Macromolecules **1999,** *32,* 4247−4253 **4247**

Synthesis and Characterization of Some Copolyformals Containing, in the Main Chain, Different Amounts of Fullerene Units

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Received January 25, 1999; Revised Manuscript Received April 16, 1999

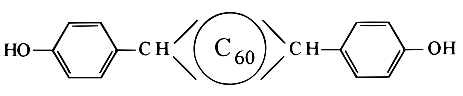
ABSTRACT: Two fullerene monomers, 61,61′-bis(*p*-hydroxyphenylmethano)fullerene[60] (**I**) and 61,61-bis(*p*-hydroxyphenyl)methano-1,2-fullerene[60] (**II**) were prepared. Polycondensations between dibromomethane and suitable mixtures of **I** or **II** and bisphenol A or 1,20-di(bisphenoxy-A)eicosane (**III**) in different molar ratios were performed to obtain copolyformals **IV**−**VII** that contain up to about 5% (molar) of fullerene units in the main chain. Composition and microstructure of these copolyformals were inferred by UV−visible and matrix-assisted laser desorption ionization−time-of-flight mass spectrometry (MALDI−TOF MS) analyses. Copolymers **IV**−**VII** are soluble enough materials and exhibit a good thermal stability; besides, the insertion of long linear aliphatic linkages along the main chain of copolyformals **VI** and **VII** produces a remarkable lowering in their glass transition temperature at about 15 °C.

Introduction

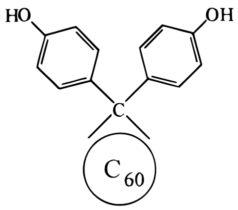
Recently the interesting physical and chemical properties of fullerenes have attracted the attention of many searchers.[1−5] The difficult tractability of these compounds, however, has stimulated an effort aimed to include fullerene units in polymeric structures in the hope to obtain more handy materials which retain useful properties for practical applications.[6−9]

In previous articles, we described the synthesis and characterization of some polymers and copolymers containing, in the main chain, special units such as porphyrins[10,11] or Schiff base complexes.[12] In the present case, we report a work about the inclusion of fullerene units in copolyether structures.

To arrange the fullerenes along the polymer chain, two suitable fullerene monomers,the 61,61′-bis(*p*-hydroxyphenylmethano)fullerene[60] (**I**) (an isomeric mixture) and the 61,61-bis(*p*-hydroxyphenyl)methano-1,2-fullerene[60] (**II**),[7,13] starting from commercial C_{60}, were prepared. Then, by a condensation reaction between dibromomethane and mixtures of the fullerene derivative **I** or **II** and bisphenol A or 1,20-bis(bisphenoxy-A)-eicosane (**III**) in different molar ratios, copolyformals **IV**−**VII** (for polymer composition, see Table 1) were obtained. In particular, monomer **III** was chosen to homogeneously insert long linear aliphatic linkages along the chain, which promote a greater molecular flexibility with a fall in the T_g value of the copolymer.[11]



I



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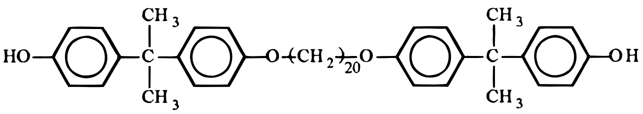
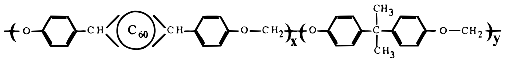


III



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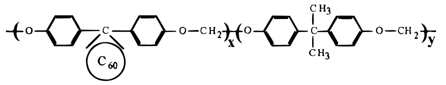
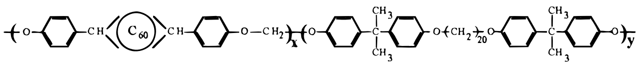
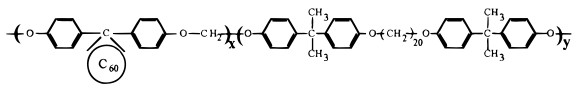


V



VI



VII

The copolymers **IV**−**VII** were characterized by UV, GPC, TG, DSC, and MALDI−TOF analyses. The obtained data show that the resulting fullerene-containing materials are soluble enough, have a fairly good molecular mass, and exhibit a good thermal stability.

Experimental Section

Materials. All the solvents and the basic materials were commercial products appropriately purified before use.

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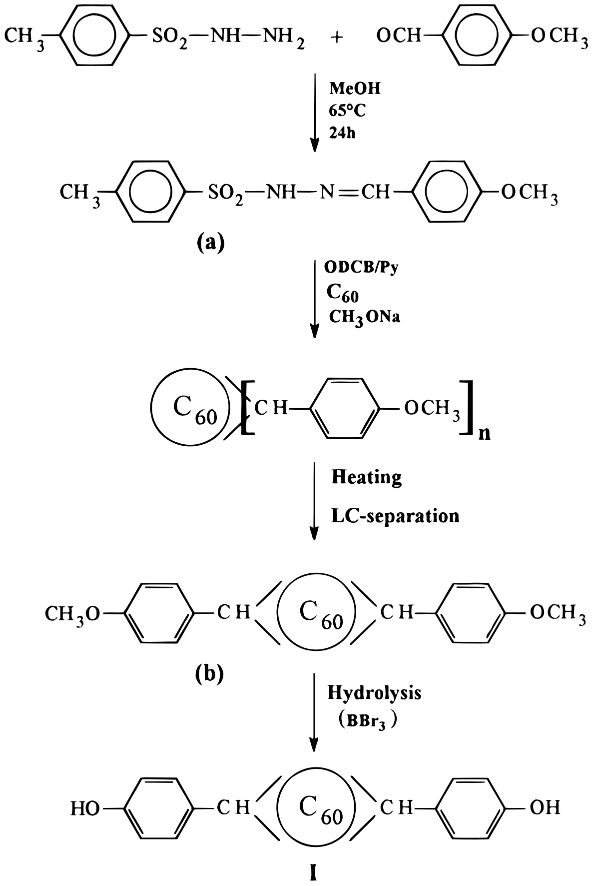
10.1021/ma990097d CCC: $18.00

