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Full Characterization of a Multiblock Copolymer Based on Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(bisphenol-A carbonate)

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ABSTRACT: Full characterization, that is the true molar mass distribution and block sequence, of a multiblock copolymer based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(bisphenol A carbonate) (PC) segments (PPO-*b*-PC), synthesized by polycondensation reaction of both diol-terminated PPO and PC samples with the bischloroformate of bisphenol A, is reported. The initial diol terminated PPO sample contains a few tetramethyl bisphenol A units in the backbone. The molar mass distribution of the starting PPO and PC homopolymers and the multiblock structure of the final PPO-*b*-PC copolymers were studied by light scattering and viscometry on-line with a SEC system, MALDI−TOF mass spectrometry, and NMR. In a previous study, we have demonstrated that homogeneous PPO-*b*-PC block copolymers having only one single T_g were obtained if low molar mass PPO and PC starting blocks were used. More important findings of this recent study are the following. MALDI−TOF analysis showed that the synthesized PPO-*b*-PC copolymers were composed of multiblock PPO-*b*-PC chains and also of some nonreacted PC oligomers terminated with methyl carbonate groups. Exhaustive and selective aminolysis of carbonate groups of the PC blocks has been also performed in order to determine the number of blocks and the average length of PPO blocks in the copolymers.

1. Introduction

In a previous study,[1] we have reported synthesis and preliminary characterization of some new multiblock copolymers based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(bisphenol A carbonate) (PC) segments, referred in short as PPO-*b*-PC copolymers. Interest for PPO-*b*-PC macromolecular systems derives from their potential mechanical, rheological and thermal properties. It is well-known that PPO homopolymer shows considerable chain stiffness, high T_g and consequently a relatively difficult processing. From a practical point of view a relatively simple method in obtaining polymeric materials based on PPO homopolymer showing good processability consists of blending it with traditional or modified polystyrene (PS).[2−4] Another classical method consists of synthesizing block copolymers based on PPO segments. In the past, General Electric Co. synthesized some di- and triblock PPO-*b*-PC copolymers based on high molar mass PPO showing two different T_g.[5,6] On the contrary, an important finding of our previous study was that these new multiblock PPO-*b*-PC copolymers show one single T_g if low molar mass starting PPO and PC blocks were used.[1−7] These new PPO-*b*-PC materials show remarkably lower dynamic viscosity of the melt compared with the PPO homopolymer having similar average molar mass. The PPO-*b*-PC copolymer could be also employed as a compatibilizer in PS/PC blends.[8]

Other than the synthesis, a previously cited article[1] described a preliminary molecular characterization together with thermal and rheological properties and the thermal stability of these new PPO-*b*-PC materials. However, a multiblock copolymer needs a fully accurate characterization of its macromolecular structure consisting both of the molar mass distribution (MMD) and of the potential complex multiblock sequence (number of blocks, average length of blocks, terminal groups, etc.). Consequently, the aim of this follow-up study is to describe both the true MMD and multiblock structure of this class of high performance materials having potentially good processability. All of the PPO-*b*-PC samples prepared, together with the starting PPO and PC low molar mass starting blocks, were studied by a multidetector size exclusion chromatography (SEC) system equipped with on-line multiangle light scattering and viscometer detectors (SEC−MALS−DV),[9] matrix assisted laser desorption ionization−time-of-flight mass spectrometry (MALDI−TOF)[10−12] techniques. Also (^{1}H and ^{13}C) NMR spectroscopy was used in defining the macromolecular structures of these PPO-*b*-PC multiblock copolymers.

2. Experimental Section

2.1. Materials. Chloroform and *N*,*N*-diisopropylethylamine (DIPEA) (99 wt % purity) were purchased from Aldrich Co. and dried over calcium hydride for 48 h. 4-(Dimethylamino)pyridine (DMAP) (99 wt % purity), 1-methylimidazole, 2,2-bis(4-hydroxyphenyl)-propane (bisphenol A, BPA), 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane (tetramethyl bisphenol A, TMBPA), and bisphenol A bis(chloroformate) were purchased from Aldrich Co. and used as received. $Cu(NO_3)_2 \cdot 3H_2O$ (analytically pure) and $NaOCH_3$ were obtained from Merck and used without further treatment. 2,6-Dimethylphenol (DMP) (Aldrich) was purified by repeated recrystallization from *n*-hexane.

