approach. In the first approach, varying numbers of hydroxyl groups were first installed onto the fullerene core to initiate the ring opening polymerization of ε-caprolactone [39–41]. In the latter approach, the PCL was first synthesized with reactive groups located at different positions along the chain, typically an azide at the chain-end or along the chain [5,42–44]. Their addition to C₆₀s gave end-capped PCL or star PCL with a C₆₀ core, depending on the stoichiometry [5,44]. The effects of conjugation on crystallization, degradation behavior, and fiber preparation by electro-spinning were studied [5,41,42,44]. The direct addition of azide-functionalized polymers to C₆₀ is a simple and straightforward method widely used in literature for the preparation of fullerene polymers [6,45–47]. It is known to proceed

Table 1
Reaction conditions and yields for Fisher esterification of fullerene alcohol **1** and **2**.

Entry	Solvent	Reactor	Fullerene alcohol	Yield
I	Toluene	Dean–Stark apparatus	1	trace
			2	trace
II	Toluene/1-Chloronaphthalene	Dean–Stark apparatus	1	34%
			2	84%
III	Toluene/1-Chloronaphthalene	Soxhlet apparatus	1	38%
			2	85%
IV	Toluene/1-Chloronaphthalene	Home-made reactor	1	92%
			2	93%

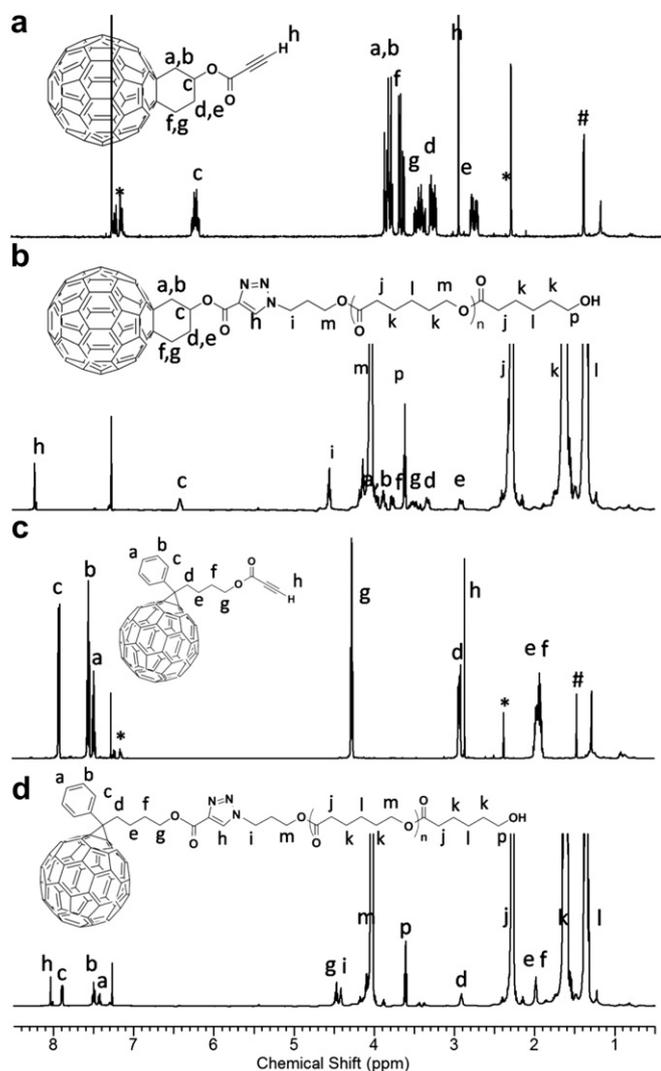


Fig. 2. ^1H NMR spectra of Fullerene01 (a), PCL-C₆₀I (b), Fullerene02 (c), and PCL-C₆₀II (d). The * and # denote the residual solvent of toluene and water, respectively.

with a less tendency toward multi-addition and crosslinking, providing sufficient control in the synthesis of fullerene polymers for most purposes. Nevertheless, well-defined structure, high C₆₀ functionality (~100%), and high molecular uniformity are highly desired for many physical studies, such as single crystal growth and

the validation of theory predictions on the phase behavior of shape amphiphiles [8,48]. Our approach offers a valuable alternative to the literature results by the possibility to prepare such model compounds by “click” chemistry.