Table 1. Composition, Molecular Mass, Thermal Stability, and Glass Transition Temperature of Copolyformals IV–VIII

copolyformal	fullerene[a] molar %	PDT[b]	T_g[c]	M_{GPC}[d]
IV	0.43	460 (430)	90.0	151 200
V	1.93	450 (360)	80.4	15 570
VI	2.51	440 (385)	19.3	18 170
VII	3.12	460 (390)	14.4	26 920
VIII	0.00	450 (410)	82.0	108 900

[a] The fullerene content (molar percent) in the copolyformals was calculated spectrometrically on the basis of the absorption value at 320 nm (**IV** and **V**) or 328 nm (**VI** and **VII**). [b] PDT values are the temperatures of maximum rate of polymer degradation from TG experiments under N_2 flow. The temperatures at which 2% of weight loss of material is observed are also reported in parentheses. [c] The glass transition temperatures were determined by DSC experiments. [d] Molecular masses measured with respect to polystyrene standards in correspondence to the maxima of the GPC curves.

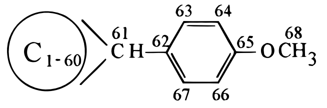
Scheme 1



Monomer I Synthesis. 61,61′-Bis(*p*-hydroxyphenylmethano)fullerene[60] (**I**) was prepared as reported in Scheme 1. The starting *p*-tosylhydrazone (**a**) was obtained by the reaction between 18.6 g of *p*-toluenesulfonylhydrazide (0.1 mol) and 12.2 g of *p*-anisaldehyde (0.09 mol) in 100 mL of MeOH maintained under stirring and refluxing conditions for 24 h. The product, recovered by cooling, was crystallized twice from MeOH to obtain colorless crystals (yield about 80%) having mp 114.0 °C (DSC, purity 99%). Its structure was confirmed by NMR (spectrum omitted for brevity) and DP–MS (molecular ion at *m*/*z* 304 as M^+) analyses.

Into a three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a tube for N_2 introduction were placed 7.6 g (0.025 mol) of **a** and 1.46 g (0.027 mol) of CH_3ONa in 200 mL of anhydrous pyridine. After 10 min under stirring and N_2 flow, a solution containing 7.2 g (0.01 mol) of C_{60}-fullerene in 300 mL of 1,2-dichlorobenzene (ODCB) was added. The mixture was then heated and maintained at 65 °C for 24 h. After cooling, the volume of the filtered solution was reduced to about 70 mL by distillation under vacuum. To convert the fulleroid compounds contained in the mixture in the thermodynamically most stable methanofullerene derivatives, the ODCB solution was then refluxed for 12 h.[14,15] The solution was successively chromatographed on silica gel column (particle size 70–230 mesh, h = 100 cm and i.d. = 4 cm) using toluene as eluant, and besides the unreacted C_{60}, two products were collected which were further purified by a second chromatographic separation (LC).

The first eluted product, having $R_f = 0.78$ (TLC in toluene), on the basis of its negative MALDI–TOF mass spectrum (molecular ion at *m*/*z* 840 as M^-) and NMR (in ODCB-d_4, at 90 °C) analysis, was identified as 61-(*p*-methoxyphenyl)-methano-1,2-fullerene[60] (i.e. the mono-C_{60} derivative; yield 1.3 g): proton signals assignments 3.710 (s, 3H, 68), 5.217 (s, 1H, 61), 6.958 and 6.998 (d, 2H, 63 and 67), 7.826 and 7.866 (d, 2H, 64 and 66);



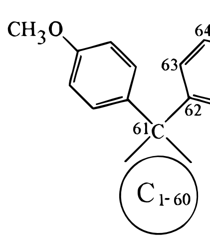
carbon signals assignments 43.418 (t, 61), 55.088 (p, 68), 76.272 (q, 1 and 2), 114.432 (t, 63 and 67), 125.300 (q, 62), 132.326 (t, 64 and 66), 135.017, 136.440, 138.543, 140.859, 141.022, 142.063, 142.106, 142.338, 142.786, 142.880, 142.902, 142.940, 142.974, 143.030, 143.641, 143.729, 144.124, 144.325, 144.350, 144.478, 144.619, 144.657, 144.798, 145.030, 145.055, 145.083, 145.133, 145.569, 145.672, 147.985, 149.943, 159.887 (q, 65). This product was subsequently used as a standard for *m*/*z* calibration in the negative MALDI–TOF mass spectrometric analysis.

