New Nanostructured Materials Based on Fullerene and Biodegradable Polyesters

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Star-shaped poly(ϵ-caprolactone) (PCL) with a fullerene (C_{60}) core, $C_{60}[N(CH_2)_{12}OPCLOH]_x$, was successfully synthesized by reaction of azide-terminated PCL with C_{60}. Both the experimental conditions and the stoichiometry were optimized, such that an average of six PCL chains was grafted per fullerene core. The molecular weight of the polyester chains directly controlled the length of the arms of the star-shaped polymers. Singlet oxygen was generated on irradiation of the $C_{60}[N(CH_2)_{12}OPCLOH]_x$ nanohybrids. These $C_{60}[N(CH_2)_{12}OPCLOH]_x$ nanohybrids were then processed in two kinds of nanomaterials. First, they were encapsulated within the core of micelles formed by biocompatible amphiphilic block copolymers. In water, the particle size distribution of these nanoparticles was narrow, and their diameter was in the range of 100 to 200 nm. Second, C_{60}-containing micro-/nanosized polymer fibers were prepared, for the first time, by electrospinning. The average diameter of the fibers was varied by tuning the PCL/$C_{60}[N(CH_2)_{12}OPCLOH]_x$ weight ratio. Grafting of polyester chains onto C_{60} is thus a suitable strategy for producing easily processable C_{60} and attractive building blocks for incorporation of C_{60} in nanomaterials.

Introduction

Fullerene-polymer conjugates deserve much interest because they can take advantage of the biologically important properties of fullerenes, such as production of singlet oxygen upon light irradiation.[1] Photosensitivity of fullerene (C_{60}) is promising in photodynamic therapy of cancer and treatment of multidrug resistant pathogens. Development of fullerene-based agents in photodynamic therapy is, however, restricted by a low solubility in biologically relevant media. This drawback can, however, be overcome by grafting suitable polymers to fullerenes. Water-soluble polyether derivatives of fullerenes[2−4] were prepared and proved to be injectable intravenously and to accumulate preferentially in tumor tissues, so making photodynamic cancer therapy possible.[5,6]

A system of conjugated double bonds accounts for the high reactivity and plurifunctionality of fullerene and for the opportunity to prepare a large range of functional fullerenes.[7,8] Well-defined polymer derivatives of fullerene were synthesized by addition reactions.[9−14] Nevertheless, when bioapplications are concerned, the C_{60}/polymer nanohybrids must be at least biocompatible, thus consisting of biocompatible chains. In this respect, poly(ϵ-caprolactone) (PCL) is a tissue-compatible, biocompatible, and biodegradable material,[15] and thus a potential substrate for application, for example, in surgery, sustained drug delivery, and tissue engineering.[16−18] Preparation of fullerene-containing nanoparticles and nanofibers of PCL is thus a valuable strategy for exploiting the potential of fullerene and derivatives.

In this paper, C_{60}/PCL nanohybrids have been first prepared by reaction of azide-terminated PCL chains with C_{60}. The photoactivity of these C_{60}/PCL nanohybrids has

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been studied with the purpose to produce singlet oxygen. Then, these nanohybrids have been incorporated in various nanomaterials. They have been encapsulated in the core of biocompatible amphiphilic diblock copolymer micelles leading to nanoparticles. Finally, fullerene-containing polyester nanofibers have been prepared by electrospinning.

Experimental Section

Materials. Buckminsterfullerene (98%), 12-bromo-1-dodecanol (99%), triethylaluminum (1.9 M in toluene), and sodium azide (99%) were purchased from Aldrich and used as received. ϵ-Caprolactone (CL; Aldrich) was dried over calcium hydride and degassed by several freeze−thaw cycles before being distilled under reduced pressure. Toluene was dried by refluxing over a sodium benzophenone complex and distilling under a nitrogen atmosphere. Dimethylformamide (DMF) was dried and distilled over P_2O_5. All polymerization experiments were performed using the classical Schlenck techniques under nitrogen. Liquids were transferred under nitrogen with syringes and stainless steel capillaries.

Synthesis of Azide-Terminated PCL. α-Azido-ω-hydroxy PCL was synthesized by ring-opening polymerization of CL initiated by ethylaluminum 12-bromo-1-dodecyl oxide, as reported elsewhere.[19] The bromo end group was converted into an azide by the common method based on a fivefold molar excess of sodium azide in dry DMF at 35 °C for 24 h. The α-azido-ω-hydroxy PCL was quantitatively isolated and purified by selective precipitation in methanol.

