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Polyether-modified fullerenes

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Summary

Polyether-modified fullerenes have been prepared under mild conditions by reacting C_{60} or C_{70} in toluene with a precursor poly(oxyethylene) or poly(oxypropylene) polymer possessing amino end-groups. In the early stages of the interaction, soluble products are formed. Later, cross-linking proceeds between the polyfunctional fullerenes and the bifunctional polyethers. The non-crosslinked fullerene derivatives are soluble both in toluene and water; by evaporation of toluene, very adhesive films are formed.

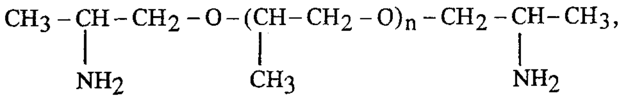
Introduction

Until recently, the main axes of fullerene research have been the study of their structure and physical properties. The recent availability of gram quantities of C_{60} has led to an increase of the chemical studies (1), leading to chemically modified fullerenes which open new prospects in the future applications of these compounds. C_{60} was found to add hydrogen (2), halogens (3,4) and amines (5). Recently, polystyrene has been covalently attached to C_{60} by reaction with a living polystyrene (6). Here we report the synthesis and characterization of amphiphilic derivatives of fullerenes obtained by reacting C_{60} or C_{70} with a precursor polymer - poly(oxyethylene) or poly(oxypropylene) - possessing amino end-groups.

Experimental

C_{60} and C_{70} were isolated from carbon soot extract purchased from MGP-ISAR, Bayonne, France (content: 85% C_{60} and 15% C_{70}, HPLC). C_{60} was separated by column chromatography on activated carbon (Norit A) according to reference (7), and C_{70} was separated on alumina (8). The fullerenes purity was checked by gel permeation chromatography (GPC) (C_{70} in C_{60}, less than 0.1%; C_{60} in C_{70}, less than 1%).

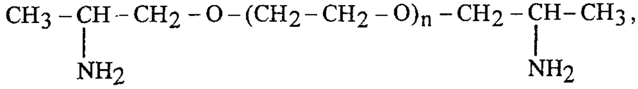
O,O'-bis (2-aminopropyl)polypropylene glyco 130 (Jeffamine D-230), O,O'-bis(2-aminopropyl)polypropylene glycol 300 (Jeffamine D-400) :



$$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_2-O-(\underset{CH_3}{\underset{|}{CH}}-CH_2-O)_n-CH_2-\underset{NH_2}{\underset{|}{CH}}-CH_3$$

, where n=2 or 5

O,O'-bis(2-aminopropyl)polyethylene glycol 500 (Jeffamine ED-600) and O,O'-bis(2-aminopropyl)polyethylene glycol 800 (Jeffamine ED-900) :



$$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_2-O-(CH_2-CH_2-O)_n-CH_2-\underset{NH_2}{\underset{|}{CH}}-CH_3$$

, where n=11 or 17

were purchased from Fluka and will be denoted further as D230, D400, ED600 and ED900.

The GPC analyses were carried out on a Waters apparatus equiped with a set of two Ultrastyragel columns of pore sizes 500 and 100 Å and double detection (differential refractometer and UV-visible detector set at 540 nm) using 1 mL/min of toluene as mobile phase at 45°C. In some cases an apparatus equipped with a photodiode array detector was used. UV-visible spectra were recorded on a Beckman Acta-MIV spectrophotometer. IR spectra were recorded on a Nicolet 710 FTIR spectrometer.

Preparation of polymer-modified fullerenes. The polymer-modified fullerenes were prepared by an interaction between C_{60} or C_{70} or their mixture (85% C_{60}, 15% C_{70}) and the polymers at polymer/fullerene molar ratios of 1:1, 50:1 or 100:1 in toluene. Syntheses were also carried out in neat diaminopolyether or in other solvents (hexane, cyclohexane, tetrahydrofuran, 1,2-dichloroethane).

$\boldsymbol{C_{60}(D230)_x}$: C_{60} (40 mg, 5.55×10^{-5} mol) was dissolved in 20 mL toluene and D230 (1.38 g, 5.55×10^{-3} mol) was added. The reaction mixture was stirred for 30 h at room temperature. The brown product was isolated by precipitation in diethyl ether (1:10 v/v) and dried under vacuum.

