Diamond Rings or Dumbbells: Controlling the Structure of Poly(ethylene glycol)−Fullerene [60] Adducts by Varying Linking Chain Length

Hin Chun Yau, Mustafa K. Bayazit, Joachim H. G. Steinke, and Milo S. P. Shaffer*

Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, U.K.

Supporting Information

ABSTRACT: Fullerene [60] (C60) and poly(ethylene glycol) (PEG) adducts were prepared via 1,3-dipolar cycloaddition of bis-azido-terminated linear PEG (N3-PEG-N3) and C60. While long chain length PEGs (Mn = 1000 and 3350 Da) yielded the cyclic diamond ring structures (C60PEG1000 and C60PEG3350), short-chain PEG (Mn = 200 Da) yielded a telechelic dumbbell structure (C60-PEG200-C60). Both dumbbell and diamond ring structures were characterized by MALDI-TOF-MS, 1H NMR, FTIR, UV−vis, and elemental analysis (EA). The results highlight the structural dependence of the PEG−C60 adducts on the chain length of the azido-terminated polymer, a factor previously neglected.

INTRODUCTION

Fullerene [60] (C60) has been a focus of scientific attention since its discovery in the mid-1980s, attracting particular interest in its rich chemistry with electron-rich reactive species including carbenes, nitrenes, and azides. The strong electron-accepting character of fullerenes and the versatility of their grafting chemistry have motivated their incorporation in diverse applications, including organic photovoltaics, as antioxidants, and as MRI agents. In many contexts, especially bulk heterojunction solar cells, fullerene’s highly hydrophobic nature has a deterministic effect on phase behavior in polymer blends. However, the low solubility of C60 in common solvents limits direct use in many circumstances. To enhance the compatibility and processability, C60 has been attached to a wide range of polymers, in many different architectures, including “pear necklace” main chain, side chain pendant, and telechelic configurations; the properties of various polymer blends incorporating C60 polymer adducts have been tested. Both mono- and double-fullerene-terminated PEGs have received particular attention as simple model systems due to their linearity and ease of preparation. PEG is an appealing backbone for C60 end-capping followed three steps: (i) the conversion of the terminal PEG hydroxyl to chloride with thionyl chloride, (ii) the formation of N3-PEG-N3 using sodium azide, and (iii) the 1,3-dipolar cycloaddition reaction of PEG-N3 with C60 to yield dumbbells. Although a well-defined synthetic protocol has been reported, the existing characterization appears ambiguous since it mainly relies on UV−vis analysis of the resulting fullerene−polymer adducts. Other core characterization data, particularly NMR and mass spectrometry characterization, have not been reported, although they are vital in determining the product geometry. In addition to dumbbells, a range of monofullerene polymer adducts, including some based on PEG, have been prepared by using end-protected polymers to limit grafting to single fullerenes only. This paper explores the established “PEG dumbbell” reaction using different molecular weight PEG chains to control both mono- and bis-fullerene end-capped poly(ethylene glycol) (PEG) adducts. The distinct nature of these products was established by fully characterizing both starting materials and products using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), nuclear magnetic resonance spectroscopy (1H NMR), Fourier transform infrared spectroscopy (FTIR), and ultraviolet visible spectroscopy (UV−vis).

RESULTS AND DISCUSSION

The C60-PEG200-C60 dumbbell was synthesized via the 1,3-dipolar cycloaddition reaction of N3-PEG-N3 with C60.
following a modified literature procedure.\textsuperscript{17} Unexpectedly, longer PEG chains produced diamond ring structures ($\text{C}_{60}$PEG\textsubscript{3350} and $\text{C}_{60}$PEG\textsubscript{1000}). In a typical reaction, bis-azido-terminated PEGs dissolved in o-dichlorobenzene (o-DCB) were treated with 20 equiv of C\textsubscript{60} at 140 °C for 24 h, followed by work-up with solvent extraction or column chromatography (see Experimental Section). Fewer equivalents of C\textsubscript{60} (2.2 equiv, as in the literature procedure) produced similar results; C\textsubscript{60} content was increased in an attempt to favor dumbbell formation. Three new PEG-C\textsubscript{60} adducts (1, 2, and 3) were obtained in 45, 59, and 86% yields, respectively (Scheme 1). The structural assignments were based on MALDI-TOF-MS data and \textsuperscript{1}H NMR spectra.

