Preparation and Characterization of Highly Water-Soluble Pendant Fullerene Polymers

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ABSTRACT: Pendant fullerene polymers were prepared by attaching methano[60]fullerene carboxylic acid (MFCA) and methano[60]fullerene phenylpropyl carboxylic acid (MFPCA) to linear poly(propionylethylenimine-*co*-ethylenimine) (PPEI−EI) via amide linkages in carbodiimide-catalyzed coupling reactions. The pendant MFCA−PPEI and MFPCA-PPEI polymers, which were characterized using NMR, gel permeation chromatography, FT-IR, and other instrumental methods, most likely have a "charm bracelet" type structure without significant cross-linking. MFCA and MFPCA were also coupled with diethylamine in the same carbodiimide-catalyzed reactions, and the methano[60]fullerene amides thus obtained were used as monomeric model compounds for the pendant polymers. UV−vis absorption spectra of the polymer-bound fullerenes, though broader, retain the characteristic features observed in monomeric methano-[60]fullerene derivatives. The pendant MFCA−PPEI and MFPCA−PPEI are highly water-soluble, with the equivalent aqueous solubilities of the polymer-bound fullerene cages significantly higher than that of the parent [60]fullerene in room-temperature toluene. Thus, the preparation of pendant fullerene polymers represents an effective approach for introducing fullerene cages into an aqueous solution or hydrophilic environment.

Introduction

Fullerene cages are highly hydrophobic, insoluble in water and most polar solvents. Several approaches have been explored for the introduction of fullerenes into an aqueous or polar environment.[1] For example, water-soluble fullerene carboxylic acid derivatives,[2−5] fullerenols,[6] and fullerene amino acid derivatives[7,8] have been prepared and used in the investigation of biochemical and medicinal activities of fullerene cages. Peptide functionalized fullerene derivatives and fullerene−oligonucleotide conjugates have also been studied for their biologically significant functions.[9−11] In addition, the preparation and properties of fullerene−protein conjugates with high fullerene/protein molar substitution ratio have been reported.[12]

The incorporation of fullerene cages into polymeric structures is another approach for aqueous solubilities.[13−16] For example, polyethers containing amino end groups were used to functionalize fullerene cages.[13] The polymeric fullerene materials thus obtained are amphiphilic, but the polymer structures are complex due to extensive cross-links.[13] To improve the selectivity in the attachment of fullerene cages to polymer, "bucky-ball-fishing" approaches on the basis of photochemical amination[14] and catalytic amidation[15] reactions were used to prepare pendant fullerene−aminopolymers without significant cross-linking. The pendant fullerene−aminopolymers thus obtained were highly water-soluble.[14,15] In the absence of cross-linking, pendant fullerene polymers are dubbed as "charm bracelet" fullerene polymers.[14,15,17−24] Generally speaking, as a result of relatively simple fullerene−polymer linkages in pendant fullerene polymers, the fullerene cages are largely unaffected following the attachment to polymer. Thus, the preparation of pendant fullerene polymers represents an effective method for introducing fullerene cages into polymeric systems in a structurally less invasive and more controllable fashion.

Here we report the preparation and characterization of highly water-soluble pendant fullerene polymers with well-defined structures. The polymers were obtained from carbodiimide-catalyzed amidation reactions of methano[60]fullerene carboxylic acid (MFCA) and methano[60]fullerene phenylpropyl carboxylic acid (MFPCA) with poly(propionylethylenimine-*co*-ethylenimine) (PPEI−EI), followed by the amidation of unused secondary amine units on the polymer backbone with propanoic acid. The specificity of the amidation reactions with respect to the fullerene−polymer linkages results in "charm bracelet" type pendant polymer structures. Also reported are results from the characterization of the pendant MFCA−PPEI and MFPCA−PPEI using ^{1}H and ^{13}C NMR, gel permeation chromatography (GPC), FT-IR, and other instrumental techniques. The polymer structures and properties are compared with those of the monomeric model compounds prepared in the same carbodiimide-catalyzed amidation reactions of MFCA and MFPCA with diethylamine. Aqueous solubilities of the pendant fullerene polymers and related issues are discussed.

Experimental Section

Materials. Fullerene C_{60} (99.5%) was obtained from the Southern Chemical Group and BuckyUSA. Toluene was distilled after being refluxed with sodium wire. CS_2 was fractionally distilled before use. All other chemicals and solvents were used either as received or after simple purification. Deuterated solvents and tetramethylsilane (TMS) for NMR experiments were obtained from Cambridge Isotope Laboratories. Polystyrene standards with molecular weights M_W of 3900−965 600 and polydispersity of 1.15 and less and poly(2-vinylpyridine) standards with molecular weights M_W of 9100, 50 000, and 243 000 and polydispersity of 1.18 and less were purchased from Polymer Source Inc.

