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Fullerene core star-like polymers
2. Preparation from fullerenes and linear or cyclic monoaminopolyethers

S. Delpeux[a], F. Béguin[a,*], N. Manolova[b], I. Rashkov[b]

[a]CRMD, CNRS-Université, 1B, rue de la Férollerie, 45071 Orléans Cedex 2, France
[b]Institute of Polymers, Bulgarian Academy of Sciences, 1113, Sofia, Bulgaria

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Abstract

Fullerene core star-like polymers have been synthesized by reacting C_{60} with methyl ethers of polyoxypropylene or polyoxyethylene and crown ethers having amino end-group. Depending on the starting mole ratio (C_{60}/polyether = 1, 3 or 10), products with different average number of polyether branches were prepared. The solubility of the derivatives was modulated by varying the number and the hydrophilicity of the grafted polyether chains.

1. Introduction

The promising properties of C_{60} stimulate an increasing interest for fullerene-containing polymers in view of applications in various fields (electronics, optics, catalysis, biomaterials) [1, 2]. Different synthesis routes have been used, such as grafting of reactive oligomers on C_{60} [3], polymerization of fullerene-containing macromonomers [4] or reaction with "living" polymers [5, 6]. Among all the possible combinations, dendritic and star polymers are expected to provide means to create fullerene materials having original properties [7]. Fullerene-terminated polystyrene star polymers have already been reported [8, 9]. The preparation of fullerene-core star polymers has been achieved by reaction of C_{60} with living polymers [10] or by the utilization of a polyhydroxylated C_{60} derivative as a core for anchoring polymer branches on C_{60} through bonding with the hydroxyl groups [11, 12].

As it was previously shown [3], the covalent attachment of polyether chains imparts water solubility to C_{60}. Such products have shown photo-induced cytotoxicity under visible light irradiation [13] and antitumor effect [14]. C_{60} derivatives prepared by interaction with bifunctional oligoethers may contain crosslinked products depending on the reaction conditions. Therefore, it seems of interest to prepare water-soluble C_{60} derivatives by addition of monofunctional reactive oligomers. Recently we have reported a simple preparation of fullerene-core star-like polymers by interaction of C_{60} and monomethyl ethers of oligomeric polyoxyethylenes having azide end-groups [15]. In the present work, the synthesis and the properties of fullerene derivatives, linear fullerene-containing polymers (LFP) or fullerene-core star-like polymers (FCSP), by reaction of C_{60} with linear or cyclic monoaminopolyethers are described.

2. Experimental

2.1. Materials

The following crown ethers (Aldrich) were used: 2-(aminomethyl)-15-crown-5 (2AM15C5)—a viscous liquid; 2-(aminomethyl)-18-crown-6 (2AM18C6)—a viscous liquid; 1-aza-18-crown (1AZA18C)—colourless

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* Corresponding author. Fax: +33 2-38-63-37-96.

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crystals, m.p. 46–49°C. The linear monoaminopolyethers used were: O-(2-aminopropyl)-O′-(2-methoxyethyl)-polyoxypropylene (Jeffamine D600, Fluka, $CH_3OPOPNH_2$) and O-(2-aminoethyl)-O′-(2-methoxyethyl)polyoxyethylene ($CH_3OPOENH_2$). The latter was prepared by interaction of O-(2-bromoethyl)-O′-(2-methoxyethyl)polyethylene glycol with NH_3 according to a known method [16]. C_{60} (Technocarbo, France) of purity 99.9% was used. The solvents, tetrahydrofuran (THF) and toluene, were of HPLC purity.

2.2. Preparation of C_{60} derivatives

The C_{60} derivatives were prepared by stirring a mixture of C_{60} and monoaminopolyethers, at polyether/fullerene mole ratio of 1:1, 3:1 or 10:1, in toluene or in THF. The syntheses were performed under argon in the dark at room temperature for 7 days. At the end of the reaction, the solution was concentrated by evaporation of the solvent under reduced pressure. The crude reaction products were recovered in acetone thus allowing unreacted C_{60}, if any, to precipitate. Then, the C_{60} derivatives obtained from crown ethers and polyoxyethylene were precipitated in 20-fold excess of diethylether in which unreacted crown ethers and polyoxyethylene are soluble. The C_{60} adducts prepared from Jeffamine D600 (brown viscous oils) were dispersed in water in order to eliminate the unreacted polyether.

2.3. Methods

UV spectra were recorded on a Beckman Acta MIV spectrophotometer in quartz cells (0.2 cm path). The concentrations were in the range 0.1–0.4 mg/ml in chloroform. FTIR spectra were recorded on thin films on a NaCl window for the viscous liquids, or as KBr pellets (1%) for the solid products, on a Nicolet 710 FTIR spectrometer. ^1H NMR spectra were obtained in $CDCl_3$ at room temperature on a BRUKER 300 MHz spectrometer, taking the signal of $CHCl_3$ at 7.24 ppm as a reference.

Size-exclusion chromatography (SEC) analyses were performed on a Waters apparatus equipped with: a set of three Waters columns, HR2, HR1 and HR0.5 for the analyses in THF as the eluent; and a set of three columns, HR3, Ultrastyragel 500 Å and Ultrastyragel 100 Å for the analyses in toluene. The flow rate was 1 ml/min and the column temperature 45°C. Dual detection was used with a Waters 410 differential refractometer and a Waters 486 absorbance detector set at 254 or at 350 nm in case of THF or toluene, respectively. Polyethylene glycol standards and C_{60} (99.98% purity) were used for calibration. The consumption of C_{60} was determined by SEC of the reaction mixtures (eluent toluene) by comparing the peak area with a calibration curve.