The PEG\textsubscript{3350}-C\textsubscript{60} adduct was selected for the most detailed characterization, as its long PEG chain gave the best solubility. Poor solubility complicated some aspects of spectroscopic analysis (especially NMR, see below) in the case of the PEG\textsubscript{1000} and PEG\textsubscript{200} fullerene adducts. In addition, the PEG\textsubscript{3350}-C\textsubscript{60} adduct is well suited for comparison with the existing literature reports\textsuperscript{12} of similar fullerene adducts prepared with PEG\textsubscript{2000} and PEG\textsubscript{3000}. The initial Cl-PEG-Cl and N\textsubscript{3}-PEG-N\textsubscript{3} derivatives were prepared following the procedure reported by Goh et al.\textsuperscript{17} The electronegativity difference of nitrogen compared to oxygen allows PEG-azide to be identified by \textsuperscript{1}H NMR, since the $\alpha$-proton chemical shift for the N\textsubscript{3}-PEG-N\textsubscript{3} appears at 3.42 ppm (lit. 3.36 ppm)\textsuperscript{20} compared to 3.75 ppm for OH-terminated PEG (see Supporting Information Figures S1−S3 for \textsuperscript{1}H NMR of HO-PEG\textsubscript{3350}-OH, Cl-PEG\textsubscript{3350}-Cl, and N\textsubscript{3}-PEG\textsubscript{3350}-N\textsubscript{3}, respectively). The transformation of chlorides into azides is confirmed by the presence of azido stretching ($\nu$(asymmetric N\textsubscript{3}) 2095 cm\textsuperscript{-1}) in FTIR (Figure 1).\textsuperscript{17} Further evidence for successful PEG end-group transformation is provided by MALDI-TOF-MS (see Supporting Information Figures S1−S3 for full MALDI-TOF spectra of Cl-PEG\textsubscript{3350}-Cl and N\textsubscript{3}-PEG\textsubscript{3350}-N\textsubscript{3}, respectively); these data are especially helpful for following the transformation from hydroxyl to chloride due to the similar electronegativity of oxygen and chlorine which makes \textsuperscript{1}H NMR assignment less conclusive. Isolated N\textsubscript{3}-PEG-N\textsubscript{3} was subsequently reacted with C\textsubscript{60} to afford C\textsubscript{60} end-capped PEG adducts.\textsuperscript{17}

Initially, following the literature protocol,\textsuperscript{17} THF extraction was used to isolate the PEG\textsubscript{3350}-C\textsubscript{60} adduct from the crude mixture (60 mL of THF per 1 g of C\textsubscript{60}). However, weak absorption bands, characteristic\textsuperscript{21} for pristine C\textsubscript{60} at ca. 2000−2500 cm\textsuperscript{-1} in the FTIR spectrum of the PEG\textsubscript{3350}-C\textsubscript{60} adduct (THF extracted) indicated the continued presence of nongrafted C\textsubscript{60} (Figure 1), presumably due to the modest solubility of pristine C\textsubscript{60} in THF (0.06 mg mL\textsuperscript{-1}).\textsuperscript{22} Instead, after THF extraction, the PEG\textsubscript{3350}-C\textsubscript{60} product was further extracted with water, exploiting the solubility imparted by its long hydrophilic chain. The FTIR spectrum of water extracted PEG\textsubscript{3350}-C\textsubscript{60} adduct (Figure 1) confirmed removal of unreacted C\textsubscript{60}. The FTIR analysis of the PEG\textsubscript{3350}-C\textsubscript{60} adduct (water extracted) also confirmed successful azide addition by the complete loss of the...
characteristic azido absorption band at 2095 cm$^{-1}$ and the appearance of a medium intensity band at 1720 cm$^{-1}$ which can be attributed to the aziridine ring (C–N) stretch (Figure 1). Free aziridine rings show a (C–N) stretch at around 1650 cm$^{-1}$, but the strain induced by the fullerene shifts the peak to higher wavenumber. The UV–vis spectrum of pure C$_{60}$ shows characteristic UV–vis absorption maxima at 336 and 409 nm, while the PEG itself is featureless in the range measured (Figure 2). The UV–vis spectrum of the PEG$_{3350}$–C$_{60}$ adduct showed strong absorbance at around 324 nm, confirming successful incorporation of C$_{60}$ onto PEG. Note that the shift to shorter wavelength is more consistent with the formation of a double addition to the fullerene than a monooadduct.$^{24,28}$