Preparation of C_{60}−[$N(CH_2)_{12}$OPCLOH]$_x$ Nanohybrids. In a typical experiment, C_{60} was reacted with α-azido-ω-hydroxy PCL in 1,2,4-trichlorobenzene (TCHB) at molar ratios of 10:1, 1:1, and 1:10, respectively, at 150 °C under stirring and nitrogen for 24 h. After solvent removal under reduced pressure, the residue was dissolved in tetrahydrofuran (THF), and unreacted C_{60} was removed by centrifugation (5000 rpm, 30 min) and filtration through a 0.45 μm membrane filter. The THF solution was concentrated under reduced pressure and subsequently poured into an excess of heptane for precipitating the nanohybrid.

Determination of the Singlet Oxygen ($^1O_2$) Generation by the Nanohybrids. The 9,10-anthracene dipropionic acid (ADPA) bleaching method[20] was used to confirm that singlet oxygen could be generated by the nanohybrids. Stock solutions of all C_{60}[$N(CH_2)_{12}$OPCLOH]$_x$ nanohybrids were prepared in THF. ADPA solution in a buffer (pH 7.5) was used as a singlet oxygen acceptor. Mixed solutions of photosensitizers (C_{60}[$N(CH_2)_{12}$OPCLOH]$_x$) and ADPA were irradiated at a well-defined wavelength (red filter), such that this radiation was selectively absorbed by the photosensitizer. The reaction was monitored spectrometrically by recording the intensity decrease of the 400 nm absorption peak of ADPA as a function of the irradiation time.

Preparation of C_{60}−[$N(CH_2)_{12}$OPCLOH]$_x$ Nanoparticles in Water. Three types of diblock copolymers PEO_{114}-*b*-PCL_9, PEO_{114}-*b*-PCL_{18}, and PEO_{40}-*b*-PCL_{14} were used to form C_{60}-containing nanoparticles in water. Stock solutions of each copolymer and each C_{60}[$N(CH_2)_{12}$OPCLOH]$_x$ nanohybrid were prepared with 1 wt % concentration in THF. Nanoparticles were prepared by the nanoprecipitation technique.[21] Water was rapidly added to the THF mixed solutions of the amphiphilic copolymer and the nanohybrid, followed by dialysis against water for 2 days to remove THF. Prepared nanoparticles were characterized by dynamic light scattering (DLS).

Preparation of C_{60}−[$N(CH_2)_{12}$OPCLOH]$_x$ (/PCL) Nanofibers by Electrospinning. Micro-/nanosized fibers from fullerene core star-shaped polymers were prepared by electrospinning. In a typical run, solutions of C_{60}[$N(CH_2)_{12}$OPCLOH]$_x$ nanohybrids alone or in the presence of a well-known amount of PCL ($\bar{M}_n$ = 80 000) in chloroform were electrospun. The total polymer concentration was 12%. The average diameter of the fibers was varied by changing the PCL/C_{60}[$N(CH_2)_{12}$OPCLOH]$_x$ weight ratio. A plastic syringe (2 mL) with a nozzle of 0.1 mm diameter was filled with 1 mL of chloroform solution. An electrode connected to a high voltage supply that generates positive DC voltages (up to 28.5 kV) was plunged into the syringe. A grounded copper plate was used as a collector.

Characterization. Size-exclusion chromatography (SEC) was performed with a SFD S5200 liquid chromatograph equipped with a set of PL-gel 5 μm columns (10^5, 10^4, 10^3, and 10^2 Å), eluted with THF (1 mL/min at 45 °C), and calibrated with polystyrene standards. Two detectors were used, that is, a RI2000 refractive index and a S3240 UV−vis detector. IR spectra were recorded with a Perkin-Elmer FT-IR spectrophotometer using KBr disks. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AM 400 MHz apparatus. UV−vis absorption spectra were recorded on a Hitachi U-3300 spectrophotometer. Thermogravimetric analyses (TGA) were carried out under nitrogen with a TA Instruments Q500 thermogravimetric analyzer in the 25−1000 °C range, at a 10 °C/min rate (HiRes method). Differential scanning calorimetry (DSC) was performed with a TA Instruments Q100 at a rate of 10 °C/min. DLS measurements were carried out with a Brookhaven instrument that consists of a BI-200 goniometer, a BI-2030 digital correlator, and an Ar ion laser (Lexel Lasers; 488 nm). The scattering angle was 90°. A refractive index matching bath of filtered Decalin surrounded the scattering cell, and the temperature was controlled at 25 °C. The size distribution was calculated by the CONTIN method, and the data were the average of five measurements. The collected nanofibers were vacuum-covered with carbon and examined in a scanning electron microscope Philips 515. The average fiber diameter was evaluated using Image J software program by measuring 20 fibers from each scanning electron microscopy (SEM) image.