Thermogravimetric analyses coupled with mass spectrometry were performed on a Setaram microbalance (type MTB 10-8) connected with an oven (Pyrox VL30) at a heating rate of 150°C/h, in the range 20–1200°C. The volatile products were continuously analyzed by a multichannel mass spectrometer (Balzers QMG420).

The vapour pressure osmometry (VPO) measurements were performed on a Knauer apparatus at 45°C. Chloroform was the solvent, and benzil and polyethylene glycol 2000 were the standards.

MALDI-TOF mass spectra were recorded on a BRUKER BIFLEX^{TM} time of flight mass spectrometer, as an average of 60 laser shots. The acceleration potential of the ions was 30 kV, in the positive mode. A 10 μl aliquot of the matrix (α-cyano-3-hydroxy-*trans*-cinnamic acid dissolved in acetone/water (90/10) at a concentration of 20 mg/ml) was thoroughly mixed with a 10 μl aliquot of the sample solution (1% solution in acetone) by vortexing. This preparation was proceeded by depositing 1 μl of the matrix/sample mixture on the probe tip, and the solvent was allowed to evaporate at room temperature.

Table 1
Aspect and solubility of the C_{60} derivatives prepared from C_{60} and aminopolyethers

Aminopolyether	Mole ratio, polyether/C_{60}	Aspect of the polymer	Solubility
$CH_3OPOENH_2$	3	Brownish viscous oil	H_2O (> 400 mg/ml), $CHCl_3$, THF, toluene, EtOH
	10	Brownish viscous oil	
	1	Brownish viscous oil	$CHCl_3$ (> 300 mg/ml), THF (> 40 mg/ml)
Jeffamine D 600	3	Brownish viscous oil	Toluene, EtOH, CH_3CN, CH_3COCH_3
	10	Brownish viscous oil	
	1	Black powder	THF, CH_3COCH_3, $CHCl_3$, toluene
2AM18C6	3	Black powder	THF, CH_3COCH_3, $CHCl_3$ (> 300 mg/ml), toluene, H_2O, PC
	10	Brownish rubber-like	H_2O (> 300 mg/ml), $CHCl_3$ (> 300 mg/ml), THF, toluene, EtOH, MeOH, PC, CH_3COCH_3

This mixture was desorbed/ionized using a pulse nitrogen laser beam ($\lambda = 337$ nm) at a repetition rate of 1.5 Hz. An external calibration was realized with the $[M + H]^+$ ions of angiotensine II (1047.20 Da), ACTH 18–39 (2466.73 Da) and bovine insulin (5734.56 Da) and/or using the peaks of the matrix.

The conductivity measurements were realized with a Consort C831 apparatus under high purity argon at 25°C, in anhydrous propylene carbonate (PC) (Aldrich, water content less than 0.005%). Pure 18-crown-6 (Aldrich) was used as a reference and titrated with dry potassium perchlorate according to the method described by Takeda et al. [17]. A PC solution of the crown ether (2×10^{-3} M, 50 ml) or its adduct with C_{60} was placed in a glass vessel and potassium perchlorate (2×10^{-2} M) was added step-by-step (0.5–1 ml) until the total concentration of the alkali metal perchlorate was approximately twice as large as that of the crown ether. The conductivity of the solution was measured after each addition of potassium perchlorate solution.

The X-ray photoelectron spectroscopy analyses were carried out with an ESCALAB MKII apparatus using Al $K\alpha_{1,2}$ radiation (1486.6 eV). The samples were dissolved in toluene or chloroform and the solutions were filtered. Films were prepared by casting onto a gold-deposited carrier. The Au 4f7/2 core level at 84 eV was used for energy calibrations. After SHIRLEY [18] background substraction, the line shapes of the individual peaks were fitted with Gauss/Lorentz line models using non-linear least squares fitting.

3. Results and discussion

Monoaminopolyethers with polyoxyethylene or polyoxypropylene chains were used for the preparation of the C_{60} derivatives. The polyethers selected were linear or cyclic and contained primary or secondary amino group. The synthesis was performed in homogeneous (toluene) or heterogeneous (THF) medium.

It is known that C_{60} is scarcely soluble in organic solvents, e.g. its solubility in chloroform and in THF is 0.5 mg/ml and 0.037 mg/ml, respectively [19]. The solubility of the prepared polymers in a number of polar and nonpolar solvents is higher than the solubility of C_{60} (Table 1). Almost all of them are water-soluble. As seen from Table 1, the solubility may be modulated by increasing the number of the branches, but also by varying their hydrophilicity (for example, the fullerene derivatives with polyoxyethylene chains are water-soluble, and those with polyoxypropylene chains are insoluble).

