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Synthesis and Characterization of C_{60} End-Capped Poly(ethylene oxide) Stars

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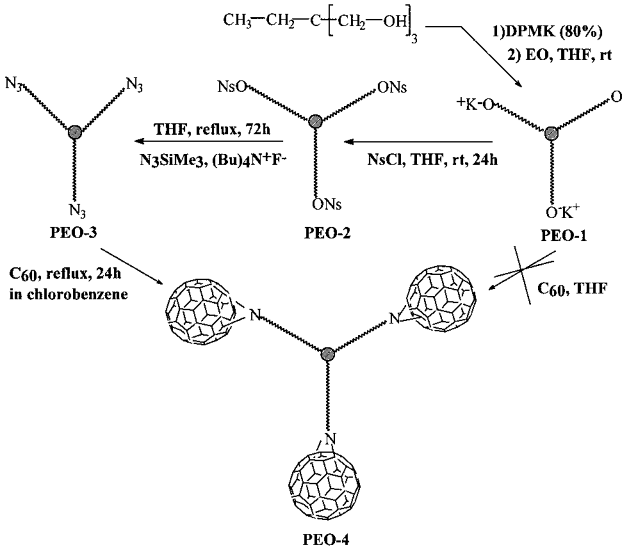
ABSTRACT: A C_{60} derivatized triarm poly(ethylene oxide) copolymer was synthesized and characterized. The soluble polymer produced spread at aqueous interfaces to form highly expanded fluid Langmuir monolayers. The onset area of 1300 Å^2/arm is likely due to the polymer disrupting cohesion between C_{60} units. Compression/expansion studies revealed a significant elastic region, beyond which the C_{60} units condensed, and a compact rigid and irreversible monolayer formed.

There are a number of recent reports dealing with the synthesis of C_{60} derivatized polymers, either by incorporating C_{60} into the backbone of polymer chains[1] or by attaching C_{60} on tailor-made functional polymers.[2] One goal of the fullerenation of polymeric materials is to combine the processability of macromolecules with the interesting physical properties of C_{60}.[3]

The polymer backbones examined to date include polystyrene, poly(methyl methacrylate), polyethylene, polynorbornene, polycarbonates, aliphatic polyesters, and even dendritic macromolecules. A hydrophilic backbone such as poly(ethylene oxide) (PEO), end-functionalized with C_{60}, which is highly hydrophobic, has been recently considered by Mathis and co-workers.[4] These authors tried to deactivate the alkoxides of "living" linear monofunctional PEO chains onto C_{60} in order to prepare star molecules with a fullerenated core. This method, however, was not quantitative since many ungrafted PEO chains were present. Arranging well-defined PEO chains within a star structure of precise functionality and end-capping the star arms with C_{60} can lead to fullerenated macromolecules in which the electronic and electrochemical properties of C_{60} are retained, as has been reported in the case of hexaarmed C_{60} end-capped polystyrene stars.[2k]

We report the preparation of C_{60} star PEO polymer through a three-step reaction starting from a well-defined tri-arm star PEO of controlled molar mass and narrow polydispersity. The aim of obtaining such amphiphilic polymers is to investigate their behavior broadly as amphiphiles and specifically in monolayers since the PEO part is expected to disorder the C_{60}, leading to fluid monolayers. Initial Langmuir monolayer results are presented.

Scheme 1. Synthetic Route to C_{60} End-Functionalized Triarmed PEO Star (EO, ethylene oxide; DPMK, $(Ph)_2CH^-K^+$; NsCl, $O_2NC_6H_4SO_2Cl$; rt, Room Temperature)



The synthetic route to the C_{60} end-functionalized tri-arm PEO star is shown in Scheme 1. The "living" anionic polymerization of ethylene oxide using 1,1,1-tris(hydroxymethyl)propane as trifunctional precursor in order to prepare well-defined PEO stars was already reported.[5] The determination of the actual molar mass of the stars was carried out by coupling a light scattering detector to a size exclusion chromatography (SEC) line in an aqueous medium and by spectroscopic measurements using ^{1}H NMR or UV.[5] In the present work, we used a 6000 g mol^{-1} star-shaped PEO.