The MALDI matrices, 2-(4-hydroxyphenylazo)benzoic acid (HABA), *trans*-3-indoleacrylic acid (IAA), 2,5-dihydroxybenzoic acid (DHB), and dithranol, were analytical-grade material, purchased from Sigma Aldrich Chemical Co. (Italy) and used as supplied.

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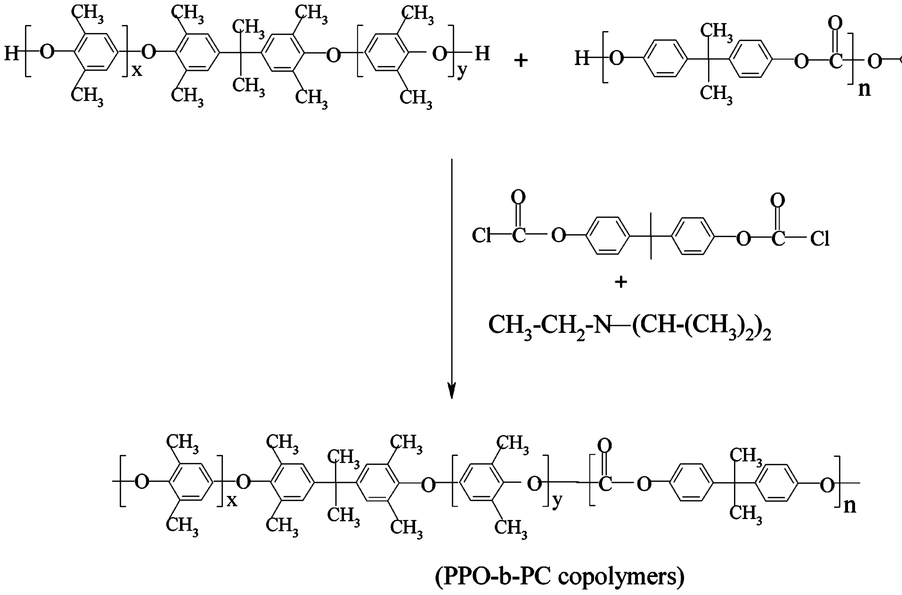
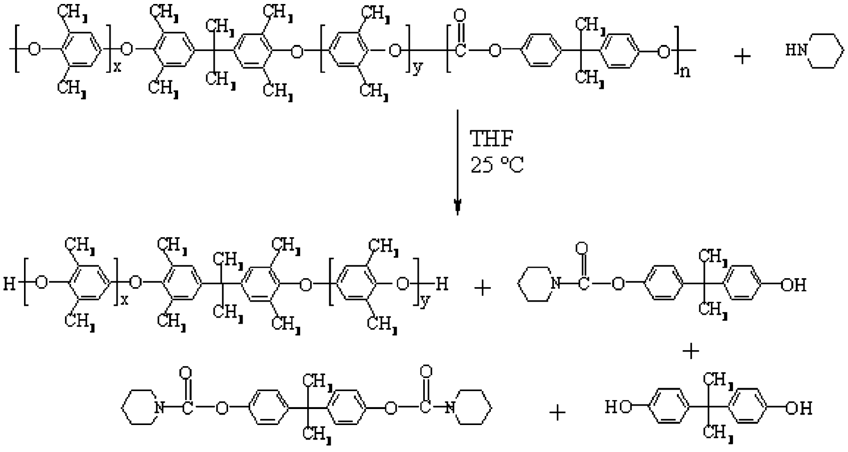
Scheme 1



Scheme 2



Deuterated chloroform ($CDCl_3$) solvent was purchased from Merck (Italy) and used as supplied.

2.2. Synthesis. The synthesis of the PC-2OH and PPO-2OH homopolymers and of the PPO-*b*-PC block copolymer was described previously[1] and will be not described in detail here. Only a brief summary will be reported.