Results and Discussion

Synthesis of C_{60} Nanohybrids. A few years ago, star-shaped polymers with a fullerene core were prepared within good yields by reaction of C_{60} with polyethers having azide end groups.[3,22] In this study, azide-terminated poly(ϵ-caprolactone) (N_3PCL) has been similarly reacted with C_{60} by nitrogen bridging with formation of "azafulleroids".[3] To prepare C_{60}/PCL nanohybrids of different molecular weights, azide-terminated PCLs with three different molecular weights ($\bar{M}_n$ = 1150, 2700, and 6900) were synthesized by ring-opening polymerization of CL initiated by triethylaluminum in the presence of 12-bromo-1-dodecanol,[19] followed by quantitative conversion of the α-bromide end group into azide, as illustrated in Scheme 1. ^{1}H NMR analyses unambiguously show the presence of the azide (−CH_2N$_3$) at a chemical shift of 3.47 ppm and the complete disappearance of the alkyl bromide (δ(−CH_2Br) = 3.52 ppm). This

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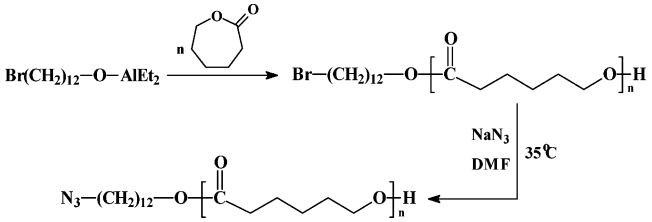
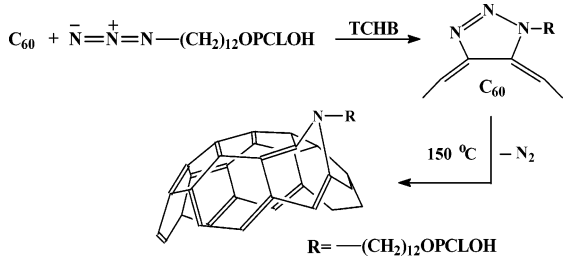
Scheme 1. Synthesis of Azide-Terminated PCL



Scheme 2. Addition of Azide-Terminated PCL to C_{60}



is additionally confirmed by the observation of an IR band at 2095 cm^{-1}, which is characteristic of the azide group of N_3PCL.

C_{60}/PCL nanohybrid was prepared by reacting C_{60} with a 10-fold molar excess of N_3PCL in TCHB at 150 °C for 24 h. C_{60} is supposed to react with N_3PCL according to the mechanism proposed for the reaction of C_{60} with alkyl azides,[9,23] thus with formation of a 1,6-aza-bridged[5,6] closed isomer, as illustrated in Scheme 2.

A change in color from violet (characteristic of C_{60} in TCHB) to red-brown was observed during the reaction. After solvent removal under reduced pressure, the residue was dissolved in THF, and unreacted C_{60} was removed by centrifugation (5000 rpm, 30 min) and filtration through 0.45 μm membrane filters. The THF solution was concentrated under reduced pressure and subsequently poured into an excess of heptane for precipitating the nanohybrid. The reaction products, $C_{60}[N(CH_2)_{12}OPCLOH]_x$, are highly viscous brownish oils or solids, soluble in THF in contrast to C_{60}. It must be noted that the polymer molecular weight decreases when the reaction time exceeds 24 h, consistent with the degradation of the PCL chains.

SEC analysis of both the starting N_3PCL and the C_{60}/PCL nanohybrids clearly shows the efficiency of the reaction (Figure 1). The SEC chromatograms for N_3PCL are systematically shifted toward lower elution volumes in line with an increase in the PCL molecular weight. The absorbance of C_{60} in the 340 nm region allows the fullerene containing polymers to be discriminated from N_3PCL by SEC using dual detection (UV and RI), because the N_3PCL does not absorb in this region. Comparison of the SEC chromatograms recorded with a RI detector and an UV detector, respectively, confirms that the products are eluted at smaller volumes than the original N_3PCL chains and are UV-absorbing and thus contain fullerene (Figure 1). Therefore, the N_3PCL chains have been successfully and quantitatively grafted onto C_{60} molecules with formation of the expected $C_{60}[N(CH_2)_{12}OPCLOH]_x$ nanohybrid. It must, however, be noted that in the case of higher molecular weight PCLs, the grafting onto C_{60} was not found to be quantitative (Figure 1) and thus these samples contain some free PCL chains together with the corresponding nanohybrids.

The average number of N_3PCL branches (x) grafted onto a C_{60} core was calculated from elemental analysis data and compared to SEC analysis. These data are listed in Table 1. They show that each fullerene core is grafted by an average of six PCL arms.

The IR absorption at 2095 cm^{-1}, characteristic of the azide group of N_3PCL, was no longer observed in the spectrum of the $C_{60}[N(CH_2)_{12}OPCLOH]_x$ products, which is an additional evidence for the success of the grafting reaction. Finally, the ^{1}H NMR signal at 3.26 ppm, characteristic of the methylene protons next to the azide group ($-CH_2N_3$), completely disappeared (Figure 2), which is expected in the case of successful addition of the N_3PCL chains onto fullerene.