Poly(propionylethylenimine) (PPEI) with an average molecular weight M_W of ∼50 000 was obtained from Aldrich and purified before use. In the purification, a PPEI sample was dissolved in acetonitrile to form a concentrated solution and

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then precipitated into diethyl ether. After repeated precipitations, the polymer sample was dried in a vacuum oven. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.46 (bs, 2 × NCH_2), 2.35 (bs, $COC\mathbf{H}_2CH_3$), 1.12 (bs, $COCH_2C\mathbf{H}_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 174 (C═O), 44 (2 × NCH_2), 26 ($CO\mathbf{C}H_2CH_3$), 9.3 ($COCH_2\mathbf{C}H_3$) ppm.

Measurements. Two GPC setups were used in the polymer analyses. One of them using chloroform as mobile phase consists of a Waters 510 analytical HPLC pump and Waters UV−vis and refractive index detectors. GPC separations were achieved by use of three Waters HT-6E linear Styragel columns connected in a serial fashion, with chloroform flow rate of 1 mL/min. Linear polystyrene standards were used as molecular weight references. The other GPC setup uses DMSO as mobile phase. It consists of a Shimadzu LC-10AS analytical HPLC pump and a Rainin Instrument UV-1 UV−vis detector. Two serially connected Waters HT-6E linear Styragel columns prepared in DMF were converted to DMSO by pumping a low volume of DMSO (0.1 mL/min) for 24 h at 75 °C. The temperature of the DMSO column and a precolumn loop was maintained by use of a tube-oven made in house. The mobile phase DMSO containing 0.2% lithium bromide salt was pumped at 1 mL/min. Linear poly(2-vinylpyridine) standards were used as molecular weight references.

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-300 MHz NMR spectrometer and a JEOL Eclipse +500 NMR spectrometer. Tetramethylsilane was used as an internal standard.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS analyses were performed on a Kratos Kompact-III mass spectrometer equipped with a nitrogen laser. Each sample was measured in positive ion mode and/or negative ion mode in reference to C_{60} as an internal standard. Several compounds including α-cyano-4-hydroxycinnamic acid, 3,5-dimethoxy-4-hydroxycinnamic acid, 2,5-dihydroxybenzoic acid, pyrene, and 9-nitroanthracene were tested as matrix materials, and pyrene was found to be the best. Thus, the results reported in this paper were obtained using pyrene as the matrix.

Absorption spectra were obtained on Shimadzu UV-2101PC and UV-3100 spectrophotometers. FT-IR spectra were measured on a Nicolet Magna-IR 550 FT-IR spectrometer. A KBr plate with the sample deposited on the surface or a KBr pellet homogeneously dispersed with the sample were used in the measurements.

Poly(propionylethylenimine-*co*-ethylenimine) (PPEI-EI). PPEI-EI random copolymer was prepared via a partial hydrolysis of PPEI under acidic conditions. In a typical reaction, 1 g of PPEI was dissolved in 50 mL of hot water. To the solution was added 2 mL of 1 M HCl solution. After refluxed with stirring for 10 h, the aqueous solution was neutralized by adding NaOH solution to adjust pH to ∼10. Upon the removal of water, PPEI-EI was extracted into chloroform. Further purification was accomplished by precipitating the polymer from a concentrated chloroform solution into hexane. After drying under vacuum at 50 °C, a glassy PPEI-EI sample was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.45 (bs, 2 × NCH_2), 2.78 (bs, 2 × $NHC\mathbf{H}_2$), 2.4 (bs, $COC\mathbf{H}_2$-CH_3), 1.12 (bs, $COCH_2C\mathbf{H}_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 174 (C═O), 48.5 (2 × $NHCH_2$), 44 (2xNCH_2), 26 ($CO\mathbf{C}H_2$-CH_3), 9.3 ($COCH_2\mathbf{C}H_3$) ppm.