The negative MALDI–TOF mass spectrum of the second eluted product exhibits only a peak at *m*/*z* 960 corresponding to the molecular ion, as M^-, of 61,61′-bis(*p*-methoxyphenylmethano)fullerene[60] (**b** in Scheme 1). The complex signals appearing in its ^1H and ^{13}C NMR spectra, compared also with those of the above-reported monoadduct, agree with a mixture of isomeric diadducts (yield 1.2 g).

Monomer **I** was finally obtained by hydrolysis of **b,** dissolved in ODCB, using an excess of BBr_3 in CH_2Cl_2 and maintaining the mixture at 0 °C under stirring and N_2 flow (yield about 70%). The reaction was stopped after about 1 h when all the *p*-methoxy-derived compound was converted (TLC analysis); the solution was then chromatographed on silica gel column using a THF/*n*-hexane (40/60) mixture as eluant. The collected fraction containing **I** was poured into MeOH, and the precipitated product was filtered, washed, and dried under vacuum (yield about 10%, calculated with respect to the starting fullerene amount; R_f = 0.26 in *n*-hexane/THF 2:1). The negative MALDI–TOF mass spectrometric analysis confirmed its structure (molecular ion at *m*/*z* 932 as M^-).

Monomer II Synthesis. 61,61-Bis(*p*-hydroxyphenyl)methano-1,2-fullerene[60] (**II**) was synthesized according to the same procedure described above for monomer **I**. 4,4′-Dimethoxybenzophenone was used to prepare the *p*-tosylhydrazone derivative, which was successively treated with the C_{60}-fullerene to obtain a mixture of methanofullerene and fulleroid adducts. Also in this case, before its LC separation, the mixture was heated and maintained at about 170 °C (in ODCB) for 12 h to convert the fulleroid compounds in methanofullerenes.

After the unreacted C_{60}-fullerene, the 61,61-bis(*p*-methoxyphenyl)methano-1,2-fullerene[60] was eluted from the chromatographic column (silica gel, particle size 70–230 mesh) using toluene as eluant (yield 16%). It was then crystallized from toluene (R_f = 0.68, TLC in toluene), and its structure was confirmed by negative MALDI–TOF mass spectrum (molecular ion at *m*/*z* 946 as M^-) and NMR analysis. Proton signals (ODCB, at 90 °C) at 3.643 (s, 6H, 68); 6.909 and 6.926 (d, 4H, 63 and 67); 8.029 and 8.046 (d, 4H, 64 and 66).

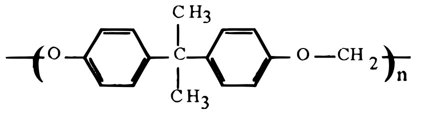


Carbon signals assignments (ODCB, at 90 °C): 55.139 (p, 68); 57.701 (q, 61); 80.196 (q, 1 and 2); 114.558 (t, 63 and 67); 132.185 (t, 64 and 66); 135.148; 138.383; 140.981; 142.195; 142.359; 142.978; 143.008 (two almost coincident signals); 143.882; 144.325; 144.647; 144.708; 144.756; 145.163; 145.230; 145.527; 148.829; 159.719 (q, 65).

The hydrolysis of 61,61-bis(*p*-methoxyphenyl)methano-1,2-fullerene[60] was performed at room temperature using an excess of BBr_3. So 61,61-bis(*p*-hydroxyphenyl)methano1,2-fullerene[60] (**II**) was collected by LC separation using the same conditions reported above for the *p*-methoxy derivative. It exhibits $R_f = 0.70$ (TLC in THF/*n*-hexane 3:2) and a molecular ion peak in the negative MALDI−TOF mass spectrum at *m*/*z* 918 (as M^-), confirming its structure (yield 12% calculated with respect to the starting fullerene amount).

Synthesis of Monomer III. 1,20-Eicosane−di(bisphenol A)ether (**III**) was prepared according to the procedure described previously[16] and summarized in the Scheme 2. The monocapped bisphenol A (**c** in Scheme 2) was obtained by reaction between bisphenol A and dihydropyrane; 1,20-Dibromoeicosane (**d** in Scheme 2) was prepared by an electrolytic procedure.[11] MALDI−TOF mass spectrometric and NMR data of compound **III** resulted in accord with its structure.

Copolyformal Syntheses. Copolyformal **IV** was synthesized in toluene/H_2O by reaction between a mixture of bisphenol A and monomer **I** (molar ratio 98/2) and a large excess of dibromomethane, according to the method described elsewhere,[10,11] using NaOH and tetrabutylammonium bromide (TBAB) as phase-transfer agent. Copolymers **V**−**VII** were prepared in *N*-methyl-2-pyrrolidinone (NMP) starting from CH_2Br_2 and mixtures of fullerene monomer **I** or **II** and suitable amounts of bisphenol A or monomer **III** in the presence of NaOH.[10] The composition of the obtained copolymers **IV**−**VII** is reported in Table 1. Pure bisphenol A polyformal **VIII** was also prepared for comparison.