Four PPO-2OH samples having different molar masses have been synthesized by oxidative coupling polymerization of a mixture of 2,6-dimethylphenol (DMP) and tetramethyl bisphenol A (TMBPA) with a different molar ratio (ranging from 18:1 up to 26:1 mol/mol), in toluene/acetonitrile solution. $Cu(NO_3)_2 \cdot 3H_2O$ and methylimidazole were employed as catalysts.[13] A ratio of TMBPA−hydroxyl groups to Cu(II) close to 1 allowed us to obtain products in which one TMBPA molecule can coordinate two Cu(II) ions and PPO chains grow from both hydroxyl groups of each TMBPA molecule.[13]

A poly(bispenol A carbonate) sample terminated with bisphenol A groups (BPA) at both ends was prepared by a polycondensation reaction between the BPA and phosgene. The reaction was carried out in chloroform in the presence of two tertiary amines: *N*,*N*-diisopropylethylamine and 4-(dimethylamino)pyridine.[1,14,15] Finally, by using the PC-2OH sample and the four PPO-2OH samples, four different PPO-*b*-PC multiblock copolymers were prepared by coupling in the presence of phosgene or bisphenol A bischloroformate. First, an oligomeric PC bischloroformate terminated was obtained by the reaction of PC-2OH with bisphenol A bischloroformate in the presence of DIPEA. Later this product was reacted with PPO-2OH in the presence of DIPEA and DMAP (see Scheme 1 and ref 1 for details).

2.3. Aminolysis of the PPO-*b*-PC Copolymers. Exhaustive and selective aminolysis of the carbonate groups[16] of the PC blocks in the PPO-*b*-PC samples has been performed by reaction of the copolymers with a large excess of the piperidine (Scheme 2) in THF solvent at room temperature for 2 h.

Typically, 300 mg of the block copolymer was dissolved in 5 mL of THF and treated with piperidine (20 mmol) at 25 °C for 2 h. Then the solution was added to 50 mol of ethyl alcohol, and the precipitated residue was filtered, washed with ethyl alcohol, and dried under vacuum for 24 h at 60 °C. Each precipitate was analyzed by ^1H NMR, MALDI−TOF, and viscosimetric techniques.

2.4. Characterization. 2.4.1. NMR. ^1H NMR and ^{13}C NMR spectra were run in $CDCl_3$ with a 600 MHz Bruker spectrometer and with a 200 MHz Bruker spectrometer (operating at 50 MHz for carbons), respectively, using TMS as internal reference. The data were elaborated with 1D Win-NMR software applying the Lorentz-Gauss enhance function using appropriate line broadening and Gaussian broadening parameters in order to improve the peaks resolution. The acquisition parameters for the ^{13}C NMR spectra, operating at 50 MHz, were optimized in order to obtain for similar carbon types similar relaxation rates; thus reliable quantification of ^{13}C NMR is possible. The carbon spectra were recorded with the following acquisition parameters: sweep width, 9615 Hz; 65 536 data points; giving a digital resolution of 0.305 Hz per point and

Table 1. Summarized Results of PC-2OH and PPO-2OH Homopolymers and PPO-*b*-PC Block Copolymers as Obtained from Conventional SEC and Thermal Analysis (DSC)

sample	M_w (g/mol)	D	T_g (°C)
PC-2OH	4110	1.8	87.2
PPO-2OH (1)	10 120	1.8	181.0
PPO-2OH (2)	8400	1.5	174.0
PPO-2OH (3)	23 700	2.9	199.3
PPO-2OH (4)	5860	1.5	154.1
PPO-*b*-PC (1)	22 730	2.1	189.2
PPO-*b*-PC (2)	21 900	1.9	189.1
PPO-*b*-PC (3)	28 930	2.8	197.9
PPO-*b*-PC (4)	18 040	2.3	164.3

an acquisition time of 2755 s. A pulse width of 4 ms and delay of 4 s were used for about 10 000 accumulations.

Quantitative ^{1}H NMR spectra were recorded using a delay of 1 s and an acquisition time of 6.5 s. These parameters were optimized using a equimolar mixture of BPA−dimethyl carbonate, TMBPA, and DMP.

The chemical shifts were accurately assigned to the specific proton and carbon atoms, using the data reported in the literature[17] and using also appropriate model compounds such as BPA−dimethyl carbonate, DMP, BPA, and TMBPA. The assignments are reported in Table 4.