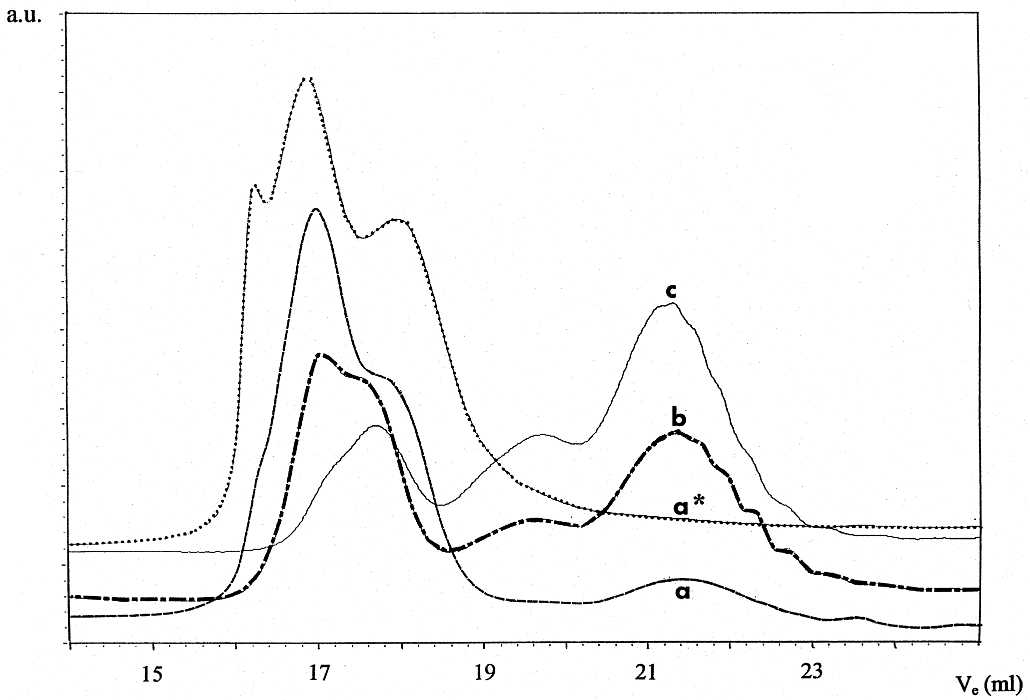

Fig. 1. Size exclusion chromatography (RI traces, eluent THF) on FCSP prepared in toluene at starting mole ratio Jeffamine D600/C_{60} equal to 1 (a), 3 (b) and 10 (c); after repeated washing with water (a*).

Table 2
Characteristics of the star-like polymers prepared from C_{60} and linear monoaminopolyethers. Molecular mass determined by vapour-pressure osmometry (VPO) and size exclusion chromatography (SEC); $\bar{x}$, average number of arms estimated from VPO, elemental analysis (EA) and thermogravimetric analysis (TGA)

Aminopolyether	Mole ratio, polyether/C_{60}	Solvent	$\bar{M}_n$ (VPO)	$\bar{M}_w/\bar{M}_n$ (SEC)	$\bar{x}$(VPO)	$\bar{x}$(EA)	$\bar{x}$(TGA)	Average formula
$CH_3OPOENH_2$	3	THF	2260	1.10	3	–	–	$(CH_3OPOENH)_3C_{60}H_3$
	10	THF	4900	1.20	7	7	–	$(CH_3OPOENH)_7C_{60}H_7$
	1	THF	–	–	–	2	1	$(CH_3OPOPNH)_2C_{60}H_2$
	3	THF	2525	1.08	3	3	3	$(CH_3OPOPNH)_3C_{60}H_3$
	10	THF	5260	1.25	7	6	6	$(CH_3OPOPNH)_6C_{60}H_6$
Jeffamine D 600	1	Toluene	–	–	–	2	–	$(CH_3OPOPNH)_2C_{60}H_2$
	3	Toluene	–	–	–	5	–	$(CH_3OPOPNH)_5C_{60}H_5$
	10	Toluene	4200	1.25	6	6	–	$(CH_3OPOPNH)_6C_{60}H_6$

New peaks growing with the consumption of C_{60} appear in the SEC chromatograms of the reaction products (Fig. 1). Since these derivatives are also absorbing in the UV and located at smaller elution volumes than the parent polyethers (the elution volume of Jeffamine D600 is 21.5 ml), it is a proof that the chains are grafted on C_{60}. As formerly mentioned [3], the elution volume of C_{60} is higher than the total column volume, thus implying a strong specific π–π interaction between C_{60} and the stationary phase of polystyrene type. The FCSP with higher average number of branches are eluted at lower volume. For example, FCSP obtained by reacting C_{60} with 2AM18C6 are eluted at 21.2, 21.8 and 22.3 ml for an average number of branches of 5, 3 and 2, respectively. The analyses of derivatives prepared at different starting mole ratio, Jeffamine D600/C_{60}, show that purification by precipitation of C_{60} in acetone and repeated washing with water is efficient to eliminate unreacted Jeffamine and residual C_{60} (Fig. 1).

Most probably, the interaction between C_{60} and polyethers having primary or secondary amine group proceeds according to the mechanism proposed for the reaction between C_{60} and alkylamines [20]. A solvating solvent like THF favours the formation of the ion pair and its role may be illustrated with the following example. The consumption of C_{60} was followed during its reaction with Jeffamine D600 in mole ratio polyether/C_{60} = 1, 3 or 10 in THF and in toluene. After a reaction time of 7 days in THF medium, the percentage of unreacted C_{60} was 6%, 1 and 0%, respectively. In the case of toluene, this percentage is higher than 20% even in the case of an important excess of polyether (mole ratio 10).