Elemental analysis (found) : C, 74.34%, H, 5.28%, N, 5.36%, indicating that the average number of D230 molecules (x) added to C_{60} was 3.

IR (KBr) $\bar{\nu}$ (wavenumber cm^{-1}): 3296 (m), 2967 (s), 2865 (s), 1651 (m), 1452 (s), 1374 (s), 1262 (w), 1101 (vs), 929 (w), 846 (w).

$\boldsymbol{C_{60}(D400)_x}$: same procedure as above and same polymer/C_{60} molar ratio (2.34 g D400 were used).

Elemental analysis (found) : C, 68.85%, H, 6.47%, N, 4.23%, indicating that the average number of D400 molecules (x) added to C_{60} was 3.

IR (KBr) $\bar{\nu}$ (wavenumber cm^{-1}): 3387 (m), 2969 (s), 2929 (sh), 2870 (s), 1653 (m), 1452 (m), 1374 (m), 1344 (sh), 1100 (vs), 933 (w).

$\boldsymbol{C_{60}(ED600)_x}$: same procedure as above and same polymer/C_{60} molar ratio (3.42 g ED600 were used).

Elemental analysis (found) : C, 62.70%, H, 6.55%, N, 2.99%, indicating that the average number of ED600 molecules (x) added to C_{60} was 3.

IR (KBr) $\bar{\nu}$ (wavenumber cm^{-1}): 3431 (br, m), 2670 (s), 1650 (br, m), 1455 (m), 1349 (m), 1298 (w), 1251 (w), 1105 (vs), 950 (m), 846 (w).

$\boldsymbol{C_{60}(ED900)_x}$: same procedure as above and same polymer/C_{60} molar ratio (4.88 g ED900 were used).

Elemental analysis (found) C, 59.84%, H, 7.47%, N, 2.36%, indicating that the average number of ED900 molecules (x) added to C_{60} was 3.

IR (KBr) $\bar{\nu}$ (wavenumber cm^{-1}): 3436 (br, m), 2871 (s), 1656 (m), 1453 (m), 1350 (m), 1299 (w), 1251 (m), 1106 (vs), 951 (m), 846 (w).

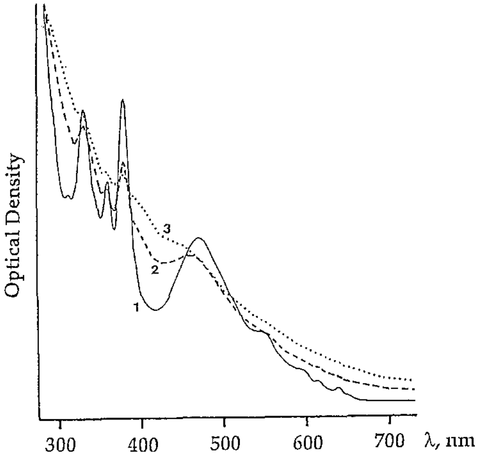
$\boldsymbol{C_{70}(D400)_x}$: C_{70} (20 mg, 2.38×10^{-5} mol) was dissolved in 15 mL toluene and D400 (1.00 g, 2.38×10^{-3} mol) was added. The reaction mixture was stirred for 30 h at room temperature and then poured into 10-fold excess (v/v) diethyl ether. The brown precipitate was dried under vacuum.

IR (KBr) $\bar{\nu}$ (wavenumber cm^{-1}) : 3362 (w), 3291 (w), 2874 (s), 2872 (s), 1668 (m), 1455 (m), 1375 (m), 1109 (vs), 1016 (w), 931 (w), 860 (w).

Results and discussion

C_{60} is insoluble in neat O,O'-bis-(2-aminopropyl)polypropylene glycols or O,O'-bis-(2-aminopropyl)polyethylene glycols but slowly interacts with them after mixing, yielding soluble products. The colourless diaminopolyethers become green-yellow and after that the whole liquid phase turns rapidly to yellow-brown.