The degree of hydrolysis x_{NH} (mole fraction of $-CH_2$-$NHCH_2-$ units in the copolymer) was controlled via varying the reaction time. The x_{NH} values were estimated using ^{1}H NMR signal integrations.[14] Since the signals at 3.45, 2.78, and 1.12 ppm are due to $C\mathbf{H}_2NCOC_2H_5C\mathbf{H}_2$, $C\mathbf{H}_2NHC\mathbf{H}_2$, and $NCOCH_2C\mathbf{H}_3$ protons, respectively, the ratio between numbers of NH and $NCOCH_2CH_3$ units r_0 can be estimated as follows.

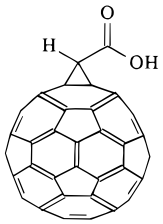
$$r_0 = I_{2.78}/I_{3.45} \quad (1a)$$

or

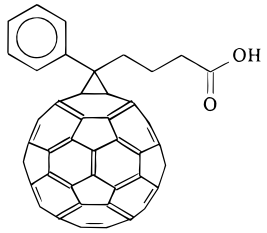
$$r_0 = {}^3/_4(I_{2.78}/I_{1.12}) \quad (1b)$$

where I represents the proton signal integrations. Thus, $x_{NH} = r_0/(1 + r_0) \times 100\%$. The results from eqs 1a and 1b agree well. PPEI−EI copolymer samples with x_{NH} of 3%, 7%, and 14% were obtained.

Methano[60]fullerene Carboxylic Acid (MFCA) and Methano[60]fullerene Phenylpropyl Carboxylic Acid (MFPCA). MFCA and MFPCA were synthesized using procedures similar to those reported in the literature.[25−28]



MFCA



MFPCA

Pendant MFCA−PPEI. MFCA was coupled with PPEI−EI to form pendant MFCA−PPEI−EI using 1-ethyl-3-(dimethylaminopropyl)carbodiimide (EDAC) as a coupling reagent.[15,29] In a typical reaction, EDAC (24 mg, 0.13 mmol) was added to a solution of MFCA (25 mg, 0.032 mmol), PPEI−EI (100 mg, x_{NH} = 3%), and triethylamine (16 μL, 0.12 mmol) in 12 mL of a bromobenzene−chloroform (3:1 v/v) mixture. The solution was stirred at 0 °C for 20 h for the formation of pendant MFCA−PPEI−EI via amidation. To obtain pendant MFCA−PPEI, unused amine units in MFCA−PPEI−EI were capped by propanoic acid using the same EDAC-catalyzed amidation reaction. For the capping, propanoic acid (0.4 mL, 5.3 mmol) was added to the reaction mixture containing MFCA−PPEI−EI, and the mixture was stirred at 0 °C for 12 h. Upon the removal of solvents, the reaction mixture was dissolved in chloroform and precipitated into hexane and dissolved in chloroform again and precipitated into acetonitrile. The polymer sample was then dissolved in water to form a brown aqueous solution. The solution was centrifuged vigorously to remove any unreacted MFCA, followed by dialysis against freshwater for 3 days to remove residual small molecules. After dialysis, water was removed to yield pendant MFCA-PPEI as a dark brown solid. The solid polymer sample was dried in a vacuum oven before characterizations.

MFCA−Diethylamine. EDAC (9.2 mg, 0.048 mmol) was added to a solution of MFCA (20 mg, 0.026 mmol) and diethylamine (6 μL, 0.06 mmol) in 12 mL of a chloroform−bromobenzene (3:1 v/v) mixture. After being stirred for 20 h, the reaction mixture was separated on a silica gel column using chloroform as eluent to yield MFCA−diethylamine as a dark solid (10 mg, 47% yield). The molecular structure of the compound was positively identified in NMR and MALDI-TOF MS analyses.[30]

Pendant MFPCA−PPEI. In a typical reaction, EDAC (14 mg, 0.073 mmol) was added to a solution of MFPCA (12 mg, 0.013 mmol) and PPEI−EI (102 mg, x_{NH} = 14%) in 5 mL of pyridine−chloroform (2:1 v/v) mixture. The coupling reaction was allowed to proceed for 48 h at room temperature. Then, propanoic acid (0.4 mL, 5.3 mmol) was added, and the reaction was allowed to proceed for an additional 16 h. Upon the removal of solvents and volatile components, the reaction mixture was dissolved in water. The brown aqueous solution was centrifuged vigorously to remove any unreacted MFPCA, followed by dialysis against freshwater for 3 days to remove residual small molecules. After dialysis, water was removed on a rotary evaporator to yield pendant MFPCA−PPEI as a dark solid. The solid polymer sample was dried in a vacuum oven at room temperature before characterizations.