With different methods (elemental analysis, VPO, TGA), it was possible to estimate the average number of branches grafted on the C_{60} core (Tables 2 and 3). Depending on the starting mole ratio, fullerene linear polymers (FLP) and fullerene core star-like polymers (FCSP) with different number of branches were obtained. At starting ratio 1 or 3, the number of poly-

Table 3
Characteristics of the star-like polymers prepared from C_{60} and cyclic monoaminopolyethers. Molecular mass determined by vapour-pressure osmometry (VPO); $\bar{x}$, average number of arms estimated from VPO, elemental analysis (EA) and thermogravimetric analysis (TGA)

Aminopolyether	Mole ratio, polyether/C_{60}	Solvent	$\bar{M}_n$ (VPO)	$\bar{x}$(VPO)	$\bar{x}$(EA)	$\bar{x}$(TGA)	Average formula
2AM15C5	10	THF	2300	6	6	–	$(2AM15C5)_6C_{60}H_6$
	1	Toluene	[a]	–	2	1	$(2AM18C6)_2C_{60}H_2$
	3	Toluene	1690	3	4	3	$(2AM18C6)_3C_{60}H_3$
2AM18C6	10	Toluene	1920	4	5	5	$(2AM18C6)_5C_{60}H_5$
	1	THF	[a]	–	1	2	$(2AM18C6)_2C_{60}H_2$
	3	THF	1210	2	2	2	$(2AM18C6)_2C_{60}H_2$
	10	THF	2630	6	6	–	$(2AM18C6)_6C_{60}H_6$
1AZA18C	10	Toluene	2300	6	6	4	$(1AZA18C)_6C_{60}H_6$
	10	THF	2350	6	6	4	$(1AZA18C)_6C_{60}H_6$

[a] Sparingly soluble in $CHCl_3$.

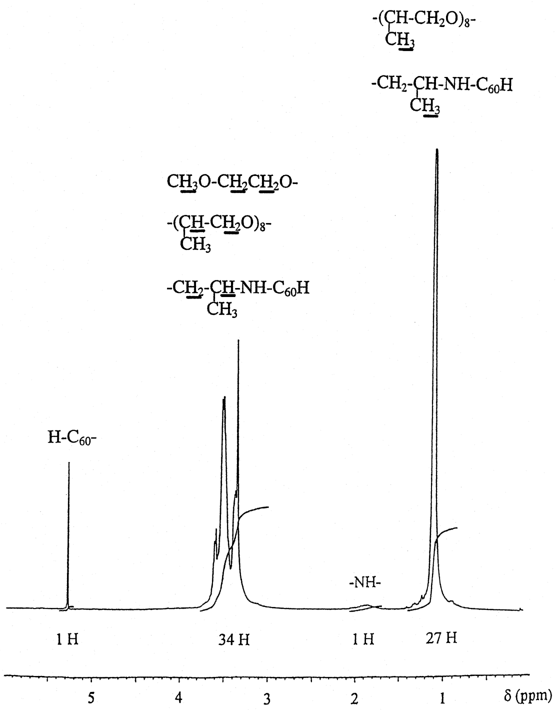

Fig. 2. ^{1}H NMR spectrum ($CDCl_3$ solution) of $(CH_3OPOPNH)_xC_{60}H_x$ ($\bar{x} = 6$) prepared from Jeffamine D600 and C_{60} in THF at mole ratio 10.

ethers branches is $\bar{x} = 2$–5, whereas it is 6–7 at starting ratio of 10.

Signals of the polyether chains are observed in the ^{1}H NMR spectra of FCSP, and a peak in the range of 5 ppm characterizes protons bound to the fullerene core [21]. An example is given for FCSP prepared from Jeffamine D600 (Fig. 2). As already observed in the case of other derivatives of Jeffamine [22], the signal corresponding to the methyl of the isopropylamino end-group is shifted in the spectra of FCSP, giving only one signal at about 1 ppm for all the methyl groups. ^{1}H NMR spectra do not allow conclusions to be drawn about the structure of the derivatives formed. The intensity ratios are independent of the number of branches added to the C_{60} core. However in all cases, whatever this average number, the ratios are compatible with the general formula $[\text{polyetherNH}]_xC_{60}H_x$.

The UV-visible spectra of the FCSP in chloroform and in acetonitrile showed absorption bands in the region 300–700 nm, but without characteristic maxima, similarly to the previously reported case of the reaction with linear polyethers having two amino end-groups [3].

In the IR spectra of FCSP, bands characteristic of the C—O—C bonds of the polyether chains were observed at 1105 cm^{-1}, and at 1373 cm^{-1} for the methyl groups of the derivatives having polyoxypropylene chains. Bands coming from the C_{60} core were only observed in the IR spectra of crown ether FLP having $\bar{x} = 2$. The lack of such bands for the other FLP may be explained either by the decrease of symmetry of the C_{60} core due to the attachment of the polyether branches or (and) by the more important relative weight of the grafted chain. On the other hand, at $\bar{x} > 2$, the bands of the C_{60} core are absent, whatever the type of polyether and the starting mole ratio.

The molecular weight of the star polymers could not be determined by the SEC analyses because of the limitations of the technique, in this particular case, when star polymers are concerned. Nevertheless, the SEC analyses showed that, using different starting mole ratio Jeffamine D600/C_{60}, all FCSP have almost the same elution volume in the case of toluene eluent, whereas in THF two overlapping peaks are observed in the V_e range 16–20 ml (at 16.9 and 17.8 ml), independently of the number of branches, up to 6–7 (Fig. 3). Moreover, with the highest number of branches, the first peak (higher hydrodynamic volume) appears as a shoulder, the second peak (at smaller hydrodynamic volume) being higher (Fig. 3c). To explain this peculiarity, we assume that the products of mono- and di-addition of polyoxypropylene chains to C_{60} form aggregates in THF, whose hydrodynamic volume is higher than that of mono- or diadducts. As it was mentioned above, C_{60} is very poorly soluble in THF. The solubility of polyoxypropylene in THF and in toluene is much higher. The binding of polyoxypropylene chains to C_{60} leads to products with increased solubility but, in the case of mono- and di-adducts, the part of C_{60} is important enough to favour the formation of aggregates with an inner C_{60} core and an outer polyether shell which is much more compatible with THF than the core.