2.4.2. Molecular Characterization. The MMD and the intrinsic viscosity [η] of homopolymers and block copolymers were characterized by a multidetector SEC system. The chromatographic system was equipped with three on-line detectors: MALS from Wyatt (Santa Barbara, CA), DV, and a differential refractometer (DRI) from Waters (Milford, MA) used as the concentration detector. The running SEC experimental conditions were as follows: two PLgel Mixed C columns, chloroform as mobile phase, 0.6 mL/min of flow rate, and 35 °C of temperature. The MALS photometer uses a vertically polarized He−Ne laser ($\lambda = 632.8$ nm) and simultaneously measures the intensity of the scattered light at 16 angles ranging in chloroform from 19.2 to 138.3°. The calibration constant was calculated using toluene as standard, assuming a Rayleigh factor of 1.406×10^{-5} cm^{-1}. The angular normalization was performed by measuring the scattering intensity of a narrow MMD PS standard ($M_p = 10.3$ kg/mol, $M_w/M_n \leq 1.03$, $R_g = 2.9$ nm) in the mobile phase assumed to act as an isotropic scatterer. It is well-known that the on-line MALS detector measures the molar mass M for each polymeric fraction eluted from the SEC columns, and when the angular dependence of the scattered light is experimentally measurable, also the molecular size generally known as gyration radius R_g may be determined. Furthermore, the on-line DV detector measures the intrinsic viscosity [η]. Consequently, for each polymeric fraction, the SEC−MALS−DV system furnishes M, R_g, and [η]. The SEC−MALS−DV system was described in detail elsewhere.[9]

The specific refractive index increment, dn/dc, for homopolymers and copolymers with respect to the mobile phase at 25 °C of temperature was measured by a KMX-16 differential refractometer from LDC Milton Roy (Riviera Beach, FL).

2.4.3. Narrow MMD Fractions of PPO-*b*-PC Copolymer. It is well-known that MALDI−TOF analysis requires narrow MMD fractions in order to obtain reliable results.[10−12] Consequently, the PPO-*b*-PC block copolymers were accurately fractionated by a conventional SEC chromatographic system equipped with a HPLC Waters 515 pump, a DRI detector, and a set of four Styragel columns (HR1−HR2−HR3−HR4) from Waters using chloroform as eluent and a flow rate of 0.6 mL/min. The fractionation of the PPO-*b*-PC block copolymers was performed by collecting 90 μL for each fraction, taking on the whole 50 fractions for each copolymer. In such a way, adequate narrow MMD fractions of the PPO-*b*-PC copolymer were obtained for the following off-line MALDI−TOF analysis.

2.4.4. MALDI−TOF. MALDI−TOF mass spectra were recorded in linear and reflectron modes, using a Voyager-DE STR instrument (Perseptive Biosystem) mass spectrometer, equipped with a nitrogen laser ($\lambda = 337$ nm, pulse width = 3 ns), working in a positive ion mode. The accelerating voltage was 25 kV, and grid voltage and delay time (delayed extraction, time lag) were optimized for each sample to achieve the higher mass resolution (fwhm). Laser irradiance was maintained slightly above the threshold.

Several matrices—2-(4-hydroxyphenylazo)benzoic acid (HABA), *trans*-3-indoleacrylic acid (IAA), 2,5-dihydroxybenzoic acid (DHB), and dithranol (1,8,9-anthracenetriol)—were used to obtain MALDI spectra of the polymer sample analyzed. The better mass spectra were obtained using HABA (0.1 M in THF solvent) for the analyses of PC and PPO-*b*-PC samples and dithranol (0.1 M $CHCl_3$) for the PPO−OH polymers.

Samples used for the MALDI analyses were prepared as follows. A 10 μL aliquot of polymer solution (3−4 mg/mL in $CHCl_3$) was mixed with 10 μL of the appropriate matrix solution. Then, 1 μL of a 0.01 M solution of CF_3COONa salt as cationizating agent, in THF solvent, was added into each polymer/matrix mixture. In the case of the analysis of the polymer SEC fractions, 10 μL of each collected fractions were mixed with 10 μL of matrix solution and with 1 μL of a 0.01 M THF solution of CF_3COONa. Then 1 μL of each analyte/matrix/salt mixture was spotted on the MALDI sample holder and slowly dried to allow analyte/matrix cocrystallization.

