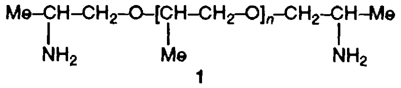
Amphiphilic Derivatives of Fullerenes Formed by Polymer Modification

Nevena Manolova,† Ilya Rashkov,† François Beguin* and Henri van Damme
CRMD, CNRS and Université d'Orléans, 45071 Orléans Cedex 2, France

Polymeric fullerene derivatives have been synthesized which are soluble both in water and toluene, by the reaction of C_{60} and C_{70} with precursor poly(oxyethylene) or poly(oxypropylene) polymers possessing amino end-groups.

Among the many derivatives of fullerenes (mainly C_{60}) which have been reported so far, only a few are polymeric.[1] Several strategies may be conceived, leading either to in-chain structures in which the fullerene cages are incorporated in 1D, 2D or 3D polymeric chains or networks, or to on-chain structures with pendant fullerene units. Polyfullerenes of the former type have been prepared by reaction of C_{60} with a living polystyrene,[2] whereas pendant polymer-bound C_{60} derivatives were prepared recently by using soluble polymers of the poly(alkylene imine) type, capable of adding to fullerene double bonds in what has been described as a 'buckyball fishing' process.[3] All these polymeric materials are insoluble in water.

Here we report the synthesis of in-chain derivatives of fullerenes with precursor polymers including O,O'-bis(2-amino-



$$\mathrm{Me{-}\underset{NH_2}{\underset{|}{CH}}{-}CH_2{-}O{-}[\underset{Me}{\underset{|}{CH}}{-}CH_2{-}O]_{\mathit{n}}{-}CH_2{-}\underset{NH_2}{\underset{|}{CH}}{-}Me}$$

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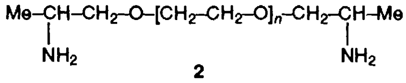

$$\mathrm{Me{-}\underset{NH_2}{\underset{|}{CH}}{-}CH_2{-}O{-}[CH_2{-}CH_2{-}O]_{\mathit{n}}{-}CH_2{-}\underset{NH_2}{\underset{|}{CH}}{-}Me}$$

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† On leave from the Institute of Polymers, Bulgarian Academy of Sciences, Sofia-1113, Bulgaria.

propyl)poly(oxypropylene) **1** and *O,O'*-bis(2-aminopropyl) poly(oxyethylene) **2**.

The polymers used were *O,O'*-bis(2-aminopropyl)polypropylene glycol 130 (Jeffamine D-230), *O,O'*-bis(2-aminopropyl)polypropylene glycol 300 (Jeffamine D-400), *O,O'*-bis(2-aminopropyl)polyethylene glycol 500 (Jeffamine ED-600) and *O,O'*-bis(2-aminopropyl)polyethylene glycol 800 (Jeffamine ED-900) from Fluka, which will be denoted as D230, D400, ED600 and ED900, respectively. The syntheses were carried out in toluene, with Jeffamine : fullerene molar ratios of 1 : 1, 50 : 1 or 100 : 1, or in neat Jeffamine or in other solvents (hexane, cyclohexane, tetrahydrofuran, 1,2-dichloroethane). In a typical preparation, such as that of $C_{60}(D230)_x$, C_{60} (40 mg, 5.55×10^{-5} mol) was dissolved in toluene (20 ml) 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 *in vacuo*. Elemental analysis (C 74.3%, H 5.3%, N 5.4%) indicated that an average number of three D230 molecules is added to C_{60}. The same molar composition was obtained with D400, ED600 and ED900.