In the MALDI-TOF spectrum of Jeffamine D600 peaks of $CH_3OCH_2CH_2[OCH_2CH(CH_3)]_nOCH_2CH(CH_3)NH_2$ homologues are observed, with values of $n = 3$–17. The most intense $[M + H]^+$ peaks at 598.3 and 656.3 m/z correspond to $n = 8$ and 9, respectively. MALDI-TOF mass spectrometry allowed estimation of the molecular mass characteristics of Jeffamine D600 according to Creel [23]. The values found are: $\bar{M}_n = 668.8$, $\bar{M}_w = 727.7$ and $\bar{M}_w/\bar{M}_n = 1.09$. MALDI-TOF analyses have been performed on the reaction products of Jeffamine D600 and C_{60} in THF, for which the average formula given by different methods is reported in Table 2. In the mass spectra of the products with average formula $\{CH_3OCH_2CH_2[OCH_2CH(CH_3)]_nOCH_2CH(CH_3)NH\}_2C_{60}H_2$ (Fig. 4a) and $\{CH_3OCH_2CH_2[OCH_2CH(CH_3)]_nOCH_2CH(CH_3)NH\}_3C_{60}H_3$, only peaks characteristic of the monoaddition are observed, and peaks corresponding to addition products with 2,

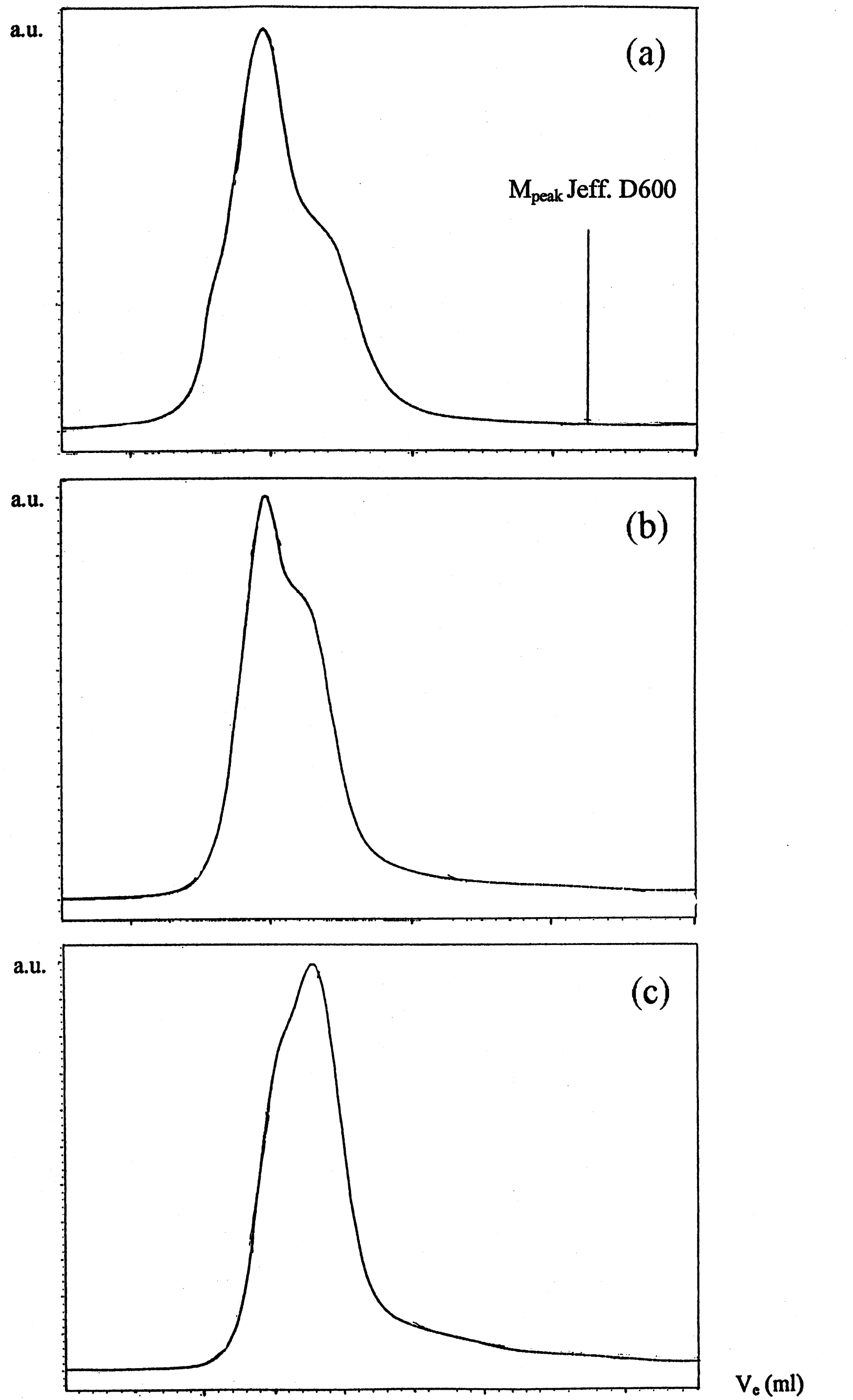

Fig. 3. Size exclusion chromatography (UV traces, eluent THF) on FCSP prepared at starting mole ratio Jeffamine D600/C_{60} equal to 1 (a), 3 (b) and 10 (c); the syntheses were performed in THF; comparison with the elution volumes of linear polyoxyethylene standards of various molecular weight (M_w).