Attempts to end-cap PEO-1 with C_{60} directly after completion of the polymerization process were unsuccessful; such reactions were previously carried out on linear PEO's by Mathis who came to the conclusion that the deactivation of oxanions by C_{60} is not controlled because of the occurrence of electron transfer.[4] A three-step sequence was then designed for the selective attachment of C_{60} to the PEO star branch ends (Scheme 1). Azide-containing polymers are reported to react selectively with C_{60} through a monoaddition reaction without noticeable side reactions.[2f,g,3−6] The preparation of a tri-arm PEO end-capped with azide function (PEO-3, Scheme 1) was then attempted. The required azidomethyl PEO star was obtained from the transformation of the PEO alkoxides into 4-nitrobenzenesulfonate (nosylate) groups followed by the substitution of the latter by azide functions (Scheme 1). The first step was carried out in THF using a 12-fold excess of commercially available 4-nitrobenzenesulfonyl chloride (NsCl) added dropwise to the solution of the tris-alkoxide PEO star. The resulting polymer (PEO-2) was recovered by two successive precipitations into a large excess of cold diethyl ether (yield = 70%). The complete replacement of the alkoxide functionality by nosylate was monitored by IR and NMR spectroscopies: the ^{1}H NMR spectrum of PEO-2 in a CD_2Cl_2 solution showed no signal at 4.3 ppm due to OH protons and the presence of two signals due to the nosylate protons at 8.2 and 8.5 ppm.

The azidation reaction was performed in THF, the nosylated PEO star polymer being allowed to react with both tetrabutylammonium fluoride (TBAF) and distilled trimethylsilyl azide (both in 9 molar excess) for 72 h under constant stirring at 70 °C. The disappearance of the protons, due to the nosylate in the NMR spectrum of the azido methyl PEO star sample as well as the appearance of the IR band at 2200 cm^{-1} characteristic of the azide functionality, attested to the occurrence of this modification step (yield: 80% after two successive precipitations in diethyl ether). The SEC trace of the recovered polymer PEO-3, obtained from either a THF solution or from a 1/1 v/v mixture of water/methanol, was basically the same as that of the starting PEO-1.

The coupling reaction between C_{60} and PEO-3 defines the final step in the synthesis of fullerene-containing PEO. The triazide PEO-3 was allowed to react with a 5-fold excess of C_{60} per azide function in a refluxing chlorobenzene solution for 24 h. The starting magenta solution turned to dark brown as conversion took place. After removal of the solvent under vacuum, THF was added to solubilize the star polymer PEO-4. The insoluble excess of C_{60} was filtered off and the THF solution was precipitated in cold diethyl ether, yielding a brown powder. The product was purified by repeated reprecipitations from chloroform into diethyl ether. During the dissolution process, the $CHCl_3$-insoluble materials were removed by filtration. The obtained polymer (yield = 30%) was found to be soluble in chlorinated solvents such as chloroform and chlorobenzene as well as in THF and toluene. Various techniques were used to confirm the covalent attachment of C_{60} to the PEO star (FTIR, NMR, and UV spectroscopies, SEC, and thermogravimetric analysis).

The FTIR spectrum of the fullerenated polymer showed the complete disappearance of the band at 2020 cm^{-1} due to the azide functionality and the appearance of a very weak band at 520 cm^{-1} characteristic of the vibration of fullerenes.

In the ^{13}C NMR, a signal at 29 ppm, absent in the parent azide polymer, was observed. This resonance can be assigned to the amino carbon CH_2-N, present in PEO-4 and formed after grafting of C_{60}. Some of the NMR spectroscopy data were found to depend on the solvent used (C_6D_6 and $CDCl_3$), likely due to the amphiphilic character of the C_{60}-derivatized PEO star; the signal at 29 ppm was indeed not detected in chloroform but was reproducibly present in benzene. Following an earlier report by Fréchet and Gitsov on tetraarmed PEO stars end-capped with hydrophobic dendritic wedges,[7] this effect can be correlated with conformation changes occurring as a function of the solvent used; being insoluble in $CDCl_3$, the C_{60} moieties tend to be enveloped by the PEO arms and can collapse in the center of a micelle. To our surprise, no resonance due to unsaturated carbon of C_{60} atoms could be detected in the aromatic region (130−150 ppm).

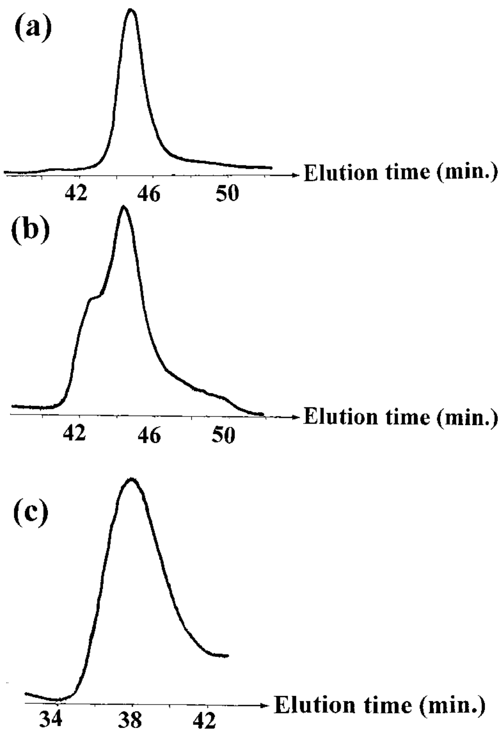


Figure 1. SEC traces: (a) triazide star PEO-3 in THF; (b) triarmed $C_{60}-$PEO-4 in THF; (c) triarmed $C_{60}-$PEO-4 in chlorobenzene.