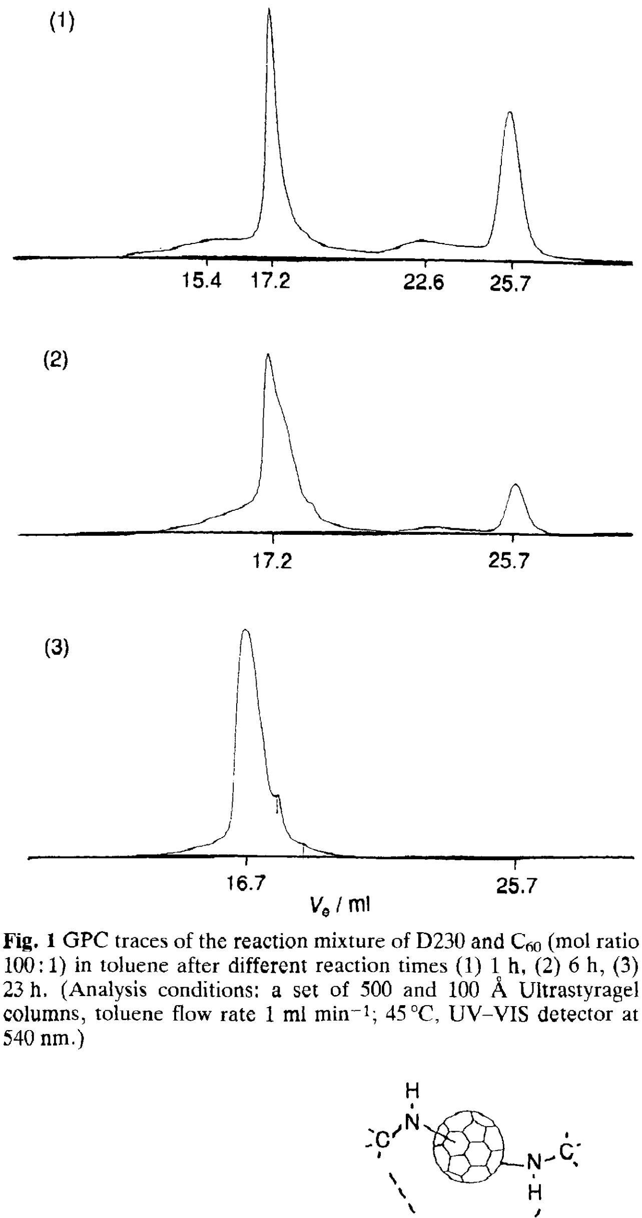


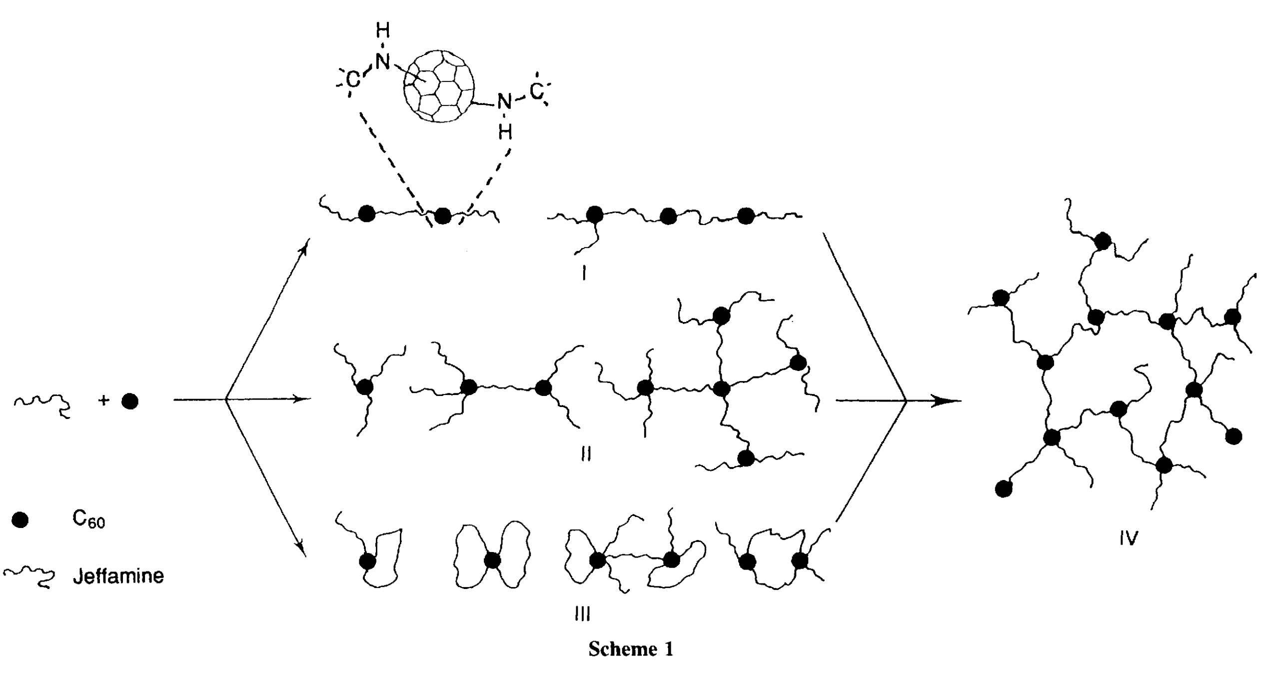
Fig. 1 GPC traces of the reaction mixture of D230 and C_{60} (mol ratio 100 : 1) in toluene after different reaction times (1) 1 h, (2) 6 h, (3) 23 h. (Analysis conditions: a set of 500 and 100 Å Ultrastyragel columns, toluene flow rate 1 ml min^{-1}; 45 °C, UV–VIS detector at 540 nm.)