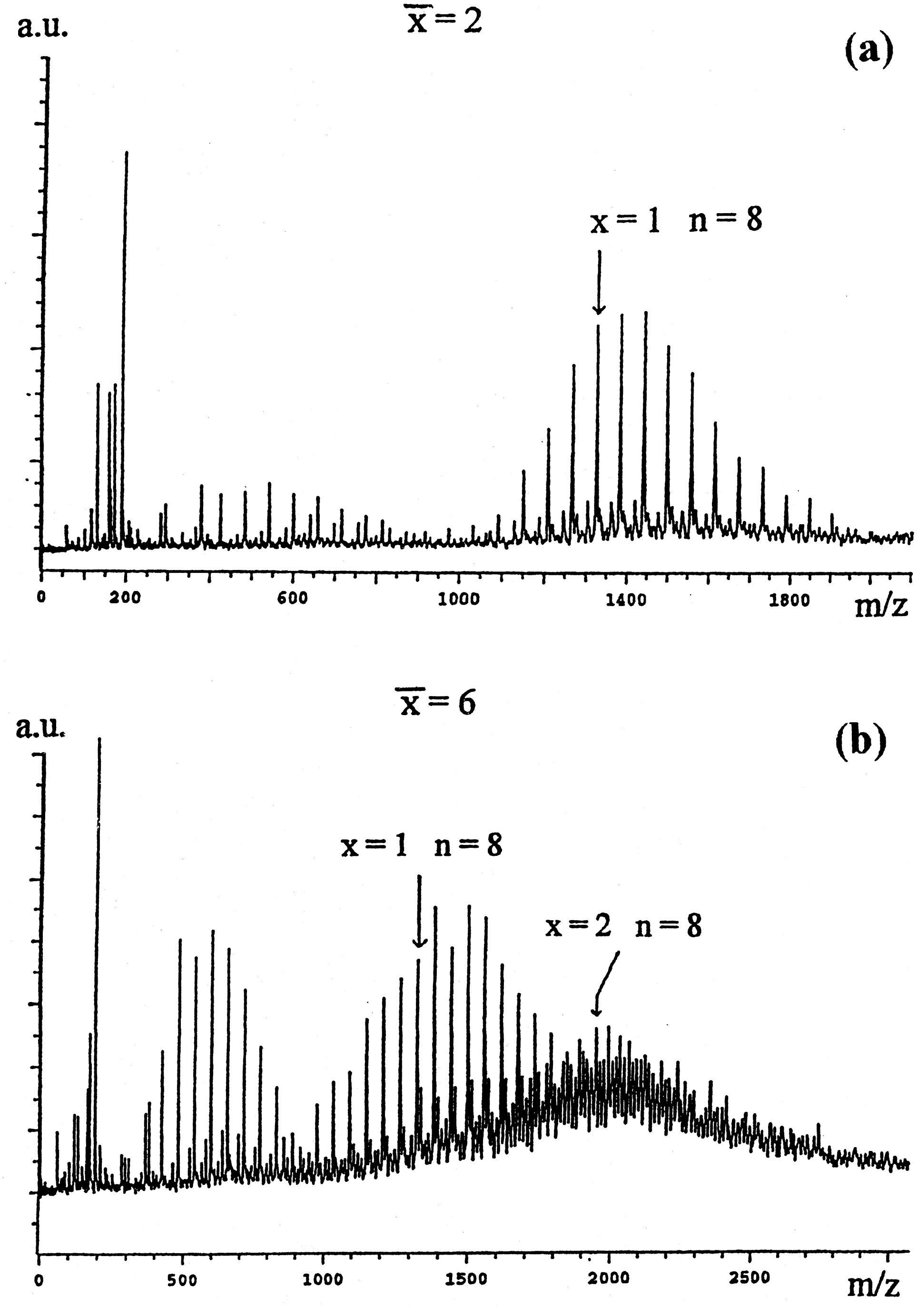

Fig. 4. MALDI-TOF analyses of star-like polymers with average formula $(CH_3OPOPNH)_2C_{60}H_2$ (a), $(CH_3OPOPNH)_6C_{60}H_6$ (b).