Further evidence for the formation of the PEG$_{3350}$–C$_{60}$ adduct is provided by $^1$H NMR (Figure 3). Compared to the parent polymer (HO-PEG$_{3350}$-OH), the $^1$H NMR spectrum of the PEG$_{3350}$–C$_{60}$ adduct shows two new signals at 4.45 and 3.80 ppm, associated with the new bond formation. Because of the conjugated, though not superaromatic, $\pi$-system, protons closer to the C$_{60}$ surface are deshielded.$^{25}$ Hence, the most deshielded new signal, at 4.45 ppm, is assigned to $\alpha$-protons and the other signal at 3.80 ppm to the $\beta$-protons (Figure 3). Despite the new signals relating to the covalently functionalized C$_{60}$, the overall structure of the adduct is not determined. The two possible geometries include either a bis-fullerene adduct with a single PEG chain connecting two fullerenes (dumbbell) or a monofullerene adduct with both ends of the PEG chain attached to the same fullerene (diamond ring). Unfortunately, $^1$H NMR does not resolve the two geometries due to the lack of protons on fullerene. No good $^{13}$C NMR data were obtained due to the long relaxation times involved.$^{26}$

Overall, the $^1$H NMR data, supported by FTIR and UV–vis, indicate successful covalent addition of N$_3$–PEG$_{3350}$–N$_3$ to C$_{60}$. However, MALDI-TOF-MS was used to confirm that the diamond ring (C$_{60}$–PEG$_{3350}$) geometry formed in preference to the dumbbell (C$_{60}$–PEG–C$_{60}$) structure; a low laser intensity (90 mW) was used to minimize any fragmentation of the polymer chain or dissociation of terminal C$_{60}$ molecules. The mass spectrum of the PEG$_{3350}$–C$_{60}$ adduct shows a Gaussian distribution of positively charged ions ranging from 2297 to 4720 m/z (Figure 4). Taking an average of 65 ethylene oxide repeating units as a representative example for the chain (equivalent to the $M_n$ derived from MALDI,$^{27}$ Figure 4), the theoretically calculated masses ([M + Na]$^+$) for diamond ring (C$_{60}$–PEG$_{3350}$) and dumbbell (C$_{60}$–PEG–C$_{60}$) can be calculated as 3660.7 and 4380.7 Da, respectively. It is clear from the mass spectrum that the reaction of N$_3$–PEG$_{3350}$–N$_3$ with excess C$_{60}$ does not yield a dumbbell structure (C$_{60}$–PEG$_{3350}$–C$_{60}$) or a double PEG chain structure (PEG$_{3350}$–C$_{60}$–PEG$_{3350}$); rather, the data indicate the formation of a diamond ring structure (single fullerene), at around 720 Da (C$_{60}$ = 720 Da) less than that of the theoretically calculated mass of C$_{60}$–PEG$_{3350}$–C$_{60}$.

**Figure 2.** UV–vis spectra of PEG$_{3350}$ and PEG–C$_{60}$ adducts and pristine C$_{60}$ recorded in toluene.

**Figure 3.** $^1$H NMR of PEG$_{3350}$ derivatives and PEG$_{3350}$–C$_{60}$ adduct.

![Diagram](https://via.placeholder.com/150)
Figure 4. MALDI-TOF of the PEG3350-C60 diamond ring. The offset high/low intensity patterns are formed by the polydispersed polymer with either Na+ or K+ as counterions.