Polymers grafted to fullerene usually exhibit an improved thermal stability.[3,4] This evolution was confirmed by TGA (Figure 3) of the C_{60} star-shaped products and the original N_3PCLs polymers, respectively. The most considerable decomposition occurs in the temperature range 300−400 °C and is due to the thermal destruction of the polyester branches. As seen, the higher the branch chain length, the higher the increase of the thermal stability of the C_{60} nanohybrid. As a result of carbonization up to 800 °C the weight loss of the $C_{60}[N(CH_2)_{12}OPCLOH]_x$ products is never 100%.

The length of the grafted chains has also an effect on the melting temperature shown by DSC. The melting temperatures of the C_{60} products increase in the following order: $C_{60}[N(CH_2)_{12}OPCL_8OH]_x$ (39.5 °C), $C_{60}[N(CH_2)_{12}OPCL_{22}OH]_x$ (50.8 °C), and $C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$ (55.5 °C). These values are considerably lower than those of the original N_3PCLs. Compared to the original azide the larger difference in melting temperature is observed when PCL is shorter (39.5 vs 48.5 °C).

The successful grafting of PCL chains onto C_{60} has thus been evidenced by all these previous experiments. Because C_{60} has a great interest as a singlet oxygen producer, the next step has been devoted to the study of this C_{60} typical property when it is included in the polyester nanohybrids.

Singlet Oxygen Production by the Nanohybrids. Fullerenes are known to produce singlet oxygen ($^1O_2$) when exposed to visible light.[20] The photooxidation of ADPA to its endoperoxide derivative by singlet oxygen (Scheme 3) is usually used for detection of $^1O_2$ generated by photosensitizers.

This ADPA bleaching method was used to prove that the C_{60}-containing nanohybrids are photoactive and thus able to produce singlet oxygen after light irradiation. Mixed solutions of photosensitizers ($C_{60}[N(CH_2)_{12}OPCLOH]_x$) and ADPA were irradiated at a selected wavelength (red filter) that was selectively absorbed by the photosensitizer. The reaction was followed spectrometrically at 400 nm by monitoring the decrease of the absorbance of ADPA in the presence of $C_{60}[N(CH_2)_{12}OPCL_{22}OH]_x$ with the irradiation time (Figure 4). The blank experiment, thus in the absence of the $C_{60}[N(CH_2)_{12}OPCLOH]_x$ nanohybrid, shows that ADPA is

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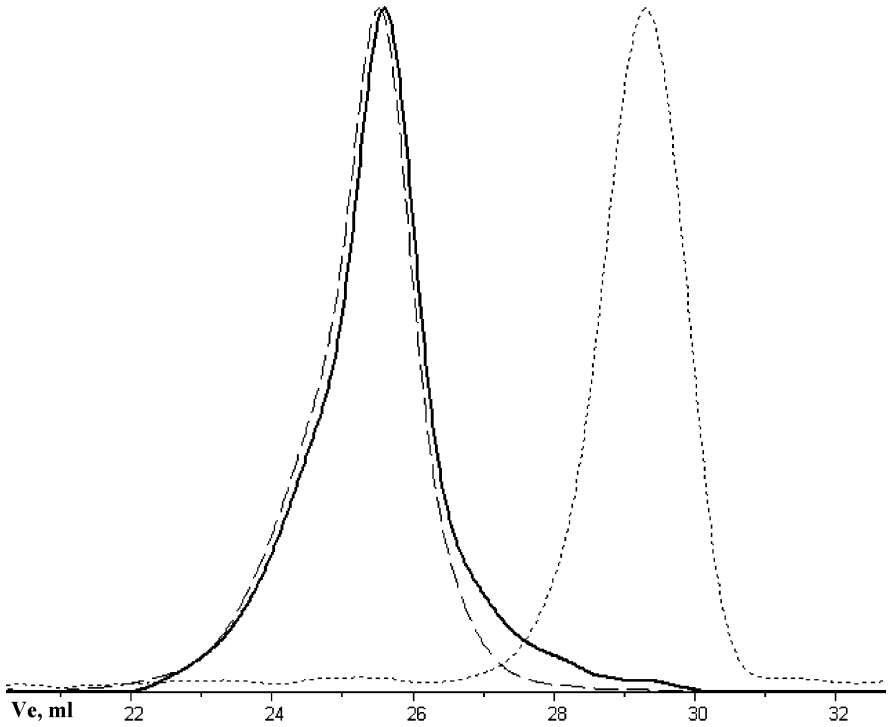

Figure 1. SEC chromatograms (eluent THF). RI traces for the N_3PCL_8 (dotted line) and RI (solid line) and UV (340 nm, dashed line) traces for the $C_{60}[N(CH_2)_{12}OPCL_8OH]_x$ products. $\bar{M}_n$ of the starting PCL is 1150 g/mol.