MFPCA−Diethylamine. EDAC (9.2 mg, 0.048 mmol) was added to a solution of MFPCA (20 mg, 0.022 mmol) and diethylamine (6 μL, 0.06 mmol) in 6 mL of a pyridine−chloroform (2:1 v/v) mixture. The reaction was allowed to proceed for 24 h at room temperature. Upon the removal of

solvents and volatile components on a rotary evaporator, the reaction mixture was separated on a silica gel column using chloroform as eluent to yield MFPCA−diethylamine as a dark solid. The solid sample was dried overnight under vacuum at 60 °C (11 mg, yield 42%). The molecular structure of the compound was positively identified in NMR and MALDI-TOF MS characterizations.[31]

Aqueous Solubility. Solubilities of the pendant polymer samples in room-temperature water were determined gravimetrically. In a typical experiment, 100 mg of pendant polymer sample was added to 1 mL of water. After sonication, the polymer−water mixture was centrifuged vigorously, followed by the removal of the clear aqueous solution. The residual polymer sample was dried, and its weight was determined and used in the solubility calculation.

Results and Discussion

PPEI and PPEI−EI polymers are highly water-soluble. In fact, the aqueous solution concentration of these polymers is limited more by viscosity than by solubility. With the covalent attachment of fullerenes, these polymers serve as carriers to introduce hydrophobic fullerene cages into water or polar solvents to form homogeneous solutions. For attaching fullerenes to the linear polymers in a structurally controllable fashion to preserve the fundamental properties of fullerene cages, the preparation of pendant fullerene−PPEI polymers represents an effective approach.

The pendant MFCA−PPEI was characterized in GPC analyses. With chloroform as mobile phase, however, significant tailing was observed in the chromatogram. Interactions beyond size exclusion were suspected as being responsible for the results. As reported recently,[32] fullerene-containing polymers in polar solvents often exhibit GPC behavior that is characteristic of polyelectrolytes, and the polyelectrolyte effects can be eliminated by adding lithium bromide salt to the mobile phase.[32] Thus, the pendant polymer was analyzed using DMSO with 0.2% lithium bromide as mobile phase. Under the GPC conditions, the tailing problem became negligible. The GPC analysis of the pendant MFCA−PPEI yielded an average molecular weight M_w of 49 000 in reference to poly(2-vinylpyridine) standards, which is comparable to that of the parent PPEI. The results suggest no cross-linking due to the attachment of MFCA to multiple PPEI polymer chains. The absence of cross-linking should be expected considering the specificity of the EDAC-catalyzed MFCA−PPEI−EI coupling reaction. Thus, the pendant fullerene polymer most likely has a "charm bracelet" type structure in which MFCA is attached to the linear PPEI chain via an amide linkage (Scheme 1).

Separately, MFCA−diethylamine as a monomeric model compound was prepared via the same EDAC-catalyzed amidation reaction (Scheme 1).

The UV−vis absorption spectrum of the pendant MFCA−PPEI is broader than those of free MFCA and the monomeric model compound MFCA−diethylamine (Figure 1). The sharp absorption peak at ∼430 nm and the weak band at ∼700 nm characteristic of MFCA and other methano-C_{60} derivatives become less pronounced in the spectrum of the polymer-bound MFCA. The UV−vis results were used to estimate the content of fullerene cages in the pendant polymer. Under a rough assumption that the total transition probability (integrated molar absorptivity) in the visible (400−750 nm) remains unchanged from the monomeric model compound to the

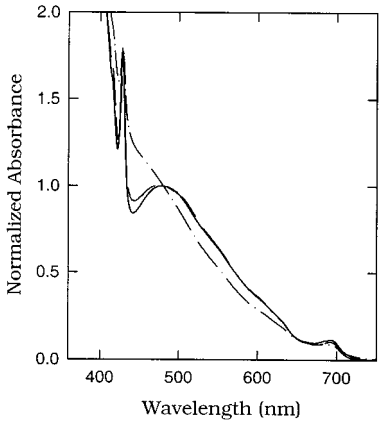
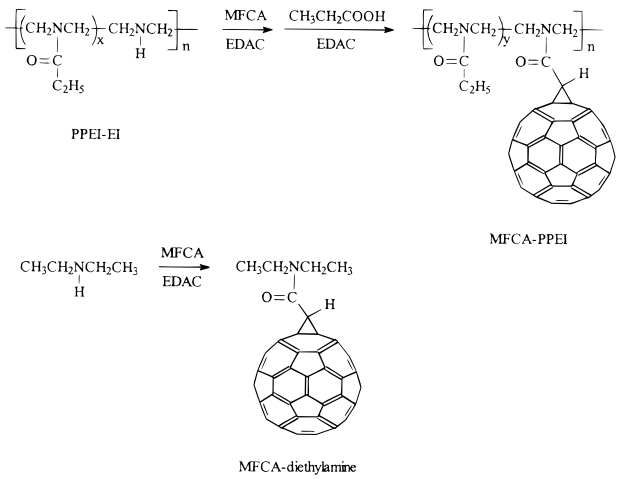