3 or more branches are completely absent. In the MALDI-TOF spectrum of $\{CH_3OCH_2CH_2[OCH_2CH(CH_3)]_nOCH_2CH(CH_3)NH\}_6C_{60}H_6$ (Fig. 4b), small peaks corresponding to products of diaddition are found together with the main contribution of monoaddition derivatives. In all the MALDI-TOF spectra two homologous groups are clearly identified, in the molecular weight range 600 for the first one and 1400 for the second one. They may be attributed to $CH_3OCH_2CH_2[OCH_2CH(CH_3)]_nOCH_2CH(CH_3)NH_2$

and $\{CH_3OCH_2CH_2[OCH_2CH(CH_3)]_n\ OCH_2CH(CH_3)NH\}C_{60}H$, respectively. The presence of a homologous series with the formula $CH_3OCH_2CH_2[OCH_2CH(CH_3)]_nOCH_2CH(CH_3)NH_2$ may be explained by a retroaddition rearrangement involving the scission of the bond between the amino group and C_{60} and the transfer of the proton bound to the adjacent carbon. Consequently the FCSP with a high number of branches loses the majority of them, and mainly the most stable monoderivative remains, explaining why multiaddition derivatives are hardly brought out by this technique. A series of peaks is observed for the monoderivative $\{CH_3OCH_2CH_2[OCH_2CH(CH_3)]_nOCH_2CH(CH_3)NH\}$-$C_{60}H$ with values of $n = 3$–17 (Fig. 4a), the most abundant fraction being with $n = 9$ and 10 ($\bar{M}_n = 1396.1$ $\bar{M}_w = 1428.5$, $\bar{M}_w/\bar{M}_n = 1.023$). Unfortunately, because of their instability, we could not find optimal conditions for studying the structure of FCSP with MALDI-TOF mass spectrometry.

During the conductivity titrations by potassium perchlorate, it was observed that the complexation of K^+ by FCSP is slower than by the corresponding free crown ether, which may be attributed to the greater concentration of crowns in a microdomain in the case of FCSP. The curves of 18-crown-6 (18C6) and of the FCSP prepared from 2AM18C6 at starting mole ratio 10 (product $(2AM18C6)_6C_{60}H_6$, Table 3) are shown in Fig. 5. There is a well-defined change of the slope at exactly $[18C6]/[K]^+ = 1$ (Fig. 5a), showing that this method is quite appropriate for the titration of the crown ether ligands. For the FCSP, the break in the slope is observed at $[FCSP]/[K^+] = 1/6$, thus showing that the average number of complexed potassium ions per star molecule is equal to 6, in good agreement with the average stoichiometry obtained from the other methods (Table 3). Assuming the formation of 1:1

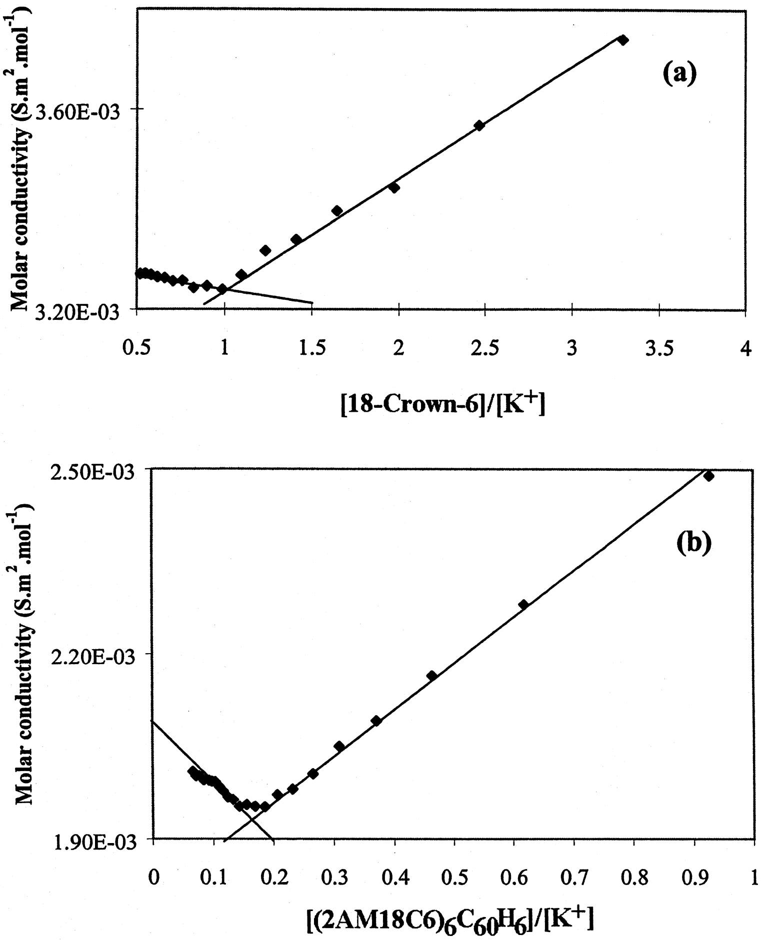

Fig. 5. Molar conductivity Λ versus $[L]/[K^+]$ curves for the crown ether 18-crown-6 (a) and $(2AM18C6)_6C_{60}H_6$ (b) in propylene carbonate at 25°C; ([L] is the ligand concentration in mol l^{-1}).

Table 4
Results of XPS analyses on $(2AM18C6)_xC_{60}H_x$ derivatives

Starting mole ratio, $2AM18C6/C_{60}$	Atomic ratio, $N_{1\,s}/C_{1\,s}$	Atomic ratio, $O_{1\,s}/C_{1\,s}$	Relative contributions, C—O/C—N/C—C in $C_{1\,s}$ peak	Average number of arms, $\bar{x}$
1	Exp.[a] 0.023	Exp. 0.138	Exp. 5.5/1/14.2	
	Calc. 0.023	Calc. 0.139	Calc. 6/1/14.5	2
3	Exp. 0.029	Exp. 0.213	Exp. 7/1/10	
	Calc. 0.030	Calc. 0.182	Calc. 6/1/9.5	3
10	Exp. 0.042	Exp. 0.270	Exp. 5.6/1/4.3	
	Calc. 0.043	Calc. 0.261	Calc. 6/1/4.5	6

[a] Exp.: experimental value; Calc.: values calculated for the average number of arms, $\bar{x}$, indicated in the last column.

complex of the crown ether branch with K^+ it was concluded that the average number of branches is 6.