ranging from m/z 2297 to 4720 (Figure 4) indicates that the observed mass values are not related to fragmentation of a dumbbell structure, as the molecule retains the full chain length distribution of the initial PEG. This finding is further supported by elemental analysis (EA) of the PEG3350-C60 adduct which has composition C (60.23 wt %) and H (7.25 wt %), with a C:H weight ratio of 8.31; the calculated composition for the diamond ring structure (65 repeating units, number-average of the distribution from 2297 to 4720 m/z) is C (63.35 wt %) and H (7.31 wt %), with a C:H ratio of 9.67; the calculated value for the dumbbell structure is C (69.41 wt %) and H (6.10 wt %), with a C:H ratio of 11.38. The calculated value for the bis-PEG/C60 adduct (PEG3350-C60-PEG3350) is C (59.27 wt %) and H (8.14 wt %), with a C:H ratio of 7.28. Only the diamond ring ratio is in good agreement with the experiment.

The MALDI and EA confirm the formation of a monofullerene-substituted PEG3350-C60 adduct. Other monofullerene-substituted linear PEG chains bearing monoazide (C60-PEG3350-NH2), amine (C60-PEG3350-NH2), or hydroxyl (C60-PEG3350-OH) end groups can also be ruled out as follows. While these alternatives vary only slightly in mass, a detailed comparison of the possible masses is only consistent with a diamond ring structure (see Supporting Information Table S1 for the calculated monoisotopic masses for C60-PEG3350-NH2, C60-PEG3350-NH2, and C60-PEG3350-OH). Furthermore, the experimental isotopic pattern for the 65 ethylene oxide repeating unit peak ([M + Na]+ = 3660.7 Da) closely matches the theoretical calculated monoisotopic mass of the diamond ring (Figure 5). The FTIR (Figure 1) excludes the formation of a monoisotopic pattern for the primary peak of the PEG3350-C60 adduct with 20 ethylene oxide repeating units (the most intense signal in the starting PEG3350 mass distribution) ([M + Na]+ = 1679.5) was consistent with the formation of diamond ring structure (see Supporting Information Figure S9 for full MALDI-TOF spectrum of PEG1000-C60).

The only difference between C60-PEG1000-C60 and C60-PEG3350-C60 is the length of the polymer backbone. However, the longer PEG chain offers a benefit in purification. As mentioned above, THF alone was not sufficient to remove all unreacted fullerene. Having a relatively long PEG chain in the fullerene/PEG adducts (PEG3350) makes the adduct water-soluble, simplifying the complete removal of free fullerene since pristine C60 is insoluble in water. Unlike the longer PEG-C60 analogues (C60-PEG1000-C60 and C60-PEG3350-C60), the PEG200-C60 adduct was not easily isolated by extraction in water or THF. The combination of the short PEG200 chain and bis-addition of fullerene (see below) makes the adduct insoluble in both water and THF; instead, unreacted fullerene was removed by column chromatography using tolune as eluent. In contrast to the PEG3350 and PEG1000/fullerene products, the mass spectrum of the isolated PEG200-C60 adduct showed no peaks related to fullerene formation, around the theoretically expected mass range (975.1 m/z for four ethylene oxide repeating units). Instead, a Gaussian mass distribution of positively charged ions ranging from 1100 to 2300 m/z was observed, consistent with the formation of dumbbell structure (C60-PEG200-C60) (see Supporting Information Figure S8 for full MALDI-TOF spectrum of C60-PEG200-C60). The UV-vis spectrum (Figure 2) for C60-PEG200-C60 shows no shift in the primary fullerene absorbance, consistent with the addition of a single PEG chain to each fullerene, in this case, rather than the double PEG addition/diamond ring structure.24,28