By allowing to react C_{60} with diaminopolypropylene glycols or diaminopolyethylene glycols in solution (toluene or hexane), the violet colour of the C_{60} solution turns red-brown. The maxima in the UV-visible spectrum characteristic of C_{60} (and C_{70}) decrease in the course of the reaction until disappearence (Figures 1 and 2).



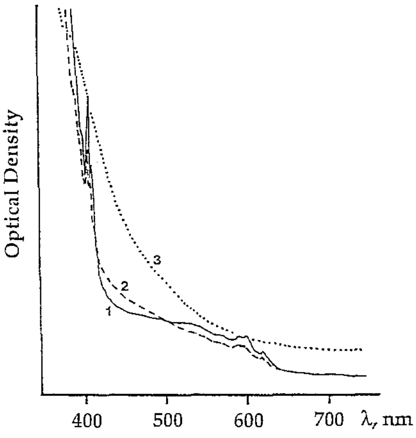


Figure 1. UV-visible spectra of the reaction mixture of C_{60} and D400 in hexane at different reaction time: (1) 5 min, (2) 48 h, (3) 60 h.

Figure 2. UV-visible spectra of the reaction mixture of C_{70} and D400 in hexane at different reaction time: (1) 5 min, (2) 1 h, (3) 1.5 h.

The reaction mixtures absorb in the region 300-700 nm but no pronounced maxima are observed. Weak structural features around 660 nm (mw, broad), different from those of C_{60}, are displayed in the spectrum of the reaction product of C_{60} in neat diaminopolyether.

The products of the interaction between C_{60} and ED600 or ED900 are water soluble and may be completely extracted with water from the toluene solution. The products of the reaction with D230 and D400 become water soluble after protonation with HClaq ($pH<4$). On adding HCl, no reverse reaction with regeneration of C_{60} was observed, contrary to what was observed in the case of other reaction products of C_{60}(9). On neutralizing the aqueous phase (with NaOH aqueous solution), the polymer adducts of C_{60} are completely re-extracted by toluene. The polyether-modified fullerenes contain hydrophilic segments - the polyether chains - and hydrophobe segments - the fullerene core. Such an amphiphilicity is typical of the surface active compounds. The soluble polypropylene glycol-modified fullerenes stabilize the toluene-water emulsions for more than ten days.

The reaction of fullerenes with diaminopolyethers was followed by the decrease in the NH_2 deformation band at 1590-1585 cm^{-1} . The broad and very strong C-O stretch absorption at 1110-1100 cm^{-1} does not allow to detect the tertiary carbon-nitrogen stretch absorption (of modest intensity) expected to appear at 1235 cm^{-1}. The consumption of C_{60} was also monitored by the decrease of the intensity of the C_{60} reflection IR bands until their disappearance (Figure 3). In the reflection IR spectrum of a C_{60} dispersion in polyethylene glycol (molar ratio 1:3), taken for comparison, bands are easily observed which are characteristic for C_{60}(10) and for the polyether.