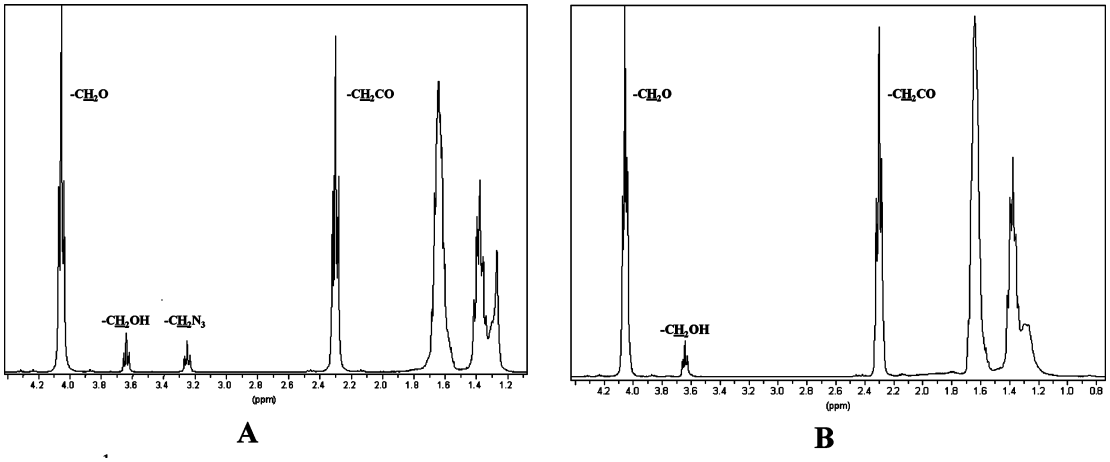

Figure 2. ^{1}H NMR spectra of N_3PCL_8 (A) and $C_{60}[N(CH_2)_{12}OPCL_8OH]_x$ products (B).

Table 1. Average Number (*x*) of PCL Arms Grafted to the Fullerene Core

sample	%N[a]	$\bar{M}_n$[b]	$\bar{M}_n$[a,c]	x[b]	x[a]
$N_3(CH_2)_{12}OPCL_{58}OH$	0.80	6 900	5 300		
$C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$	0.44	40 400	27 000	6	5
$N_3(CH_2)_{12}OPCL_{22}OH$	1.48	2 700	2 900		
$C_{60}[N(CH_2)_{12}OPCL_{22}OH]_x$	0.68	20 000	15 000	7	5
$N_3(CH_2)_{12}OPCL_8OH$	3.28	1 150	1 300		
$C_{60}[N(CH_2)_{12}OPCL_8OH]_x$	1.09	6 750	6 900	6	5

[a] Determined by elemental analysis. [b] Determined by SEC chromatography. [c] The degree of polymerization (n) of the starting $N_3(CH_2)_{12}OPCL_nOH$ was calculated from the equations $\%N = (aA/M_n) \times 100$ and $\bar{M}_n = 243 + n114$, where a is the number of nitrogen atoms ($a = 3$) and A is the atomic weight of nitrogen atom. Then the $\bar{M}_n$ value of $C_{60}[N(CH_2)_{12}OPCL_nOH]_x$ nanohybrids was calculated using the equation $\bar{M}_n = 720 + (215 + 114n)x$, where x is the average number of grafted PCL branches.

stable toward irradiation at this wavelength. Therefore, the singlet oxygen generation results from the irradiation of the $C_{60}[N(CH_2)_{12}OPCLOH]_x$ solution. Clearly, a significant quantity of singlet oxygen was produced during the 1 h irradiation of $C_{60}[N(CH_2)_{12}OPCLOH]_x$ products, as expressed by the decrease in the absorption intensity of ADPA. The five to six nitrogen bridges resulting of the PCL−azide reaction with C_{60} do not modify significantly the electronic properties of the fullerene allowing still its use for singlet production and biomedical applications. Therefore, the objective is now to include these PCL based nanohybrids within biocompatible nanomaterials.