The azide-functionalized PCLs were prepared from 3-bromo-1-propanol by ring opening polymerization of ϵ -caprolactone and subsequent nucleophilic substitution in a procedure similar to literature reports (see Supporting Information) [5]. The ring opening polymerization of ϵ -caprolactone catalyzed by Sn(Oct)₂ is known to proceed in a controlled fashion [49,50]. The presence of halogen functionality, such as chloro or bromo, does not interfere with the polymerization [5,43]. The polymer was obtained with a molecular weight of 3.6 kg/mol and a polydispersity of 1.18 as determined by size exclusion chromatography. The presence of bromo end-functionality is demonstrated by the triplet in the ^1H NMR spectrum at δ 3.48 ppm. After conversion to azide by stirring with sodium azide at 60 °C in DMF overnight, the peak completely shifts upfield to δ 3.39 ppm. The characteristic absorption band of azide in FT-IR spectrum is also evident at 2098 cm⁻¹ (see Supporting Information, Fig. S5). As a modular feature, the azide-functionalized PCL (PCL-N₃) (1 equivalent) was reacted with fullerenes (1.05 equivalents) under identical conditions to give PCL-C₆₀I and PCL-C₆₀II, respectively for Fullerene01 and Fullerene02. The “click” procedure was as simple as mixing the reactants with catalyst, degassing, and stirring at room temperature overnight (see Supporting Information). After chromatographic removal of excess fullerenes and residual catalyst followed by precipitation into methanol, PCL-C₆₀S were obtained as brown powders in high yields (85% and 86% for PCL-C₆₀I and PCL-C₆₀II, respectively).

The success of the reaction was evidenced by the complete disappearance of the characteristic absorption band of azide at 2098 cm⁻¹. The chemical structures were confirmed by ^1H NMR (Fig. 1), ^{13}C NMR (Fig. S4), and MALDI-TOF mass spectrometry (Fig. 3). The comparison of ^1H NMR spectra of fullerenes and corresponding fullerene polymers is shown in Fig. 2. For PCL-C₆₀I, the formation of a triazole ring was demonstrated by the sharp peak appearing at δ 8.23 ppm in the ^1H NMR spectrum, and the signal assignable to methylene protons adjacent to the azide shifts from δ 3.39 ppm completely to δ 4.56 ppm. The rest of the protons on Fullerene01 can be clearly visible at δ 6.42, 3.29, and 2.90 ppm, while some of them overlap with protons on the PCL backbone. For PCL-C₆₀II, the proton on the triazole ring can be seen as a sharp peak at δ 8.04 ppm, and the signal assignable to methylene protons adjacent to the azide shifts from δ 3.39 ppm completely to δ 4.47 ppm, which overlaps with the methylene group of the ester group on Fullerene02 (proton g). The other

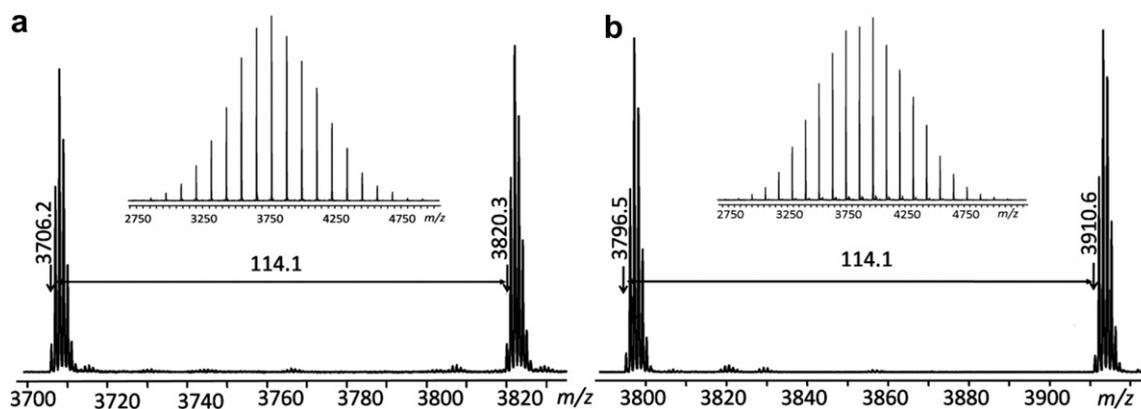


Fig. 3. MALDI-TOF mass spectra of PCL-C₆₀I (a), and PCL-C₆₀II (b). The insets are the corresponding overview of the spectra.