For PC and PPO-*b*-PC polymer samples, the better MALDI mass spectra were obtained in reflectron mode, whereas for PPO-2OH samples were obtained in linear mode.

3. Results and Discussion

Block copolymers are polymeric materials with very interesting properties from both scientific and technological points of view. Recently, several original routes for synthesis of block copolymers were proposed and numerous combinations of chemically different chains were prepared. As a result, a number of new interesting block copolymers were synthesized. Unfortunately, the molecular characterization of block copolymers (true and not relative MMD, block sequence, number and length of blocks, and terminal groups) is often incomplete and substantially inadequate. Considering the notable progress in the synthesis of block copolymers and the resultant new opportunities, this is an important drawback. PPO-*b*-PC is a relatively new block copolymer. In a previous article,[1] we have reported the synthesis and the preliminary characterization of some PPO-*b*-PC multiblock copolymers showing one single T_g and lower melt dynamic viscosity η compared to starting PPO homopolymer having similar average molar mass. These thermal and rheological properties are very important because are characteristic of high performance PPO-*b*-PC materials having potential good processability compared to the PPO homopolymer. The more important molecular characteristics of all prepared samples, both PPO-2OH incorporating some TMBPA units in the backbone and PC-2OH homopolymers and PPO-*b*-PC copolymers, are summarized in Table 1 (data from ref 1). It is important to note that the molar mass parameters of Table 1, i.e., the weight-average molar mass M_w and the polydispersity index $D = M_w/M_n$, were obtained by a conventional SEC method using a DRI detector and a relative calibration constructed with some PS narrow standards. Differently, in this study we have used a multidetector SEC−MALS−DV system, NMR and MALDI−TOF techniques for the full characterization of both MMD and multiblock structure of this new class of high performance PPO-*b*-PC materials. Substantially, we have used the more powerful "absolute" techniques for the full characterization of these PPO-*b*-PC copolymers including the multiblock structure and terminal groups. The more important molecular characteristics of the starting blocks, PC-2OH and PPO-2OH, and the final PPO-*b*-PC copolymer using SEC−MALS−DV, NMR, and MALDI−TOF methods are sum-

Table 2. Summarized Results of PC-2OH and PPO-2OH Homopolymers and PPO-*b*-PC Copolymers as Obtained from SEC−MALS−DV, MALDI−TOF and NMR Techniques

sample	d*n*/d*c* (mL/g)	$M_n{}^a$ (g/mol)	$M_w{}^a$ (g/mol)	$M_n{}^b$ (g/mol)	$[\eta]^c$ (dL/g)	molar composition PPO/PC^d	PPO block fraction^e	av length of PPO blocks
PC-2OH	0.140	2010	2980	2300	0.092			
PPO-2OH (1)	0.155	6640	9380	6200	0.150			
PPO-2OH (2)	0.155	4970	7010	4500	0.130			
PPO-2OH (3)	0.156	7850	22 000	7300	0.293			
PPO-2OH (4)	0.155	4080	6120	4200	0.126			
PPO-*b*-PC (1)	0.152	9160	22 900		0.259	82/18	39	51
PPO-*b*-PC (2)	0.152	7600	21 990		0.228	85/15	56	38
PPO-*b*-PC (3)	0.152	11 770	30 600		0.321	80/20	40	60
PPO-*b*-PC (4)	0.152	6300	16 150		0.175	82/18	49	35

[a] SEC-MALS data. [b] Evaluated with ^{1}H NMR signals using eqs 1 and 2 for PC-2OH, and eqs 3 and 4 for PPO-2OH; [c] SEC-DV data. [d] Evaluated with ^{1}H NMR signals at 2.04 and 1.68 ppm. [e] Evaluated with ^{1}H NMR signals at 6.47 and 1.68 ppm and M_n from SEC-MALS.

marized in Table 2. It is important to note that NMR and MALDI−TOF results were obtained on quasi-homogeneous fractions after an accurate fractionation using some SEC columns (see Experimental Section for details). We define such PPO-*b*-PC polymeric fractions "quasi-homogeneous" because it is well-known that after a mono-dimensional SEC steric fractionation some residual chemical and chain length nonuniformity could exists again.