Figure 1. UV−vis absorption spectra of the pendant MFCA−PPEI in chloroform (-・-), the monomeric model compound MFCA−diethylamine in chloroform (- - -), and free MFCA in chloroform−DMSO (—).

Scheme 1



pendant polymer, there are the following relationships.

$$\text{transition probability} \propto \int(\epsilon/\lambda)\,d\lambda \approx (1/\lambda_{AVE})\int\epsilon\,d\lambda \quad (2)$$

where λ_{AVE} represents the average wavelength for the wavelength range. Thus,

$$\int\epsilon_{MFCA,P}\,d\lambda = \int\epsilon_{MFCA,M}\,d\lambda \quad (3)$$

$$\epsilon_{MFCA,P} = A_{MFCA,P}(x_{MFCA}C_{W,POLYMER})^{-1}M_{MFCA} \quad (4)$$

where the subscripts P and M denote polymer-bound and monomeric MFCA, $A_{MFCA,P}$ is the observed absorbance corresponding to the pendant polymer weight concentration $C_{W,POLYMER}$, and M_{MFCA} represents the MFCA molecular weight. Thus, the MFCA content in the pendant MFCA−PPEI can be calculated as follows.

$$x_{MFCA} = [\int(A_{MFCA,P}C_{W,POLYMER}{}^{-1}M_{MFCA})\,d\lambda]/[\int\epsilon_{MFCA,M}\,d\lambda] \quad (5)$$

The MFCA content in the polymer sample thus estimated is ∼11% (wt/wt), which corresponds to the C_{60} cage content of ∼10% (wt/wt) in the pendant MFCA−PPEI.

The FT-IR spectrum of the pendant MFCA−PPEI is rather similar to that of the parent PPEI, except for an additional weak absorption peak at ∼527 cm^{-1} due to functionalized C_{60} cage in the polymer-bound MFCA. A similar absorption peak is in the FT-IR spectrum of the monomeric model compound MFCA−diethylamine. It should be noted that the IR absorption at ∼527 cm^{-1} is characteristic of the C_{60} cage. The peak is one of the four signals in the FT-IR spectrum of C_{60} and is always preserved in the C_{60} cage functionalization. FT-IR spectra of different classes of C_{60} derivatives[33] and the C_{60} dimer[34] all show the peak at ∼527 cm^{-1}.

The pendant MFCA−PPEI was characterized using ^1H and ^{13}C NMR methods for more direct structural information on the polymer. The ^1H NMR spectrum of the pendant MFCA−PPEI[35] is essentially the same as that of the parent PPEI, except for an additional weak and broad peak at ∼4.6 ppm, which may be attributed to the methano proton in the polymer-bound MFCA. The same proton signal is at 5.1 ppm in the spectrum of free MFCA and 4.92 ppm in the spectrum of the monomeric model compound MFCA−diethylamine.[30] The ^{13}C NMR spectrum of the pendant MFCA−PPEI[36] is also similar to that of PPEI, but with weak peaks in the fullerene region. These somewhat broad fullerene peaks may be assigned to polymer-bound fullerene cages and used as evidence for the attachment of MFCA to PPEI. However, a more detailed analysis of the effects associated with the pendant polymer formation was hindered by the quality of the ^{13}C NMR spectrum. An improvement of the NMR signal quality for polymer-bound fullerene carbons was limited by the concentration of fullerene cages in the NMR solution. In principle, the concentration of fullerene cages may be increased by increasing the content of fullerene cages in the pendant polymer and/or the polymer solution concentration. In practice, however, the pendant polymer with a higher fullerene cage content is significantly less soluble, whereas the higher polymer concentration makes the solution too viscous for NMR measurements.