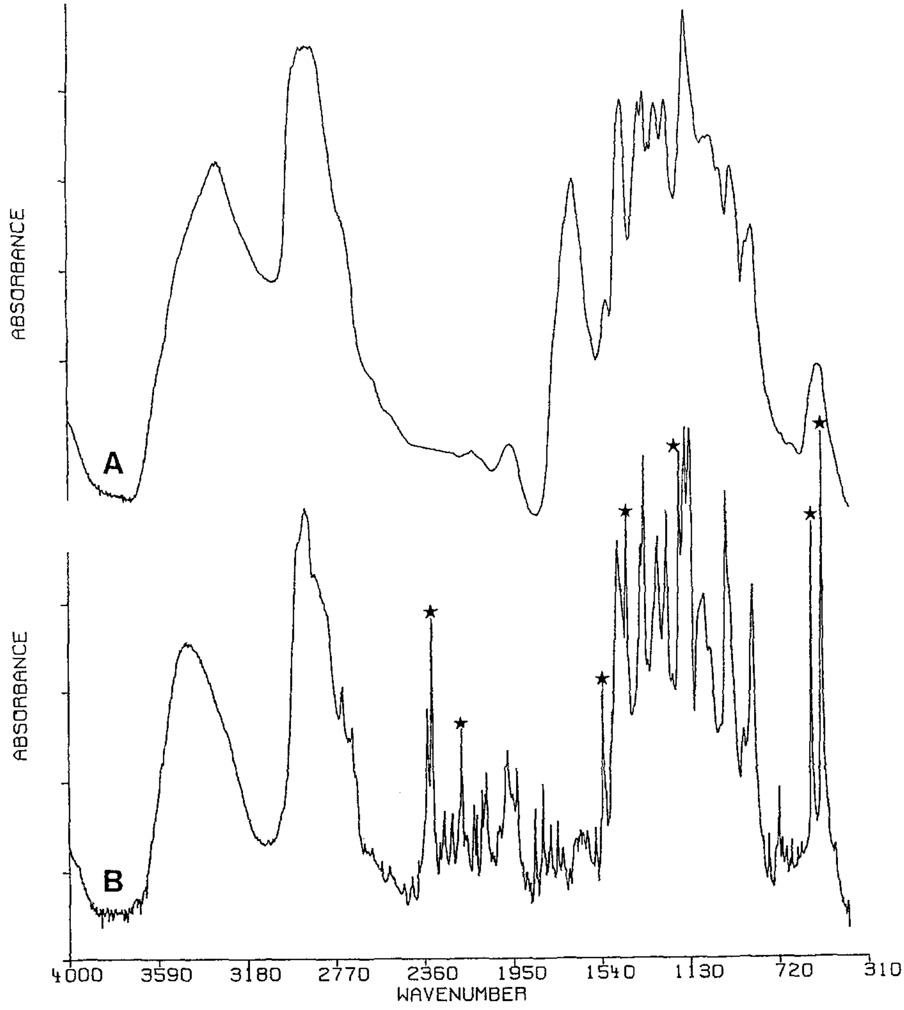


Figure 3. IR reflexion spectra of films of: A - $C_{60}(D230)_x$; B - C_{60} dispersion in polyethylene glycol; * - characteristic reflection IR bands of C_{60}

The interaction between the fullerenes and diaminopolyethers was conveniently followed by GPC. The elution volumes of C_{60} and C_{70} (25.7 mL and 27.7 mL at 45°C and at 60°C; 26.1 mL and 28.1 mL at 25°C) are larger than the total permeation limit. These facts are in agreement with earlier observations(11,12) and imply that hydrophobic interactions or adsorption phenomena are involved rather than size exclusion.

The GPC chromatograms of the reaction mixtures show the decrease in fullerene concentration with time and the appearance, at smaller elution volume, of new products (Figure 4).