This result was confirmed by the XPS spectra of the derivatives prepared by addition of 2AM18C6 to C_{60}. After correction of the space charge effects, the chemical states are, for carbon: C—C at 284.6 eV, C—N at 285.7 eV and C—O at 286.2 eV; for nitrogen: N—C at 399.5 eV; and for oxygen: C—O at 532.5 eV. The number of branches on the C_{60} core could be deduced from the relative areas C1 s/N1 s, C1 s/O1 s and from the relative contributions C—C/C—N/C—O in the C1 s peak. The values found for the average number of cyclic branches were $\bar{x} = 2$, 3 and 6, respectively, for the reaction products synthesized at starting mole ratio $2AM18C6/C_{60} = 1$, 3 and 10 (Table 4).

The thermogravimetric analyses of FCSP (Fig. 6) reveal an increased thermal stability, of about 60°C, of FCSP as compared with the starting polyether. The weight loss on heating the starting Jeffamine D600 is 15% at 172°C and 50% at 230°C. For the FCSP prepared from Jeffamine D600, the values of 15% and 50%, due to destruction of the polyether chains, are attained at 220 and 300°C for $(CH_3OPOPNH)_2C_{60}H_2$, at 230 and 290°C for $(CH_3OPOPNH)_3C_{60}H_3$, and at 230 and 290°C for $(CH_3OPOPNH)_6C_{60}H_6$, respectively. The most important decomposition occurs in the temperature range 200–400°C and the main gases evolving are CO_2 and H_2O. This important weight loss corresponds to the destruction of the polyether branches and their average number could be deter-

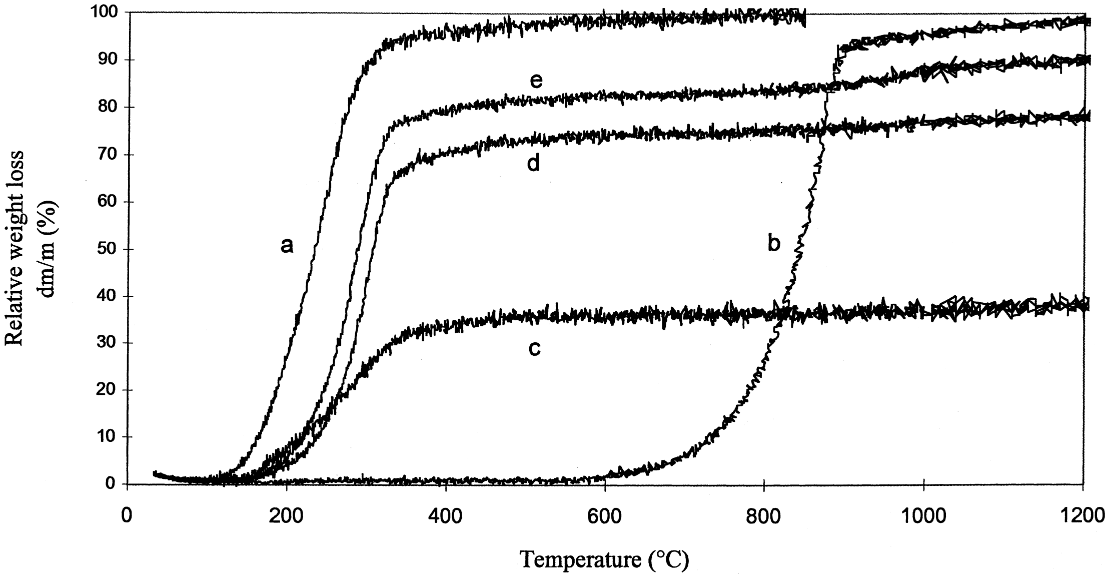

Fig. 6. Thermogravimetric analyses of FCSP prepared from C_{60} and Jeffamine D600. Jeffamine D600 (a), C_{60} (b), $(CH_3OPOPNH)_2C_{60}H_2$ (c), $(CH_3OPOPNH)_3C_{60}H_3$ (d), $(CH_3OPOPNH)_6C_{60}H_6$ (e).

mined (Tables 2 and 3). Due to carbonization processes, the total weight loss at 1000°C is lower than 100%. Similar behavior was observed earlier for FCSP with polyoxyethylene branches [15].

4. Conclusion

The synthesis of fullerene core star-like polymers (FCSP) with polyether branches, by addition of monofunctional linear or cyclic aminopolyethers, is a simple method of imparting solubility, and even water solubility to C_{60}. Certain obstacles to the exploitation of the promising properties of C_{60} can be overcome in this way. FCSP are amphiphilic and those with linear branches show a strong stabilizing effect on emulsions. They have film-forming properties; no phase separation is observed, thus showing that C_{60} is solubilized in its own polymeric matrix. Derivatives with cyclic branches are of particular interest because of their alkali metal ion complexation ability. In FCSP, the polyether branches are thermostabilized by ca. 70°C, thus implying that the C_{60} core acts as a radical inhibitor. Finally, the anti-tumoral effect of such derivatives, which was demonstrated by Y. Tabata et al. [14], constitutes a potential biological application, such as in phototherapy.

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