^1H NMR is certainly a more sensitive method, but it still has significant problems with the characterization of the pendant MFCA−PPEI. While the methano proton in MFCA may be used as a label, its signal at ∼4.6 ppm in the spectrum of the pendant MFCA−PPEI is close to those broad and intense peaks of protons on the polymer backbone,[35] making it a less reliable proton label in the ^1H NMR characterization of the pendant polymer. As a result, a modification to the fullerene structure to include a functional group whose ^1H NMR signals do not overlap with those of PPEI was considered. Since there are no aromatic protons in PPEI, the methano-C_{60} derivative MFPCA with a phenyl group at the methano bridge was selected for the preparation of pendant MFPCA−PPEI polymer. The phenyl protons serve as labels for the polymer-bound fullerene in ^1H NMR characterization. With the carboxylic acid group in MFPCA farther away from the fullerene cage, it is more reactive, and its coupling reaction with the secondary amine units in PPEI−EI is more efficient and controllable. Similarly, MFPCA−diethylamine as a monomeric model compound was prepared in the same EDAC-catalyzed amidation reaction to simulate the formation of pendant MFPCA−PPEI (Scheme 2).

The UV−vis absorption spectrum of the pendant MFPCA−PPEI is also broader than those of free MFPCA and the monomeric model compound MFPCA−diethylamine but retains some of the features that are characteristic of methano-C_{60} derivatives (Figure 2). Under the same rough assumption that the total transition probability in the visible (400−750 nm) remains unchanged from the monomeric model compound MFPCA−diethylamine to the pendant MFPCA−PPEI, a MFPCA content of 13% (wt/wt) in the polymer was estimated in terms of eq 5, which corresponds to a C_{60} cage content of 10.5% (wt/wt) in the pendant MFPCA−PPEI.

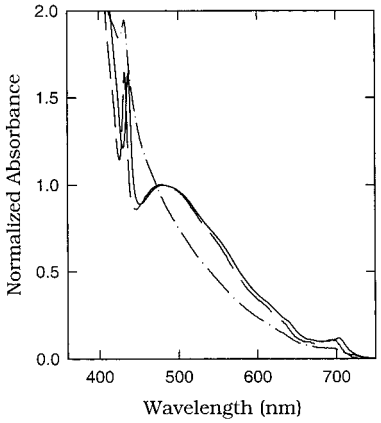
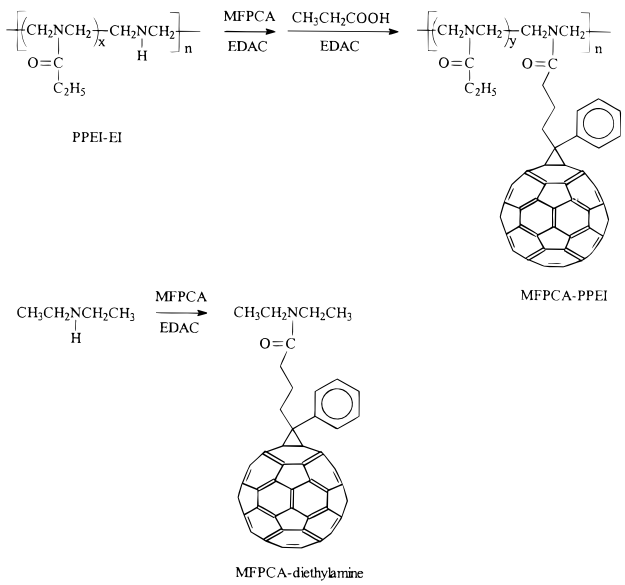


Figure 2. UV−vis absorption spectra of the pendant MFPCA−PPEI in chloroform (-·-), the monomeric model compound MFPCA−diethylamine in chloroform (- - -), and free MFPCA in CS_2 (—).

Scheme 2



The ^1H NMR spectrum of the pendant MFPCA−PPEI in $CDCl_3$[37] is similar to that of the parent PPEI, except for the aromatic region. A comparison of the ^1H NMR spectra of the pendant polymer, the monomeric model compound MFPCA−diethylamine, and free MFPCA is shown in Figure 3. The aromatic proton signals due to the phenyl group in polymer-bound MFPCA are downfield shifted and significantly broader. The ^1H NMR spectrum of the pendant MFPCA−PPEI was also used to estimate the MFPCA content in the polymer. According to the integration of the aromatic proton signals in reference to that of the peak at 3.45 ppm ($NCOCH_2C\mathbf{H}_3$), the MFPCA content of 14% (wt/wt) thus estimated, which corresponds to the C_{60} cage content of 11% (wt/wt), is in good agreement with the value estimated in