Figure 5. Experimental isotopic pattern for the primary peak of the PEG3350-C60 adduct (top) compared with the simulated monoisotopic pattern for PEG3350-C60 diamond ring with 65 ethylene oxide repeating units (bottom), both including [Na]+.
It appears that the PEG chain length determines the molecular structure of the resulting PEG-C_{60} adducts. Simple space filling models of C_{60}-PEG-C_{60} and C_{60}-PEG based on four ethylene oxide repeating units demonstrate that the PEG_{200} chain is insufficiently long enough to wrap around the fullerene for trans-I addition (the conformation requiring longest PEG chain, Figure 6). Other regioisomers may be unfavorable due to the relatively bulky PEG substituents which may hinder the addition at an adjacent position. In this case, with diamond ring formation suppressed, the dumbbell is the favored conformation. Previous literature suggests that the use of large excess of monoprotected linear polymer favors the addition of two or more polymer chains to each fullerene (10:1 equiv of grafting polymer to C_{60}). In the current experiment, excess C_{60} (1:10 relative to azide chain ends) was used in an attempt to favor dumbbell formation. Nevertheless, the diamond ring structure was favored when the PEG chain was sufficiently long. Most examples of more than one polymer attached to fullerene in the literature are synthesized via multiple azomethine ylide addition of independent substituents. A recent example suggests that the use of large excess of monoprotected linear polymer favors the addition of two or more polymer chains to each fullerene (10:1 equiv of grafting polymer to C_{60}).

The main focus of current paper is to demonstrate the geometrical control of the resultant structure of the fullerene derivative via telechelic reactive groups. This new type of fullerene diamond ring structure is potentially relevant to polymer blend and organic bulk heterojunction photovoltaics, as a means to increase the fullerene loading or control the critical phase separation of the charge carrying components. Fullerene aggregation remains a major challenge in the polymer/fullerene active layer in bulk heterojunctions (BHJ) photovoltaics (PV). Controlling the resultant structure of the fullerene derivative may provide an alternative route to enhance current fullerene-based PV performance since dumbbell and diamond ring structures are believed to have different degrees of aggregation. If dumbbells are specifically required, more rigid spacers such as polythiophene or polyphenylene might restrict the formation of the diamond ring structure, as well as providing specific electronic function.

**EXPERIMENTAL SECTION**

**Materials and Methods.** C_{60} (purity >99%) was obtained from SES Research, Houston, TX. PEG with M_n = 200, 1000, and 3350 Da were purchased from Sigma-Aldrich and azeotropically dried overnight using toluene. Azeotropic distillation was performed with Dean–Stark trap and reflux condenser under N_2. As water is denser than toluene, residual water is trapped in the bottom of the Dean–Stark trap. Sodium azide (99%), tetrabutylammonium iodide (≥99.5%), toluene (HPLC grade), anhydrous dichlorobenzene (o-DCB), anhydrous dimethylformamide (DMF), and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (≥98%) were obtained from Sigma-Aldrich. Thiouyl chloride (≥99.5%) was obtained from Fluka. All other solvents were purchased from VWR and used without further purification.

H NMR spectra were acquired on a Bruker 400 MHz NMR spectrometer operating at 9.4 T. The recycle delays for all spectra were one second, with 16 scans per spectrum unless otherwise specified. Fourier transform infrared spectra were recorded on a PerkinElmer ATR Spectrum 100 spectrometer with a resolution of 4 cm\(^{-1}\) and 32 scans per spectrum. Elemental analysis was determined by Mr. Stephen Boyer at London Metropolitan University, Science Centre, Elemental-Analysis service. UV–vis spectra were recorded on PerkinElmer Lambda 950 spectrometer in toluene. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) data were acquired on a Waters MICROMASS MALDI micro MX with a nitrogen laser at 333 nm in the positive reflection mode with delayed extraction. Samples (1–2 mg) dissolved in toluene (10 μL) were added to the mixture of 10 μL of predissolved matrix (10 mg/mL DCTB in THF) and 3 μL of NaI (3 mg/mL in THF). Small aliquots of mixture were loaded on to a stainless steel target plate and allowed to air-dry at room temperature. The instrument was calibrated in the range of 500–5000 Da using a standard poly(ethylene glycol). The simulated isotopic peak patterns were constructed using online software MoE - Molecular Mass Calculator v2.02 (http://rna-mdb.ca/albany.edu/RNAmods/masspec/mol.htm).