C_{60} is insoluble in neat Jeffamines but slowly interacts with them after mixing, yielding soluble products. The colourless Jeffamines become green–yellow and after that the whole liquid phase turns rapidly to yellow–brown. When the reaction is performed in toluene or hexane solution, the violet colour of the C_{60} solution turns red–brown. The maxima in the UV–VIS spectrum characteristic of C_{60} (and C_{70}) decrease during the reaction until disappearance. 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 Jeffamine.

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 aqueous HCl (pH < 4). Upon addition of 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}.[4] On neutralizing the aqueous phase (with aqueous NaOH), the polymer adducts of C_{60} are completely reextracted by the organic phase.

The reaction of fullerenes with Jeffamines was followed by the decrease in the IR NH_2 deformation band at 1590–1585 cm^{-1} until complete consumption of the amine and disappearance of this band. The broad and very strong C–O stretching absorption at 1110–1100 cm^{-1} does not allow the tertiary carbon–nitrogen stretching absorption (of modest intensity), expected to appear at 1235 cm^{-1}, to be detected.

The interaction between the fullerenes and Jeffamines was conveniently followed by GPC. The elution volumes of C_{60}



Scheme 1

and C_{70} (25.7 and 27.7 ml at 45 °C) are larger than the total permeation limit. These facts are in agreement with earlier observations[5,6] and imply that hydrophobic interactions or adsorption phenomena are involved rather than size exclusion. The GPC traces of the reaction mixtures show the decrease in fullerene concentration with time and the appearance, at smaller elution volume, of new products (Fig. 1). All fractions are characterized by an absorption smoothly increasing from 700 to 300 nm without any well defined maxima, similar to the spectra of the total reaction mixtures.

It is known that the interaction between bifunctional oligomers and polyfunctional agents yields crosslinked and insoluble products. This is a stepwise process and initially, 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 rings, may interact with each other or with the unconsumed starting diamine thus forming a network.

At low starting Jeffamine : C_{60} ratio (1 : 1), soluble products are formed only after long reaction times (3 weeks). Their GPC traces 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 ring-containing). In this case, the formation of insoluble products is negligible. At higher Jeffamine : C_{60} ratio (100 : 1 or 50 : 1), soluble products are obtained at the early stages of the reaction (30 h) only. The GPC traces of the reaction mixture exhibit a narrower molecular mass distribution which indicates that one type of product predominantly is 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 is 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 revert to 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 between 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.

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