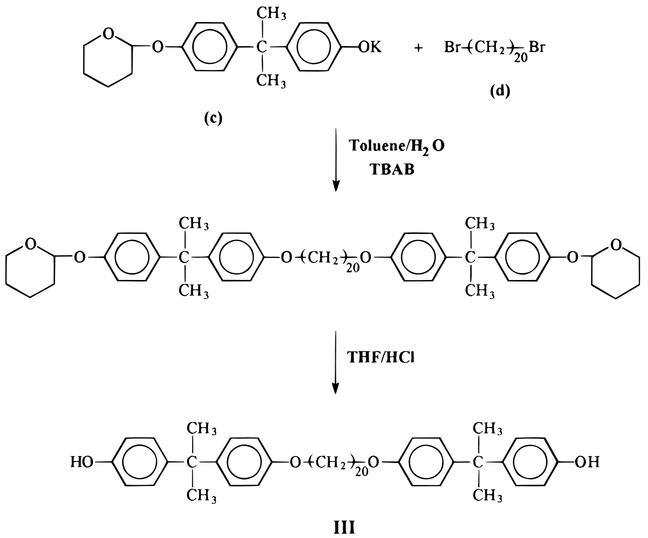


VIII

GPC Analysis. A PL-GPC 110 (Polymer Laboratories) thermostated system, equipped with three PL-gel 5 μm columns (two Mixed-D and one Mixed-E) attached in series, was used. The analyses were performed at 35 ± 0.1 °C using THF as eluant at a flow rate of 1 mL/min. A differential refractometer (Polymer Laboratories) and/or an UV−visible spectrometer (Hewlett-Packard series 1050) were used as detectors. The instrument was calibrated with a mixture of 12 polystyrene standards (Polysciences; molecular masses between 2000 and 1200000) using PL-Caliber GPC software for the determination of average molecular masses and polydispersity of the polymer samples.

UV−Visible Spectrophotometric Analysis. UV−visible spectra of copolyethers **IV**−**VII** were recorded on a Shimadzu spectrophotometer Model 1601 at room temperature using THF as solvent. The fullerene content in copolymers **IV** and **VI** was evaluated by considering the absorption values at 320 nm, using Beer's law and a molar absorption of 38472 (L mol^{-1} cm^{-1}) determined for 61,61′-bis(*p*-methoxyphenylmethano)-fullerene[60] (**b** in Scheme 1) which was used as standard. Analogously, for copolymers **V** and **VII**, the fullerene content was calculated considering the absorption values at 328 nm using a molar absorption of 35301 (L mol^{-1} cm^{-1}) calculated for 61,61-bis(*p*-methoxyphenyl)methano-1,2-fullerene[60]. The fullerene content in each copolyether is reported in Table 1.

Scheme 2



c) obtained according to the Williams et al. (Ref: 16)
d) prepared by an electrolytic procedure (Ref: 11).

^{1}H NMR and ^{13}C NMR Analyses. ^{1}H NMR and ^{13}C NMR spectra were obtained on a ^{UNITY}INOVA Varian instrument operating at 500 (^{1}H) and 125 (^{13}C) MHz and using VNMR for software acquisition and processing. Samples were dissolved in ODCB-d_4 or $CDCl_3$ and the chemical shifts expressed in ppm by comparison with the signal of TMS used as an internal standard.

Thermal Properties. Thermogravimetric analyses (TG) were performed with a Perkin-Elmer TGS-2 apparatus in a N_2 atmosphere with a flow rate of 60 mL/min and a heating rate of 10 °C/min. The temperatures of maximum polymer degradation rate (PDT) and those at which 2% of weight loss of material is observed are reported in Table 1.

Differential scanning calorimetry (DSC) was performed to determine melting points and glass transition temperatures (T_g) by using a Mettler DSC-20 instrument. The heating rate was 10 °C/min, under N_2 atmosphere.

MALDI−TOF Mass Spectrometric Analysis. The MALDI−TOF mass spectra were acquired using three mass spectrometers: a Bruker Reflex [with continuos extraction (30 kV) and detection in reflection mode (31.4 kV)], a Perseptive Voyager DE [with pulsed extraction (20 kV applied after 1 μs and a potential gradient of 454.54 V/mm) and detection in linear mode], and a Perseptive Voyager DE-STR [with a simultaneous delay extraction (20 or 25 kV applied after 150 or 250 ns with a potential gradient of 2840.91 or 2636.36 V/mm, respectively) and detection in reflection mode]. All the instruments were equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 or 8 ns).

In particular, with the Perseptive Voyager DE-STR, MALDI−TOF mass spectra with a very high mass resolution up to about 18 000 (fwhh), determined using Grams software from Perseptive Biosystems, were obtained (as an example, see insert in Figure 3).

In each MALDI experiment, the sample was prepared by loading about 0.1 nmol of polymer and 40 μmol of matrix (*trans*-3-indoleacrylic acid, IAA) onto the probe tip, using THF as a solvent. For positive MALDI−TOF mass spectra, both 5,-10-di(*p*-dodecanoxyphenyl)-15,20-di(*p*-hydroxyphenyl)porphyrin ($C_{68}H_{78}N_4O_4$, 1014 Da) and tetrakis(*p*-dodecanoxyphenyl)-porphyrin ($C_{92}H_{126}N_4O_4$, 1350 Da)[11] were used as standards for *m*/*z* calibration. Instead, for *m*/*z* negative MALDI−TOF spectra calibration, 61-(*p*-methoxyphenyl)methano-1,2-fullerene-[60] ($C_{68}H_8O$, 840 Da) and 61,61-bis(*p*-methoxyphenyl)methano-