**Synthetic Procedures.** Synthesis of Cl-PEG-Cl and N3-PEG-N3. Cl-PEG-Cl and N3-PEG-N3 were synthesized following the literature procedure reported by Goh et al. In brief, the bis-hydroxyl-terminated PEG was first converted to bis-chloro-terminated PEG (Cl-PEG-Cl) by reaction with thionyl chloride. The Cl-PEG-Cl was then reacted with sodium azide to afford bis-azido-terminated PEG (N3-PEG-N3).

Synthesis of the C_{60} Terminated PEG-Molten Diamond Ring (C_{60}-PEGSSSO). Azido-terminated PEG_{3350} (0.1 g, 1 equiv) was dissolved in 15 mL of o-dichlorobenzene in a two-necked 50 mL round-bottom flask fitted with a condenser and connected to a vacuum line. C_{60} (0.43 g, 20 equiv) was dissolved in 20 mL of o-dichlorobenzene and transferred into a pressure equalizing dropping funnel and fitted to the round-bottom flask. The C_{60} solution was then added dropwise into the stirring PEG solution to ensure the mixture...
was mixed thoroughly. Once addition of azide was completed, the mixture was then heated to 140 °C and stirred for 24 h. Solvent was evaporated in vacuo, and 25 mL of THF was added to the remaining solid. The THF solution was stirred at room temperature overnight and filtered under gravity to yield a dark brown solid. The solid was then dissolved in 20 mL of water to give a yellow solution and unreacted C60 was filtered off under gravity. The water was evaporated in vacuo, and the solid was then freeze-dried in vacuo (liquid nitrogen, 0.11 mbar, overnight) to yield a dark brown solid CPEG3350 (0.08 g, 86%). Characterization data for CPEG3350: Rf = 0.26 toluene/methanol (9/1 v/v). 1H NMR (400 MHz, CDCl3, δ 4.48 (t, 4H, J = 4 Hz, C60-CH2-CH2-CH3), 3.80 (t, 4H, J = 4 Hz, C60-CH2-CH2-O-) 3.67 (m, 292H, main PEG) ppm. FT-IR (ATR) ν/cm−1: 3462, 2859, 2871, 1728, 1468, 1361, 1342, 1281, 1242, 1150, 1102, 1062, 961, and 843. MALDI-TOF m/z: C150H290O20N2Na [M + Na]+ calc 3660.7310; found 3660.9 Da. EA calcd for C192H264O65N2: C, 63.33; H, 7.31; N, 0.77; O, 28.58. Found: C, 60.23; H, 7.25; N, 0.90; O, 31.62. All values are given as percentages.

Synthesis of the C60-Terminated PEG1000 Diamond Ring (CPEG1000). The C60-terminated PEG1000 was synthesized following the same procedure described above for CPEG3350. The resulting crude product after solvent removal was extracted by THF (3×) since it was not water-soluble. Removal of THF in vacuo afforded a dark brown solid CPEG1000 (0.056, 59%). Characterization data for CPEG1000: Rf = 0.34 toluene/methanol (9/1 v/v). FT-IR (ATR) ν/cm−1: 3391, 2972, 2877, 1729, 1463, 1431, 1384, 1353, 1292, 1249, 1184, 1105, 1044, 954, 856, and 752. MALDI-TOF m/z: C192H264O65N2Na [M + Na]+ calc 3661.7515; found 3661.9 Da. EA calcd for C192H264N2O65: C, 63.33; H, 7.31; N, 0.77; O, 28.58. Found: C, 60.23; H, 7.25; N, 0.90; O, 31.62. All values are given as percentages.

**REFERENCES**

(15) Tai, Q.; Li, J.; Liu, Z.; Sun, Z.; Zhao, X.; Yan, F. J. Mater. Chem. 2011, 21, 6848.

**ASSOCIATED CONTENT**

Supporting Information

Full MALDI-TOF-MS and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: m.shafer@imperial.ac.uk (M.S.P.S).

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors commemorate the late Dr. Joachim H. G. Steinke (1964–2013) for his contribution to this work and to the polymer chemistry field. We acknowledge the EPSRC for the EPSRC research grant EP/G007314/1 and the EPSRC UK National Mass Spectrometry Service at Swansea. M.K.B. is particularly grateful to the Scientific and Technological Research Council of Turkey (TUBITAK) for postdoctoral research permission.