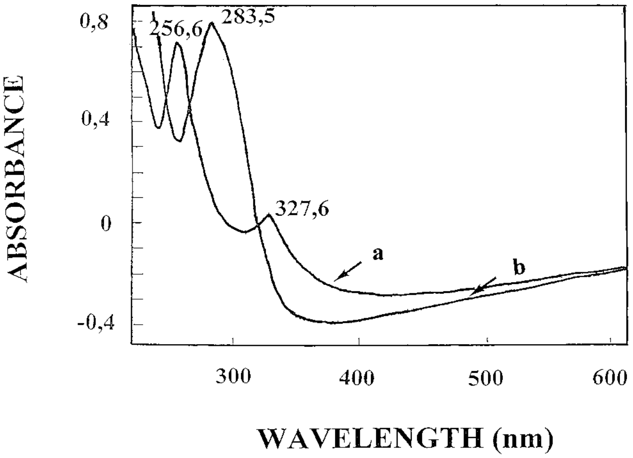


Figure 2. UV/vis spectrum in THF of triarmed $C_{60}-$PEO-4 (a) and triazide star PEO-3 (b).

Additional information about the monoaddition of C_{60} to the azido−PEO is given by the SEC trace of the fullerenated polymer (Figure 1). While in a solvent such as THF, the SEC trace showed a multimodal distribution, probably because of the intermolecular aggregation of several C_{60} moieties.[4] The SEC trace in chlorobenzene, however, revealed a single peak with a polydispersity index of 1.15, providing the evidence of selective cycloaddition without the occurrence of cross-linking.

The UV−vis absorption spectra (Figure 2) for the THF solutions of $C_{60}-$PEO (PEO-4) and the parent azido polymer (PEO-3) differed in the presence of a band at 328 nm (which is a characteristic absorption for C_{60}) in the PEO-4 spectrum. A simple test was performed to make sure that this absorption was only due to fullerenated PEO-4 and not due to free C_{60}. THF, previously

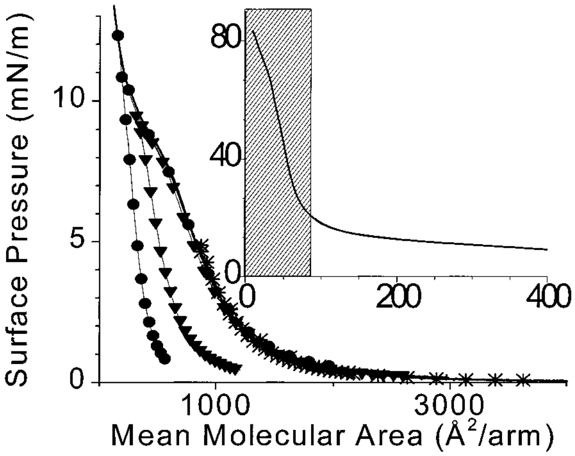


Figure 3. Isotherms obtained at room temperature. Units are identical between the outer and inset graphs. The outer graph is one compression isotherm overlayed with 3 hysteresis curves. Thick solid line indicates isotherm; symbols are as follows: *, ▼, and ● indicate compression and expansion to 5, 10, and 13 mN/m, respectively. For clarity of presentation only 1 of every 45 data points are shown. The inset shows compression data at lower surface areas; compression curves from the two regions superimpose. Experiments were performed on a KSV 5000 Langmuir trough.

treated with C_{60}, was characterized: no absorption was detected in the 300 nm region, attesting to the total insolubility of C_{60} in this solvent. The band at 328 nm can therefore be assigned to a covalent link between C_{60} and the PEO chain. No other specific band could be detected in the visible region, although the polymer was found to absorb in this region as indicated by the long tail ending around 450−500 nm.

Thermogravimetric analysis (TGA) showed the decomposition of the PEO part between 200 and 450 °C; this was confirmed with the TGA of the starting PEO-3 material. It is clear that the thermally stable material remaining beyond 450 °C corresponds to C_{60}, which undergoes only minor weight loss up to 800 °C. The relative weight percents of each part (71.2% PEO and 28.8% C_{60}) estimated from TGA fell very close to the theoretical ones (73.5% PEO and 26.5% C_{60}), assuming that each branch of the star molecule reacted selectively through a monoaddition with C_{60} as indicated by the SEC analysis (Figure 1).