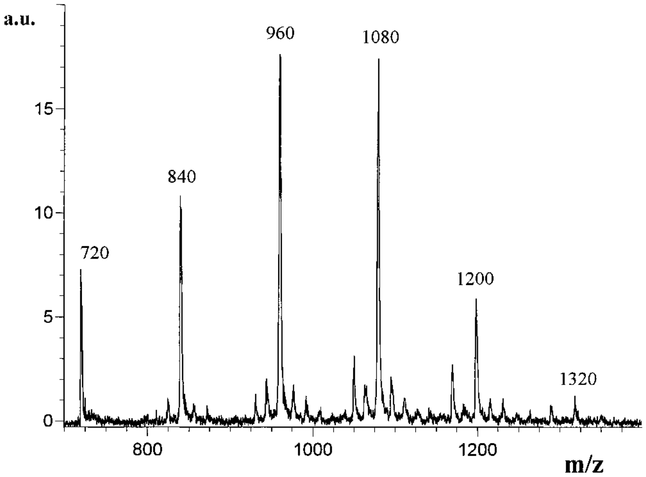


Figure 1. Negative MALDI−TOF mass spectrum of the mixture of (*p*- ethoxyphenylmethano)fullerene[60] derivatives.

1,2-fullerene[60] ($C_{75}H_{14}O_2$, 946 Da) were used as standards. The *m*/*z* values reported in the spectra and in the text refer to values corresponding to ions containing the more abundant isotope of each element present in the molecules.

Results and Discussion

To introduce fullerene units into copolyformal main chains, two appropriately dihydroxyl-functionalized C_{60}-derivatives, **I** and **II**, were prepared. Scheme 1 describes the synthesis of the bis(*p*-hydroxyphenylmethano)-fullerene[60] **I**. A mixture of C_{60}-derivatives was initially obtained by reaction of C_{60} with the *p*-tosylhydrazone of the *p*-methoxybenzaldehyde. A negative MALDI−TOF mass spectrum of this mixture, reported in Figure 1, showed that it contained, besides unreacted (peak at *m*/*z* 720), mono-, bis-, tris-, and tetra(*p*-methoxyphenyl-methano)−C_{60} derivatives (peaks at *m*/*z* 840, 960, 1080, and 1200 corresponding to the molecular ions as M^-); peaks at higher *m*/*z*, due to more heavy adducts, were also present with little intensity in the spectrum.

After protracted heating, to convert the fulleroid structures in the thermodynamically most stable methanofullerene derivatives, the bis(*p*-methoxyphenylmethano)fullerene[60] adduct was separated by LC and hydrolyzed to finally obtain monomer **I** (which is a mixture of isomers). Different from the precedent case, 61,61-bis(*p*-hydroxyphenyl)methano-1,2-fullerene[60] (**II**), which was prepared in the same manner as **I** using the *p*-tosylhydrazone of 4,4′-dimethoxybenzophenone, was a pure product corresponding to the monomethanofullerene adduct.

Copolyformals **IV** and **V** were synthesized by a condensation reaction between dibromomethane and a mixture of bisphenol A and monomer **I** or **II**. To prepare copolyformals with a lower glass transition temperature (Table 1), long linear aliphatic linkages [$-(CH_2)_{20}$] were homogeneously inserted in the polymer chain using, in the copolymer synthesis of **VI** and **VII**, 1,20-di(bisphenoxy-A)eicosane (**III**) rather than bisphenol A. The fullerene content in the starting monomeric mixtures was maintained in all syntheses under 5% (molar) in the attempt to obtain more soluble polymeric materials; however, in this work, only the soluble NMP fractions of the polymers (about 70−80% of the materials) were examined.

Because fullerene groups show similar absorption spectra in both monomeric and copolymeric form and bisphenol linkages do not absorb light above 310 nm (determinated examining the UV−visible spectrum of bisphenol A polyformal **VIII**), the actual fullerene content in the copolyformals was evaluated spectrometrically (see Experimental Section). The calculated compositions of the copolymers are reported in Table 1.

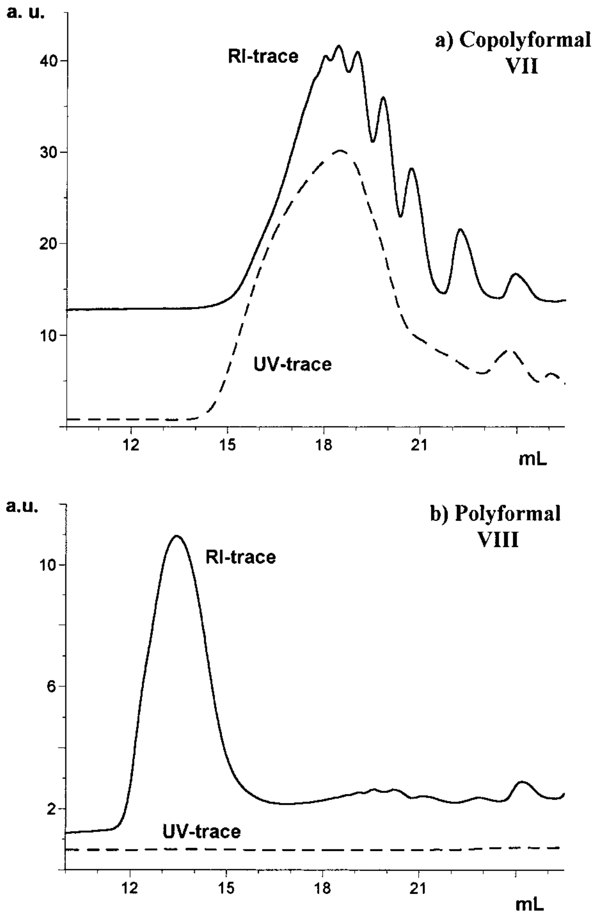


Figure 2. GPC traces obtained using both UV−visible and differential refractometer detectors connected in parallel of (a) copolyformal **VII** and (b) polyformal **VIII**.