Nanohybrids in Biocompatible Nanoparticles. Preparation of nanoparticles containing fullerene core star-shaped PCLs was achieved by nanoprecipitation.[21] This method consists of formation of nanoparticles from nonionic amphiphilic block copolymers by fast addition of water to solution of copolymers in water-miscible organic solvent. This is a convenient method for incorporation of hydrophobic drugs in nanoparticles. Attachment of PCL arms to the C_{60} core makes fullerene soluble in THF thus making possible the nanoprecipitation technique to be used for the preparation

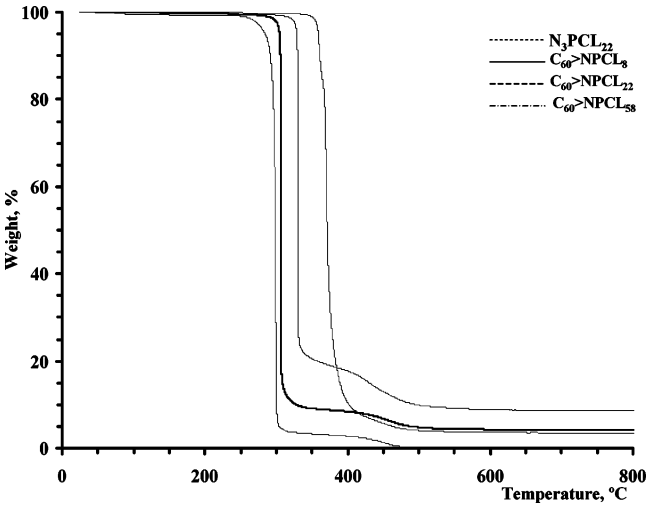

Figure 3. TGA curves for original N_3PCL and the $C_{60}[N(CH_2)_{12}OPCLOH]_x$ products.

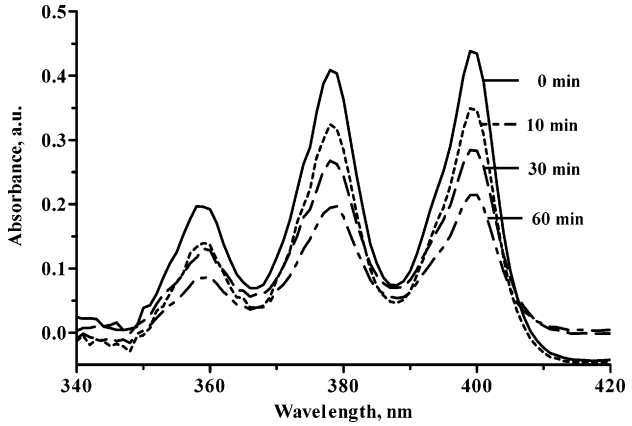

Figure 4. Absorption spectra of ADPA in the presence of $C_{60}[N(CH_2)_{12}OPCL_{22}OH]_x$.

of nanoparticles with incorporated C_{60}. The particles are stabilized by the amphiphilic copolymers PEO-*b*-PCL. As it is widely recognized, blocks of PEO efficiently stabilize the particles in the aqueous medium, being in addition to that biocompatible and nontoxic. All of the prepared nanohybrids were incorporated in the nanoparticles formed by nanoprecipitation of the mixed $C_{60}[N(CH_2)_{12}OPCLOH]_x$ and PEO-*b*-PCL solutions (Table 2).

The average particle diameter and polydispersity index of the nanoparticles prepared with different PEO-*b*-PCL/$C_{60}[N(CH_2)_{12}OPCLOH]_x$ ratios were measured by DLS. The data reported in Table 2 show that the diameter of the fullerene-containing nanoparticles decreases when the molecular weight of the PCL block of the stabilizing diblock increases at constant PEO block. A substantial increase in the nanoparticle diameter was observed upon increasing the length of the PCL arms grafted to C_{60}, all the other conditions being the same (Table 2). The polydispersity index was low and quite comparable for all the prepared nanoparticles. Dispersion of these nanoparticles in water was stable against dilution. Grafting of fullerene C_{60} with PCL chains was thus beneficial to its THF solubility, polymer (PCL) affinity, and thus the incorporation in nanoparticles.

Nanohybrids in Biocompatible Nanofibers. Electrospinning is an efficient technique to prepare polymer nano-

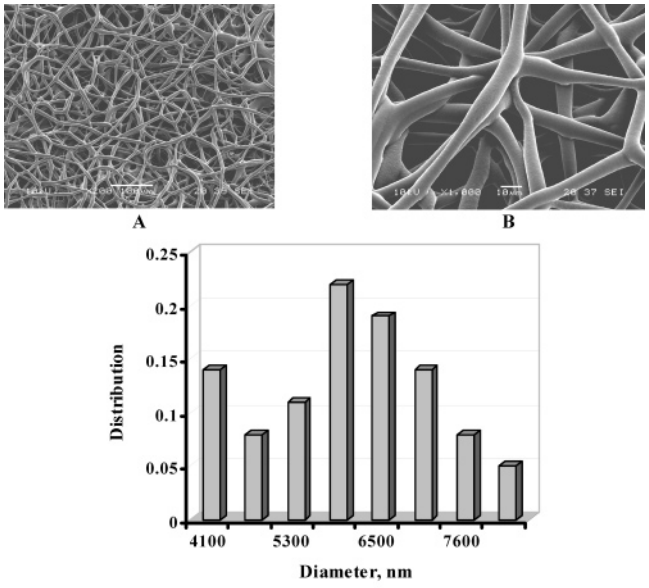

Figure 5. SEM micrographs of electrospun mats of PCL/$C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$ (2:1, w/w) ×200 (A) and ×1000 (B), and diameter distribution of the fibers (C). Total polymer concentration is 12%. Applied field strength 1.0 kV/cm.