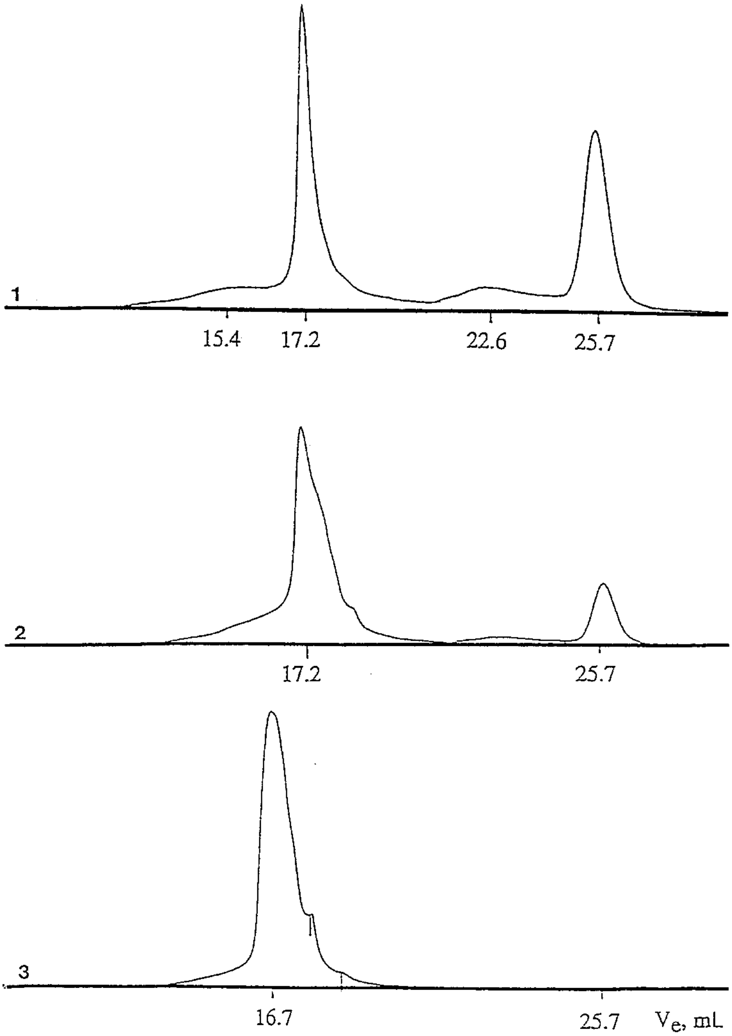


Figure 4. GPC chromatograms of the reaction mixture of D230 and C_{60} (mol ratio 100:1) in toluene at different reaction time : (1) 1h, (2) 6h, (3) 23h (UV-visible detector at 540 nm).

All the fractions are characterized by an absorption smoothly increasing from 700 to 300 nm without any well defined maxima (Figure 5), with spectra similar to those of the total reaction mixtures.

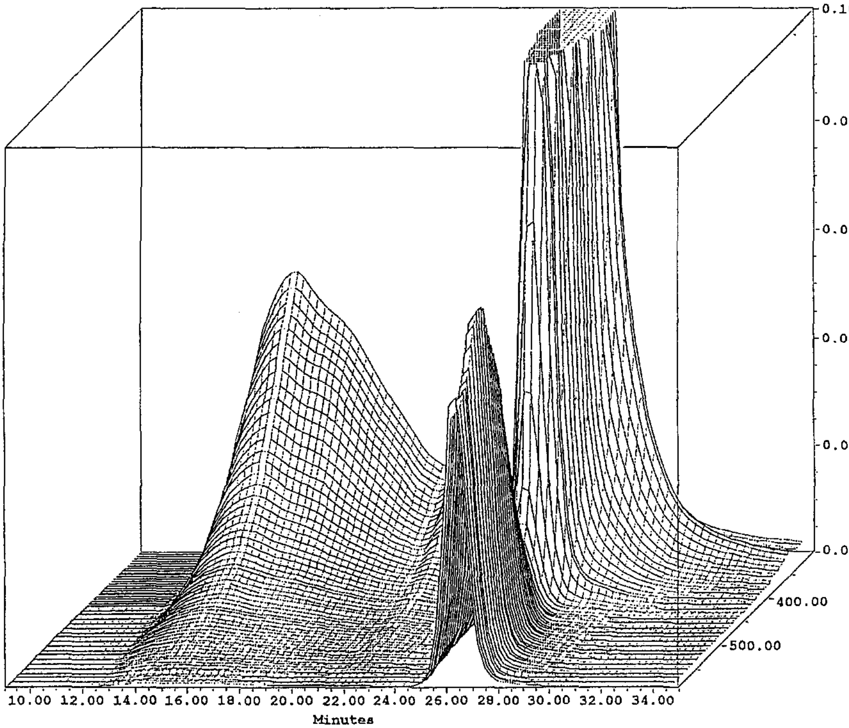


Figure 5. GPC chromatograms-UV-visible spectra of the reaction mixture of D230 and C_{60} (mol ratio 1:1) in toluene at a reaction time of 3 weeks (photodiode array detector).