Copolyformals **IV**−**VII** are thermostable materials exhibiting a starting decomposition temperature (calculated in correspondence with the 2% weight loss, in a nitrogen atmosphere) between 360 and 430 °C (Table 1); the thermal degradation occurs in one stage with a temperature of maximum decomposition rate (PDT) of about 450 °C, leaving a thermostable residue between 10 and 20%. Their glass transition temperature varies from 14 to 90 °C (Table 1) as a consequence of the different chain flexibilities due to the bisphenol A (copolymers **IV** and **V**) or di(bisphenoxy)eicosane (copolymers **VI** and **VII**) groups present in the macromolecules.

The GPC-average molecular weight values of copolyformals (estimated with respect to polystyrene standards) lie between 15 000 and 150 000 (Table 1). The homogeneous fullerene arrangement in the macromolecules was also ascertained by GPC experiments performed using both differential refractometer and UV−visible (set at 320 or 328 nm) detectors connected in parallel.

In this way, the refractometer, which is an absolute detector, records all the eluted molecules of the polymeric sample. On the other hand, since the bisphenol A groups absorb only below 310 nm, the UV spectrometer detects only molecules that contain at least one fullerene unit in the chain.

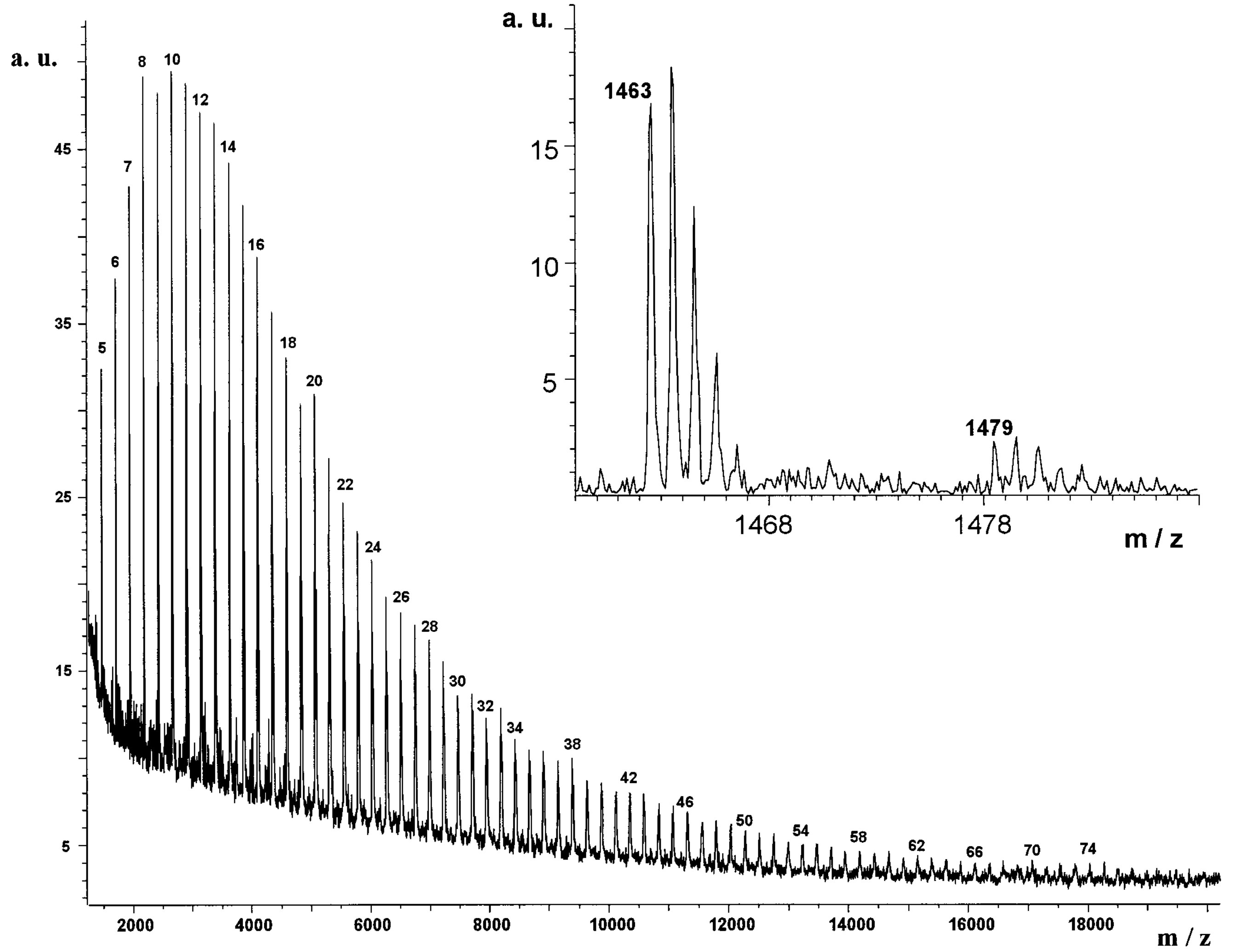


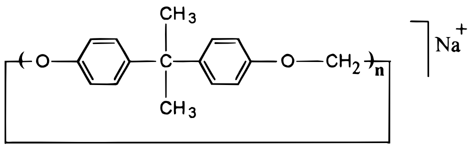
Figure 3. Positive MALDI−TOF mass spectrum of copolyformal **IV**. The number reported in correspondence to each peak represents the number of bisphenoxy-repeating units present in the molecule. In the insert, a region of the spectrum obtained by Voyager DE-STR instrument is reported.