Scheme 3. Photooxidation of ADPA

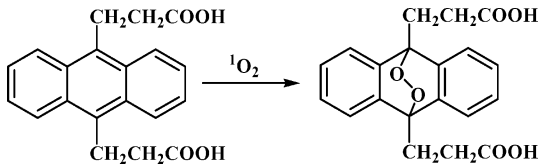

Table 2. Diameter and Polydispersity Index of C_{60}-Containing Nanoparticles Prepared at PEO-*b*-PCL: $C_{60}[NPCL]_x$ Weight Ratio of 1:1

samples	diameter, nm (polydispersity index)		
	$C_{60}[NPCL_8]_x$	$C_{60}[NPCL_{22}]_x$	$C_{60}[NPCL_{58}]_x$
PEO_{114}-*b*-PCL_9	149.1 ± 0.06 (0.11)	184.7 ± 0.02 (0.09)	218.2 ± 0.06 (0.14)
PEO_{114}-*b*-PCL_{18}	135.6 ± 0.03 (0.12)	162.7 ± 0.04 (0.09)	206.5 ± 0.21 (0.14)
PEO_{40}-*b*-PCL_{14}	168.3 ± 0.08 (0.11)	185.5 ± 0.02 (0.10)	202.5 ± 0.08 (0.09)

fibers,[24−26] which are very promising materials in a wide range of applications, from composite materials and filter media to tissue engineering and drug delivery.[27] This paper is the first report on the preparation of fullerene-containing micro- and nanosized polymer fibers by electrospinning. Solutions of $C_{60}[N(CH_2)_{12}OPCLOH]_x$ either alone or in the mixture with PCL were electrospun. Figure 5 shows SEM micrographs and diameter distribution of the fibers prepared by electrospinning of a mixed solution of PCL and $C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$. The average diameter was then 6.3 μm. The diameter of the fibers is not uniform along the fiber. This average diameter changed with the PCL/$C_{60}[N(CH_2)_{12}OPCLOH]_x$ weight ratio. For instance, it in-

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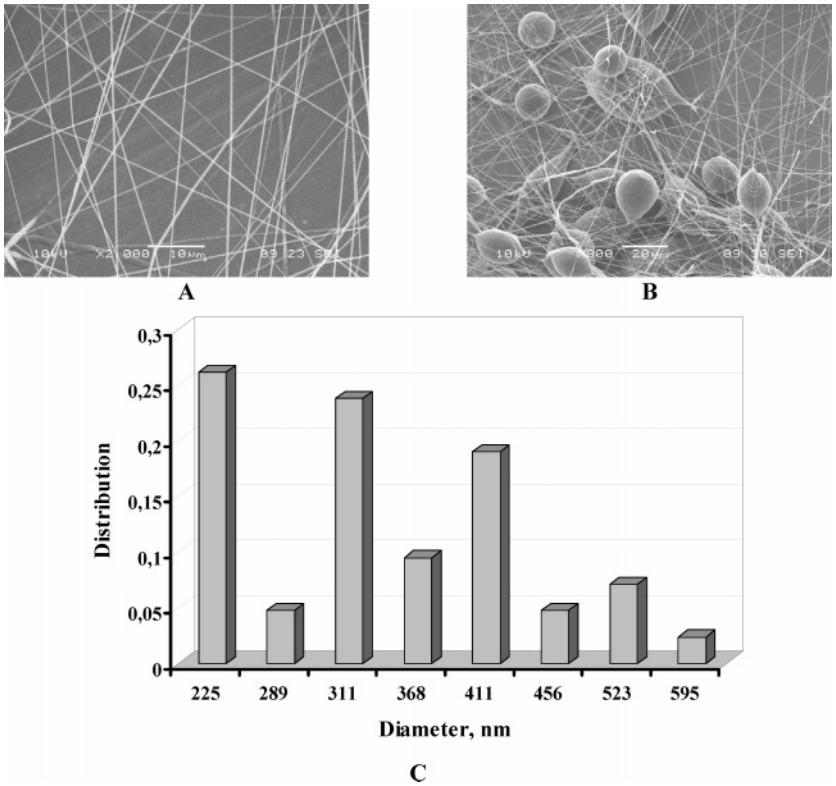

Figure 6. SEM micrographs of electrospun mats of PCL/$C_{60}[N(CH_2)_{12}OPCL_8OH]_x$ (2:1, w/w) ×2000 (A, B), and diameter distribution of the fibers (C). Total polymer concentration is 12%. Applied field strength 1.0 kV/cm.