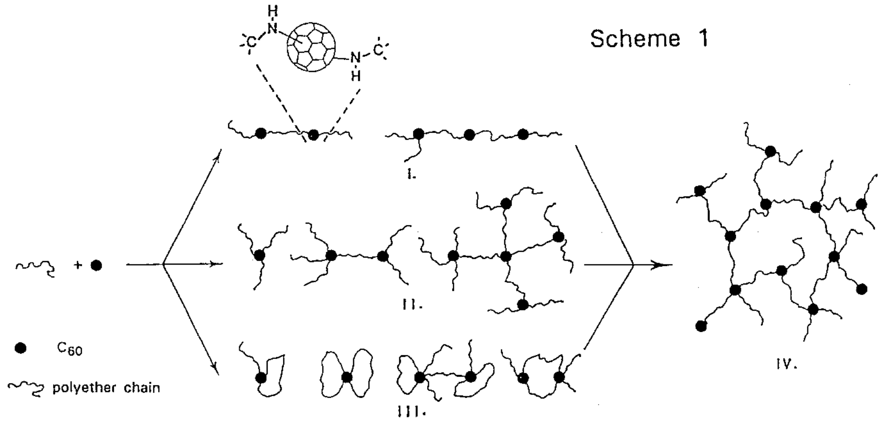
The reaction between C_{60} and diaminopolyethers was carried out also with C_{60} pre-adsorbed on activated carbon (0.1 g C_{60} per gram activated carbon with specific surface area 2000 m^2g^{-1}). Upon addition of diaminopolyether to a suspension of activated carbon containing pre-adsorbed C_{60} the colourless liquid phase turns brown in colour showing that the chemical modification changes the type of interaction with the carbon adsorbent. The GPC chromatograms show the appearance of the addition products.

The molecular weight of the reaction products was calculated from the elemental analysis data for three polyether chains added to C_{60}. Their elution volume estimated from the calibration curve is smaller than measured (Table I). This difference may be explained by the assumption that the addition of the polymer chains to the fullerenes does not completely exclude the hydrophobic interaction between the crosslinked polystyrene packing and the fullerene core. It may also be assumed that the hydrodynamic volume of the modified fullerenes is much smaller than that of the linear polyethers with comparable molecular weights. This may be the case for star-shaped or branched molecules.

Table I. Molecular weight (MW) and elution volume (V_e) of the polymer-modified C_{60}

Product	MW calc.	V_e, mL calibr. curve	V_e, mL found
$C_{60}(D230)_3$	1470	13.0	16.7
$C_{60}(D400)_3$	1986	12.5	14.7
$C_{60}(ED600)_3$	2568	12.0	14.2
$C_{60}(ED900)_3$	3360	11.5	13.9

It is known that the interaction between bifunctional oligomers with polyfunctional agents yields crosslinked and insoluble products. This is a stepwise process and first, particularly in dilute solutions, soluble products (linear, star-shaped or branched) may be formed. The low concentration of the reagents also favours the formation of cyclic species. The fullerenes are polyfunctional compounds and because of their low solubility the reactions are carried out in dilute solutions. That is why we propose Scheme 1 for the interaction between diaminopolyethers and fullerenes. The products shown in this scheme, even those containing cycles, may interact with each other or with the unconsumed starting diamine thus forming a network.



Scheme 1

At low starting diaminopolyether : C_{60} ratio (1:1), soluble products are formed even at long reaction time (3 weeks). Their GPC chromatograms exhibit large peaks and a polymodal distribution which may be explained by the formation of a mixture of products with different structures (linear, branched, star-shaped or cycle-containing). In this case, the formation of insoluble products is negligible. At higher polymer:C_{60} ratio (100:1 or 50:1), soluble products are obtained at the early stages of the reaction (30 hours) only. The GPC chromatograms of the reaction mixture exhibit a narrower molecular weight distribution (Figure 5) which indicates that one type of product is predominantly first formed. At long reaction time (3 weeks), separation of sol-gel fractions occurs in the toluene solution of ED600 and C_{60} (50:1 molar ratio). The gel fraction represents a highly swollen gel with very poor mechanical properties. A six-fold decrease of the gel volume was observed after solvent evaporation. The gel did not take back its initial dimensions by swelling in toluene, which implies that an additional cross-linking proceeds during the solvent removal. On casting the toluene solutions on glass or metal surfaces, highly adhesive films are formed.

The results show that the reaction betwen diaminopolyethers and C_{60} is kinetically controlled. A steric control cannot be excluded since it is possible that the polymer chains attached to the fullerene core may hinder some of the fullerene reactive sites.

Acknowledgments

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