As expected, in the case of copolyformal **VIII**, the refractive index trace (RI in Figure 2b) shows an intense signal with a maximum at a low eluted volume (characteristic of a polymeric material at high molecular mass) whereas the UV trace (UV in Figure 2b) is at the zero value.

Contrarily, for copolyformal **VII** (likewise for copolymers **IV**−**VI**, omitted for brevity) RI and UV traces in Figure 2a are very similar, pointing out the insertion of the fullerene units in the macromolecules in the entire molecular mass range (i.e. the concentration of C_{60} units in the copolymer does not change with the molecular mass).

A fine structural characterization of copolyformals **IV**−**VII** was attempted by MALDI−TOF mass spectrometric analysis. Data obtained with three MALDI instruments, adopting a continuos extraction procedure and a mirror device (Bruker Reflex), a delayed extraction system and detection in linear mode (Perseptive Voyager-DE), or both a delayed extraction and a detection in reflection mode (Perseptive Voyager-DE STR), were compared. Bruker Reflex allowed the detection of peaks up to higher *m*/*z* values, but Perseptive Voyager-DE STR gave spectra with a very high mass resolution which helped in the exact peak identification.

The positive MALDI−TOF spectrum of copolyformal **IV**, obtained by the Bruker mass spectrometer, is reported in Figure 3. As expected, considering that the formation of cyclic oligomers in the synthesis of polyformals is well-known,[10,16] the spectrum essentially consists of a series of peaks at *m*/*z* 263 + *n*240 with *n* = 5 (*m*/*z* 1463) − 74 (*m*/*z* 18 023), corresponding to molecular ions, as $M_n(Na^+)$, of cyclic formals containing only bisphenol A units; peaks due to $M_n(K^+)$ ions also appear in the spectrum (see insert in Figure 3, which is a part of the spectrum obtained by Voyager DE STR having a mass resolution of about 18 000) but with little intensity. It can be observed that no peaks corresponding to compounds containing fullerene units were detected here, as in all the other positive spectra obtained for copolymers **IV**−**VII**. On the contrary, due to the easier detection of fullerene-containing compounds as negative ions (behavior noticed when examining intermediate synthetic products for which positive MALDI−TOF gave weak and unresolved peaks), negative MALDI−TOF mass spectra of copolyformals **IV**−**VII** resulted, constituted of only peaks corresponding



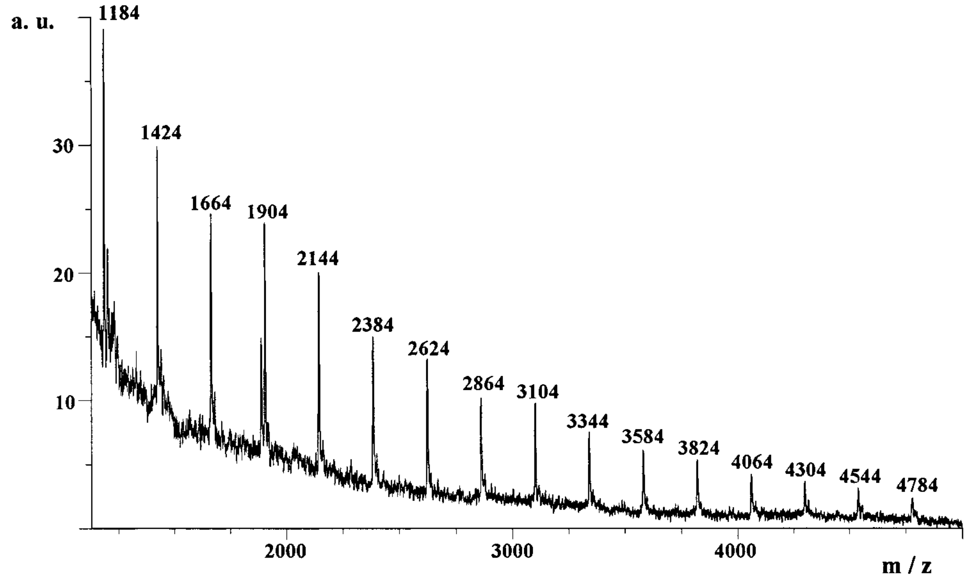


Figure 4. Negative MALDI–TOF mass spectrum of copolyformal **IV**.