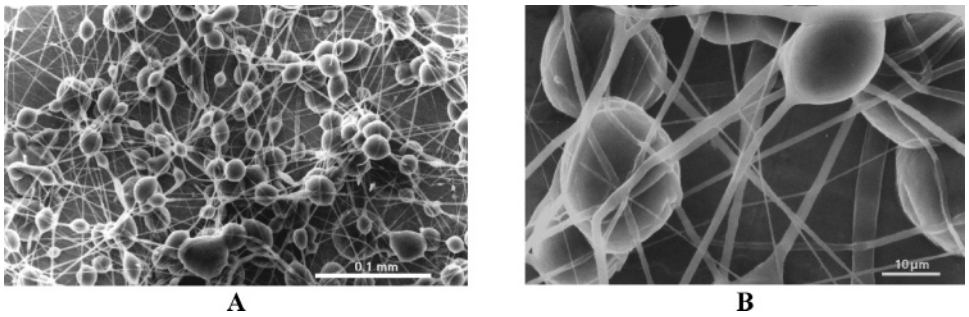

Figure 7. SEM micrographs of electrospun mats of $C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$ ×300 (A) and ×1500 (B). Total polymer concentration is 20%. Applied field strength 1.0 kV/cm.

creased from 3 μm to 7 μm when the PCL/$C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$ ratio was varied from 2 to 9.

SEM micrographs and diameter distribution of fibers prepared by electrospinning of the PCL/$C_{60}[N(CH_2)_{12}OPCL_8OH]_x$ mixture are shown in Figure 6. Spindle-like defects are observed along the fibers and nonconnected beads, as well (Figure 6B). It must be noted that this fullerene with the lower molecular weight arms leads to fibers with the smaller average diameter of 350 nm (Figure 6A,C). The average length of the spindle-like defects is 16.3 μm, and the average width is 15 μm. The average diameter of the nonconnected beads is 15 μm.

When solutions of $C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$ were electrospun alone, fibers with a considerably smaller diameter (average diameter 1100 nm) were prepared (Figure 7) as compared to the electrospinning of mixed solutions of PCL/$C_{60}[N(CH_2)_{12}OPCL_8OH]_x$. All along the $C_{60}[N(CH_2)_{12}OPCL_{58}OH]_x$ fibers, a considerable number of spindle-like defects were observed with an average length of 24 μm, and an average width of 19 μm is observed.

It is known that above a well-defined concentration flexible polymer chains form enough intermolecular entanglements ($n_{e(sol)} - 2.5$) that a three-dimensional physical network is stabilized.[28] Such a network is a prerequisite for the proper formation of micro- and nanofibers by electrospinning. However, the network formation depends on molecular weight polydispersity, flexibility (bulky substituents), and topology (linear, branched, and star-shaped) of the chains. Below a critical molecular weight, the three-dimensional physical network cannot be formed even at high concentrations, and electrospraying is then usually observed instead of electrospinning. Moreover, linear polymers are better suited to the chain networking than branched and star-shaped polymers of the same molecular weight. It might, therefore, be expected that solutions of fullerene-core star-shaped polymers should be more concentrated than usual for the electrospinning to be successful. Bearing in mind the

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topology of the PCL chains and their low molar mass (<90 000), the actual concentration needed in this work (12%) is low. This observation suggests that contributions other than the physical entanglements of the chains are involved in the formation of the physical polymer network. Hydrophobic $\pi-\pi$ interactions between fullerene cores more likely contribute to the network stabilization and fiber formation.

Conclusions

Clearly, the reaction of azide-terminated PCL with C_{60} is a very successful route to prepare C_{60}-containing polycaprolactones, particularly under the experimental conditions used in this work. An average of six PCL chains per fullerene core was grafted as a result of the reaction of azide-terminated PCL with C_{60}. Lack of chemical cross-linking and retention of the fullerene's electronic properties make this procedure a simple and versatile method for the synthesis of well-defined fullerene-core starlike polymers. Upon photoactivation, the C_{60} containing products generate singlet oxygen in a reasonable quantity. The C_{60} star-shaped polymers have successfully been encapsulated into PEO-*b*-PCL copolymers by the nanoprecipitation technique. For the first time, micro- and nanosized C_{60}-containing fibers were prepared by electrospinning. Therefore, the herein prepared C_{60}-derivatives are promising materials for photodynamic therapy of cancer and treatment of multidrug resistant pathogens.

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