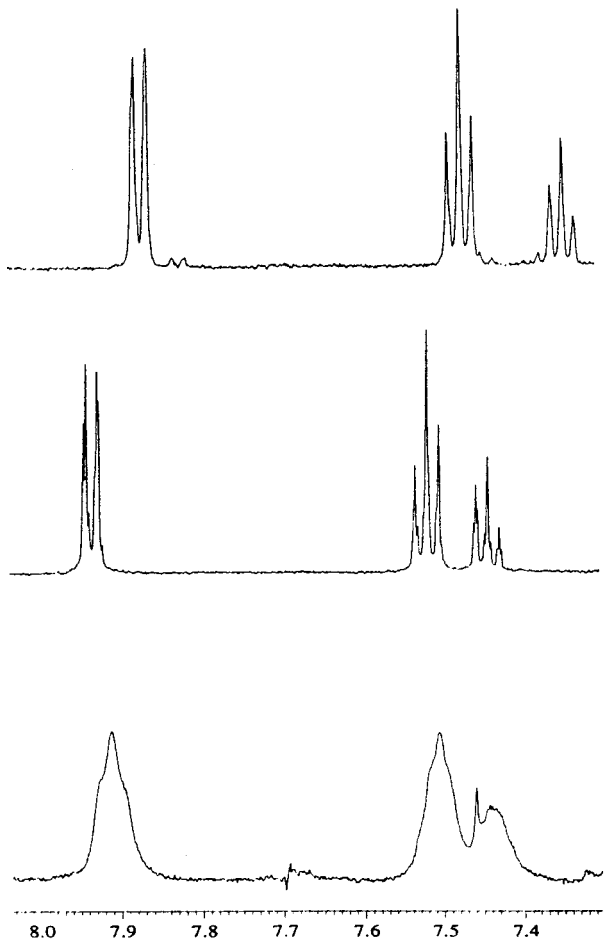


Figure 3. A comparison of the aromatic proton signals in the ^{1}H NMR spectra (500 MHz, TMS internal standard) of the pendant MFPCA−PPEI in $CDCl_3$ (bottom), the monomeric model compound MFPCA−diethylamine in $CS_2/CDCl_3$ (middle), and free MFPCA in CS_2 (top).

terms of eq 5 for the UV−vis absorption results. Such a good agreement is significant. While it may not validate the rough assumption that the total transition probability in the visible wavelength region is unchanged from the monomeric model compound to the pendant polymer, it suggests that the errors associated with the rough assumption may have fortuitously been canceled in the estimate of the fullerene content in MFPCA−PPEI. Thus, as long as the calculations (eqs 1−5) for MFCA−PPEI and MFPCA−PPEI are subject to similar errors, the rough estimate of the fullerene content in MFCA−PPEI in terms of the absorption results is probably not far from the correct value.

The ^{13}C NMR spectrum of the pendant MFPCA−PPEI[38] is again dominated by signals of the PPEI backbone, though there are clearly structured peaks in the fullerene region due to polymer-bound fullerene cages. The aromatic carbon signals due to the phenyl group in the polymer-bound MFPCA are also shifted from those of the monomeric model compound MFPCA−diethylamine and free MFPCA.

Both pendant MFCA−PPEI and MFPCA−PPEI polymers are soluble in water, forming dark colored aqueous solutions. The equivalent aqueous solubilities of C_{60} cages in the pendant MFCA−PPEI and MFPCA−PPEI are 9.5 and 10 mg/mL, respectively, which are significantly higher than the solubility of the parent C_{60} in room-temperature toluene (~3 mg/mL).[39] The pendant fullerene polymers are also highly soluble in chloroform and more polar solvents such as DMSO. The high equivalent aqueous solubilities of the polymer-bound C_{60} cages show that the pendant polymers are effective vehicles for the introduction of fullerenes into water or a hydrophilic environment.

The mole fraction of amine units in PPEI−EI has little effect on the preparation and properties of pendant fullerene−PPEI polymers. For the PPEI−EI copolymer samples of different x_{NH} values (3%, 7%, and 14%), their EDAC-catalyzed amidation reactions with MFCA and MFPCA yielded pendant polymers with similar properties.