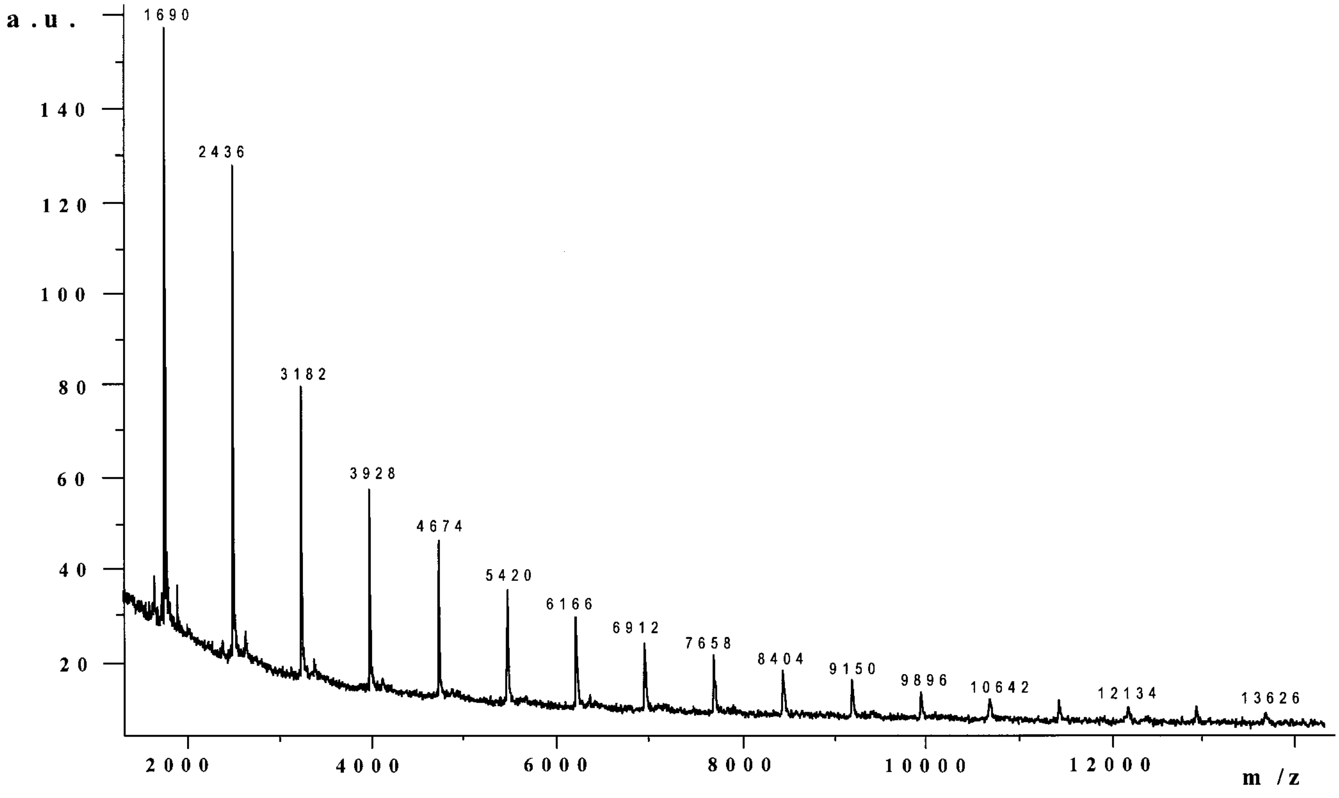
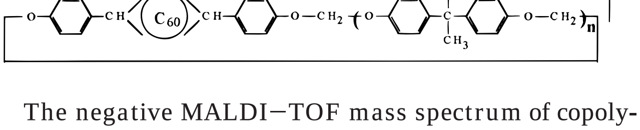


Figure 5. Negative MALDI–TOF mass spectrum of copolyformal **VI**.

to formals containing a fullerene unit in the molecule. As an example, in Figure 4, the negative MALDI spectrum of copolyformal **IV** is shown. Peaks appear at *m*/*z* 944 + *n*240 values corresponding to molecular ions (as M^-) of cyclic compounds containing, besides one 61,-61′-bis(phenoxymethano)-1,2-fullerene[60] group, an increasing number (1–15) of bisphenol A units.



The negative MALDI–TOF mass spectrum of copolyformal **VI**, based on di(bisphenoxy)eicosane and methanofullerene **I**, is reported in Figure 5. Also in this case the spectrum only shows a series of peaks at *m*/*z* 944 + *n*746 with *n* = 1 (*m*/*z* 1690) – 17 (*m*/*z* 13 626), corresponding to molecular ions, as M^-, of compounds containing one fullerene **I** unit and *n* di(bisphenoxy)-eicosane groups.

MALDI–TOF mass spectra of copolyformals **V** and **VII** (omitted for brevity), which contain the methanofullerene **II** unit, exhibit a similar behavior.

In previous works,[17] MALDI–TOF mass spectrometric analysis was also used to direct determination of average molecular mass of several polymeric materials. However, in the present case, this procedure was avoided because, on the basis of the above-reported data, neither positive nor negative MALDI−TOF spectra are representative of all molecular species present in each fullerene copolymer sample so that mistakes in the molecular mass valuation can be made.

In conclusion, on the basis of GPC (using both RI and UV detectors) and MALDI−TOF data, it can be conclude that, as was stated as our purpose, soluble bisphenolic copolyformals containing different amounts of fullerene units inserted in the main chain and a variable T_g value were obtained.

Acknowledgment. Partial financial support from the Italian Ministry of University and Scientific and Technological Research (ex-40 and ex-60%) and CNR-Rome are gratefully acknowledged.

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MA990097D