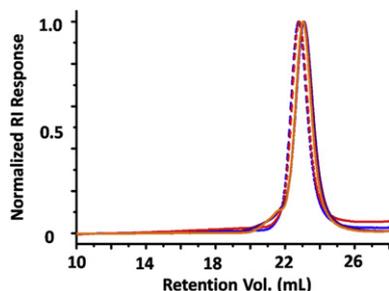


Fig. 4. SEC overlay of PCL-Br (dashed blue), PCL-N₃ (dashed red), PCL-C₆₀I (solid purple), and PCL-C₆₀II (solid orange).

protons on Fulleryne02 essentially remain at the same chemical shifts, at δ 7.90, 7.48, 2.91, and 1.71 ppm, respectively. In ¹³C NMR spectra of both samples (Fig. S4), the sp² carbons appear around δ 125–150 ppm, which are due to the presence of the C₆₀ cage in the polymer. In FT-IR spectra (Fig. S3), the characteristic sharp absorption at 527 cm⁻¹ from the vibration of C–C bonds on C₆₀ can also be seen. The most convincing evidence comes from MALDI-TOF mass spectrometry. The spectra are shown in Fig. 3. For both PCL-C₆₀I and PCL-C₆₀II, only a major single distribution was observed in addition to several very minor distributions. The *m/z* values of the major distribution match the calculated monoisotopic mass of the fullerene polymers very well. Since PCL-C₆₀I and PCL-C₆₀II have the same precursor PCL-N₃, the peak of maximum intensity for both samples are both found to be the 25-mer. The calculated monoisotopic mass for the 25-mer of PCL-C₆₀I is 3819.8 Da ([M₂₅·Na]⁺) and the observed *m/z* equals 3820.3. The experimental *m/z* for PCL-C₆₀II is 3910.6, which fits the calculated monoisotopic mass of 3909.9 ([M₂₅·Na]⁺) for the 25-mer. The minor distributions of very low intensity should be PCLs and/or PCLs fragments with different chain end-groups that are possibly generated during the ionization or post-source process. The clean MALDI-TOF mass spectra without signals of homopolymers and higher addition products are prime evidence of the products' high purity and high C₆₀ functionality. The chemical structures of PCL-C₆₀ fullerene polymers are thus unambiguously proven. There is only one C₆₀ per chain connected with the polymer in a well-defined linkage as proposed in the scheme. The polydispersity calculated from the MALDI-TOF spectra is 1.01 for both PCL-C₆₀I and PCL-C₆₀II, which is very narrow.

Fig. 4 shows the SEC overlay of PCL-Br, PCL-N₃, PCL-C₆₀I, and PCL-C₆₀II. The elution profile of both PCL-Br and PCL-N₃ is a monomodal, symmetric peak with relatively narrow molecular weight distribution (PDI = 1.18). Notably, although the attachment of a C₆₀ to the PCL chain significantly increases the overall molecular weight, the elution volumes of fullerene polymers remain essentially the same as that of PCL-N₃. The polydispersity determined by SEC is 1.09 and 1.03 for PCL-C₆₀I and PCL-C₆₀II, respectively, which is lower than that of the precursor PCL-N₃ (PDI = 1.18), but higher than that determined by MALDI-TOF mass spectrometry. This is because direct mass spectrometric analysis is known to underestimate the molecular weight and polydispersity of the materials [51]. In addition, there appears a high molecular weight shoulder in the SEC trace of PCL-C₆₀s. This is very likely due to the aggregation of PCL-C₆₀s in THF (a typical non-solvent for C₆₀), which is consistent with previous reports on fullerene polymers [52]. To verify that it is due to aggregate formations rather than multi-adducts, the samples were also analyzed by linear mode MALDI-TOF mass spectrometry since it generally has higher sensitivity than reflectron mode [53]. No high molecular weight impurities could be observed in this case (Fig. S8). Therefore, the

shoulder in SEC trace could only be attributed to the formation of aggregates.