The EDAC-catalyzed amidation reactions between methano-C_{60} carboxylic acids and the polymer-bound secondary amines are specific, forming most likely "charm bracelet" type pendant polymer structures. Because of the presence of amines, however, the possibility of thermal nucleophilic amine−fullerene addition as a competing reaction should be considered. In a control experiment, *tert*-butyl methano-C_{60} carboxylate was stirred with PPEI−EI under similar experimental conditions as those used for the EDAC-catalyzed amidation. No meaningful reaction between the carboxylate and PPEI−EI was observed. The results from the control experiment indicate that thermal nucleophilic amine−fullerene addition is insignificant in the solution containing methano-C_{60} cages and PPEI−EI polymers. In addition, the solution environment in the EDAC-catalyzed amidation is acidic, making the competing nucleophilic addition more difficult. The absence of nucleophilic amination of fullerene cages under the experimental conditions for EDAC-catalyzed amidation is consistent with the GPC results that suggest no meaningful cross-linking of linear PPEI chains in the pendant polymer samples.

In the pendant fullerene polymers prepared via the EDAC-catalyzed amidation, the fullerene cages are largely undisturbed. UV−vis absorption spectra of the polymer-bound methanofullerenes, though broader, retain the characteristic features observed in the spectra of monomeric methanofullerene derivatives. However, mechanistic details concerning the spectral changes upon the attachment of fullerene cages to the polymer remain to be understood. Since there are abundant amino groups in biological systems, the same carboxylic acid−amine coupling reaction may be used to introduce fullerene cages into biomacromolecular structures. In fact, it has been reported recently that methano-C_{60} dicarboxylic acids may be coupled to amino groups in the natural protein bovine serum albumin (BSA) to yield fullerene−protein conjugates.[12]

In summary, pendant MFCA−PPEI and MFPCA−PPEI were prepared via carbodiimide-catalyzed amidation reactions of methano-C_{60} carboxylic acids with polymer-bound secondary amine units. The pendant polymers were characterized by GPC, NMR, and other instrumental methods. The polymer structures are most likely of the "charm bracelet" type, without meaningful cross-linking of linear PPEI chains. With the pendant polymers being highly water-soluble, the equivalent aqueous solubilities of the polymer-bound fullerene cages are significantly higher than that of the parent C_{60} in toluene. Thus, the preparation of pendant fullerene polymers represents an effective approach for introducing fullerene cages into an aqueous solution or highly polar environment.

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Supporting Information Available: Synthetic procedures for MFCA and MFPCA. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) ^{1}H NMR (300 MHz, CS_2/C_6D_6): δ 4.91 (s, 1H), 3.98 (q, 2H), 3.68 (q, 2H), 1.59 (t, 3H), 1.33 (t, 3H) ppm. ^{13}C NMR (75 MHz, CS_2/C_6D_6): δ 164.11, 148.15, 147.27, 145.49, 145.35, 145.06, 145.05, 145.04, 144.55, 144.53, 144.53, 144.16, 143.84, 143.58, 143.21, 142.83, 142.65, 142.36, 143.16, 141.97, 141.05, 140.81, 139.19, 136.37, 72.03, 42.64, 41.56, 40.98, 14.83, 13.17 ppm. MALDI-TOF MS: 833.
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(34) ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.6 (bs, weak), 3.47 (bs, 2 × 2H), 2.40 (bs, 2H), 1.12 (bs, 3H) ppm.
(35) ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 173.8, 148−145 (weak), 46.9, 44.5, 25.8, 9.3 ppm.
(36) ^{1}H NMR (500 MHz, $CS_2/CDCl_3$): δ 7.94 (d, 2H), 7.54 (t, 2H), 7.45 (m, 1H), 3.38 (q, 2H), 3.29 (q, 2H), 2.95 (m, 2H), 2.52 (t, 2H), 2.23 (m, 2H), 1.16 (t, 3H), 1.13 (t, 3H) ppm. ^{13}C NMR (125 MHz, $CS_2/CDCl_3$): δ 171.2, 149.1, 148.1, 145.9, 145.3, 145.2, 145.0, 144.7, 144.6, 144.5, 144.4, 144.1, 143.8, 143.3, 143.2, 143.0, 142.5, 142.4, 142.3, 142.2, 141.2, 140.9, 138.1, 137.5, 137.2, 132.25, 128.49, 128.29, 80.2, 52.0, 42.0, 40.0, 36.0, 33.0, 22.0, 13.0, 12.0. MALDI-TOF MS: 951.
(37) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (bs, 2H), 7.51 (bs, 2H), 7.44 (bs, 1H), 3.42 (bs, 2 × 2H), 2.3 (bs, 2H), 1.1 (bs, 3H) ppm.
(38) ^{13}C NMR (125 MHz, $CDCl_3$): δ 175, 174.6, 145−141 (weak), 132.0, 128.6, 128.5, 46, 43.5, 26, 9.5 ppm.
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