Further investigation confirmed the amphiphilic nature of the polymer. After being dried under vacuum, the material was difficult to solubilize, requiring several hours of aggressive sonication in heated chlorobenzene. It was readily concentrated or diluted once solubilized, forming clear brownish solutions which were used for the monolayer experiments.

The polymer spreads to form highly compressible monolayers at the air/water surface. Figure 3 shows several isotherms recorded at 22 °C set to different scales to illustrate various features. The onset of surface pressure is observed at a value of about 3000 Å^2/arm, each attached to one C_{60} unit. This value is much larger than that reported[8] for pure C_{60} as well as several fullerene derivatives that seem to form monolayers.[9] Its very expanded behavior is reminiscent of that observed by Sauer and co-workers[10] for a 252 kg/mol fraction of pure PEO, where a plateau at 10 mN/m was assigned to the collapse pressure. They ascribed this constant pressure, combined with a constant ellipsometrically determined film thickness, to the solubilization of PEO segments into the aqueous phase, defining PEO as a hydrophilic substance. This finding compares well with the plateau observed in these C_{60}−PEO's. The molecular weight is lower, but the ends are capped with the bulky hydrophobic C_{60} groups. These two effects cancel each other out, and the plateau is observed around 10 mN/m. The most expanded set of curves in Figure 3 also shows a linear region at pressures between 3 and 7 mN/m; extrapolating to zero pressure, yields an area of about 1830 Å^2. The above behavior indicates that the packing at low surface pressures is dominated by the polymeric nature of the molecule, the region between about 1−7 mN/m likely being testament to the 2D compressibility of the surface-tethered PEO chains.

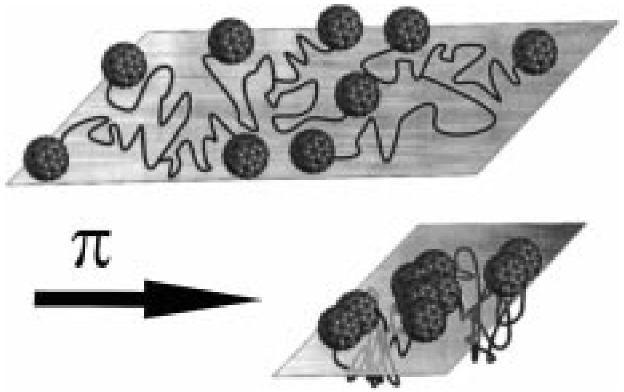


Figure 4. Cartoon of molecular packing at low and high surface pressures.

The fluid monolayer showed little hysteresis after compression to pressures less than about 7 mN/m. This differs from unsubstituted C_{60}, which has been reported to form rigid monolayer rafts or multilayer domains[11] at aqueous surfaces. At lower surface pressure, the suspended PEO generates sufficient 2D osmotic character to inhibit cohesion of the initially spread C_{60} units as illustrated in the left side of Figure 3. Compression to surface pressure of 10 mN/m and above resulted in significant hysteresis upon expansion, likely due to both C_{60} cohesion and solubilization of the PEO. The inset to Figure 3 shows the isotherm behavior at a more compressed state and higher pressures. Extrapolation of the higher pressure region leads to a value of about 121 Å^2/C_{60} unit, similar to values reported in crown ether substituted-C_{60} monolayer studies.[12] The shaded region at 87 Å^2 corresponds to our calculated close-packed area of C_{60} assuming a van der Waals diameter[13] of 10.02 Å and hexagonal packing. It is difficult to state an exact collapse pressure or area from the isotherm, though a kink at about 65 mN/m is observed.

An attempt to estimate the molecular weight of the polymer with a 2D analogue of the Van't Hoff equation failed, likely due to 2D solution nonideality even at high areas. Nonideality could be caused either by local aggregation of the C_{60} units, as shown schematically in Figure 4, or to the fact that the very expanded molecules do not collide as hard spheres even though the areas approach those one might consider to be 2D gaslike. At higher surface pressures the PEO units are likely solvated and submersed in the subphase as depicted in Figure 4. The hysteresis results, however, indicate that the more expanded phase observed at lower pressures cannot form spontaneously. Integrating the area under the compression isotherm and subtracting the expansion curve after aggregation may allow a rough estimation of the energy of cohesion. Further investigations are underway to better quantify the energy of cohesion and the effect of molecular architecture on the surfactant character of these compounds.

In conclusion, this study clearly shows that C_{60} can be incorporated selectively to the end-linked azide functions of well-defined triarmed PEO stars, leading to amphiphilic branched polymers of controlled molar mass and narrow polydispersity. The resulting polymer is soluble in common solvents but difficult to resolubilize upon removal of solvent. The polymer forms interesting highly expanded Langmuir monolayers. A detailed investigation of the solution properties of compounds with various compositions in C_{60} is currently in progress.

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