3. Conclusions

In summary, we have successfully extended the scope of Fischer esterification to fullerene derivatives for the efficient synthesis of fullerynes including Fulleryne01 and Fulleryne02 in excellent yields. A non-typical solvent, 1-chloronaphthlene, was used as the reaction medium to increase the molar concentration of the reactants. A special reactor was designed to allow the continuous circulation of toluene to remove the water by azeotropic distillation and moisture adsorption with molecular sieves. These readily available fullerynes can serve as versatile building blocks in the modular and efficient construction of fullerene polymers, as demonstrated by the synthesis of PCL-C₆₀I and PCL-C₆₀II. These fullerene polymers possess well-defined structure and high degree of functionality of C₆₀ (~100%). They can serve as model compounds in the study of the physics of fullerene polymers. Relevant work currently under intense investigation in our group includes the phase behavior of shape amphiphiles and the use of self-assembly of polymers, such as single crystal growth and micellization, as templates to manipulate the ordered structure formation of C₆₀ in multiple dimensions across different length scales.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.07.026.

References

- [1] Kadish KM, Ruoff RS. Fullerenes: chemistry, physics, and technology. New York: Wiley-Interscience; 2000.
- [2] Martin N, Giacalone F. Fullerene polymers: synthesis, properties and applications. Weinheim: Wiley-VCH; 2009.
- [3] Hirsch A, Brettreich M. Fullerenes: chemistry and reactions. Weinheim; Great Britain: Wiley-VCH; 2005.
- [4] Weis C, Friedrich C, Mulhaupt R, Frey H. Macromolecules 1995;28(1):403–5.
- [5] Stoilova O, Jerome C, Detrembleur C, Mouithys-Mickalad A, Manolova N, Rashkov I, et al. Chem Mater 2006;18(20):4917–23.
- [6] Giacalone F, Martin N. Chem Rev 2006;106(12):5136–90.
- [7] Date RW, Bruce DW. J Am Chem Soc 2003;125(30):9012–3.
- [8] Glotzer SC, Horsch MA, Iacovella CR, Zhang ZL, Chan ER, Zhang X. Curr Opin Colloid Interface Sci 2005;10(5–6):287–95.
- [9] Zhang W-B, Li Y, Li X, Dong X, Yu X, Wang C-L, et al. Macromolecules 2011; 44(8):2589–96.
- [10] Lotz B, Kovacs AJ, Bassett GA, Keller A, Kolloid Z. Polym 1966;209:115–28.
- [11] Zheng JX, Xiong HM, Chen WY, Lee KM, Van Horn RM, Quirk RP, et al. Macromolecules 2006;39(2):641–50.
- [12] Chen WY, Li CY, Zheng JX, Huang P, Zhu L, Ge Q, et al. Macromolecules 2004; 37(14):5292–9.
- [13] Bhargava P, Tu YF, Zheng JX, Xiong HM, Quirk RP, Cheng SZD. J Am Chem Soc 2007;129(5):1113–21.
- [14] Bhargava P, Zheng JX, Li P, Quirk RP, Harris FW, Cheng SZD. Macromolecules 2006;39(14):4880–8.
- [15] Zhang WB, Tu Y, Ranjan R, Van Horn RM, Leng S, Wang J, et al. Macromolecules 2008;41(3):515–7.
- [16] Huisgen R. Angew Chem Int Ed 1963;2:565–98.
- [17] Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. Angew Chem Int Ed 2002; 41(14):2596–9.
- [18] Meldal M, Tornøe CW. Chem Rev 2008;108(8):2952–3015.
- [19] Fazio MA, Lee OP, Schuster DI. Org Lett 2008;10(21):4979–82.
- [20] Nierengarten JF, Iehl J, Oerthel V, Holler M, Illescas BM, Munoz A, et al. Chem Commun 2010;46(22):3860–2.
- [21] Li CH, Hu JM, Yin J, Liu SY. Macromolecules 2009;42(14):5007–16.

- [22] Steinmetz NF, Hong V, Spoerke ED, Lu P, Breitenkamp K, Finn MG, et al. *J Am Chem Soc* 2009;131(47):17093–5.
- [23] Inglis AJ, Pierrat P, Muller T, Brase S, Barner-Kowollik C. *Soft Matter* 2010;6(1):82–4.
- [24] Iehl J, Osinska I, Louis R, Holler M, Nierengarten JF. *Tetrahedron Lett* 2009;50(19):2245–8.
- [25] Iehl J, Nierengarten JF. *Chem Eur J* 2009;15(30):7306–9.
- [26] Zhang W-B. Soft fullerene materials: "Click" chemistry and supramolecular assemblies. Department of Polymer Science, Ph.D. Dissertation, Akron: The University of Akron, 2010.
- [27] Huisgen R. *Angew Chem Int Ed* 1963;2:633–45.
- [28] Padwa A. 1,3-Dipolar cycloaddition chemistry. New York: Wiley; 1984.
- [29] Jewett JC, Sletten EM, Bertozzi CR. *J Am Chem Soc* 2010;132:3688–90.
- [30] Neises B, Steglich W. *Angew Chem Int Ed* 1978;17(7):522–4.
- [31] Blush JA, Park J, Chen P. *J Am Chem Soc* 1989;111(24):8951–3.
- [32] Nagel M, Hansen HJ. *Helv Chim Acta* 2000;83(5):1022–48.
- [33] Fischer E, Speier A. *Chem Ber* 1895;28:3252–8.
- [34] Otera J. Esterification: methods, reactions and applications. Weinheim; Cambridge: Wiley-VCH; 2003.
- [35] Pirrung MC. The synthetic organic chemist's companion. Hoboken, NJ: Wiley-Interscience; 2007.
- [36] Louisiana State University Macromolecular Studies Group Server. <http://macro.lsu.edu/HowTo/solvents/toluene.htm> (accessed July 2011).
- [37] Hadjichristidis N, Iatrou H, Pispas S, Pitsikalis M. *J Polym Sci. Part A Polym Chem* 2000;38(18):3211–34.
- [38] Uhrig D, Mays JW. *J Polym Sci. Part A Polym Chem* 2005;43(24):6179–222.
- [39] Zhou L, Gao C, Zhu D, Xu W, Chen FF, Palkar A, et al. *Chem.Eur.J* 2009;15(6):1389–96.
- [40] Kai WH, Hua L, Zhao L, Inoue Y. *Macromol Rapid Commun* 2006;27(19):1702–6.
- [41] Peng QY, Kang F, Li JA, Yang XL. *Chin Sci Bull* 2010;55(29):3279–82.
- [42] Kai W, Hua L, Dong T, Pan P, Zhu B, Inoue Y. *Macromol Chem Phys* 2008;209(12):1191–7.
- [43] Kai WH, Hua L, Dong TL, Pan PJ, Zhu B, Inoue Y. *J Appl Polym Sci* 2008;107(6):4029–35.
- [44] Kai WH, Hua L, Dong TL, Pan PJ, Zhu B, Inoue Y. *Macromol Chem Phys* 2008;209(1):104–11.
- [45] Hawker CJ. *Macromolecules* 1994;27(17):4836–7.
- [46] Hawker CJ, Saville PM, White JW. *J Org Chem* 1994;59(12):3503–5.
- [47] Hawker CJ, Wooley KL, Frechet JMJ. *Chem Commun*; 1994:925–6 (8).
- [48] Iacovella CR, Horsch MA, Zhang Z, Glotzer SC. *Langmuir* 2005;21(21):9488–94.
- [49] Kowalski A, Duda A, Penczek S. *Macromol Rapid Commun* 1998;19(11):567–72.
- [50] Penczek S, Duda A, Kowalski A, Libiszowski J, Majerska K, Biela T. *Macromol Symp* 2000;157:61–70.
- [51] Liu XM, Maziarz EP, Heiler DJ, Grobe GL. *J Am Soc Mass Spectrom* 2003;14(3):195–202.
- [52] Taton D, Angot S, Gnanou Y, Wolert E, Setz S, Duran R. *Macromolecules* 1998;31(18):6030–3.
- [53] Guttman CM. Mass spectrometry. *Encyclopedia of polymer science and technology*. Wiley-Interscience; 2001.