3.1. Synthesis and Characterization of PC-2OH Homopolymer. The low molar mass poly(bispenol-A carbonate) with both bisphenol A (BPA) ends (referred as PC-2OH) was accurately characterized by FT-IR, SEC−MALS−DV, MALDI−TOF and NMR techniques. The FT-IR spectra were in good agreement with the PC structure; see ref 1. Substantially the PC-2OH homopolymer shows a M_n of about 2000 g/mol, a M_w of about 3000 g/mol and about 0.1 dL/g of intrinsic viscosity $[\eta]$ (see data in Table 2**)**.

For the synthesis of multiblock PPO-*b*-PC copolymers a PC block with two BPA terminal groups was essential. Consequently, an accurate characterization of terminal groups is also required. The MALDI−TOF mass spectrum of the PC-2OH sample, Figure 1, shows well mass resolved and mass calibrated peaks from 1000 g/mol up to 7000 g/mol. It reveals three different families of homologous peaks that can be assigned to the sodiated ions of three different families of PC oligomers terminated with different end groups. Each mass series of peaks was assigned to the corresponding PC oligomers which structures are reported in Table 3. Their masses corresponds to the equation $Mi_n = n254.2 + m_\theta + 23$, where Mi_n is the molar mass of the i-oligomers with n repeating units terminated with the groups θ having the mass m_θ, 254.2 is the mass of the PC repeating unit, and 23 is the mass of the Na$^+$ cation used as cationizing agent. One expanded portion of the mass spectrum is reported in the inset of Figure 1, and the structures of the corresponding macromolecular species are summarized in Table 3. The intense peaks labeled with the symbol α corresponding to the expected PC oligomers terminated with BPA groups at both end chains (species α, in Table 3). The peaks labeled with the symbol β, which appear with an intensity similar to that of mass series α, corresponds to the PC oligomers terminated with BPA groups at one end and with a methyl carbonate groups at the other end (species β in Table 3). The third mass peak series labeled with the symbol χ corresponds to the PC oligomers terminated with methyl carbonate groups at both ends (species χ in Table 3). According to the synthesis procedure[1] the formation of PC chains terminated with only BPA-OH groups (species α) should be expected; the presence in the MALDI spectrum of PC-2OH sample (Figure 1) of the peaks due to the oligomers having methyl carbonate end groups (species β and χ in Table 3) suggest that these products were formed during the precipitation of the PC solution in methanol owing the reaction between the BPA chloroformate reactive ends of PC chains, and the methanol. Unfortunately, the formation of the PC chains terminated with methyl carbonate at both chains (oligomers χ in Table 3) has opposite effect to the formation of PPO-*b*-PC copolymers since cannot be react with diol terminated PPO polymers and bisphenol A bis(chloroformate) during the synthesis procedure followed for the preparation of the PPO-*b*-PC copolymers. The presence of the PC oligomers terminated with methyl carbonate group was confirmed by ^{1}H NMR analysis that shows the characteristic singlet at 3.9 ppm (see Table 4). The assignments of the proton signals present in the ^{1}H NMR spectrum of the PC-2OH sample are reported in Table 4. The signals of ^{13}C NMR spectra are in agreement with the ^{1}H NMR data and are reported in Table 4 too. The average M_n of this sample was calculated from ^{1}H NMR spectrum applying the eqs 1 and 2: using the integrated area of the quartet in the range 7.13−7.28 ppm due to the eight aromatic protons indicated as 4 and 5 in Table 4, that of the doublet at 6,70−6.74 ppm corresponding to the aromatic protons 4′ of the BPA ends, and the integrated area of methyl carbonate protons (labeled as 9 in Table 4). In these equations with $\%_{(6.60-6.74)}$ and with $\%_{3.9}$, we indicate the percent of the four aromatic protons 4′ of the BPA ends and the six methyl carbonate protons, respectively. These percentages were calculated using the integrated area of the corresponding proton peaks.

$$X_n = \frac{I(7.13 - 7.28)}{\dfrac{I(6.70 - 6.74)\ \%\ (6.60 - 6.74)}{4} + \dfrac{I3.9\ \%\ 3.9}{6}} \qquad (1)$$

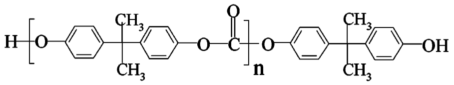
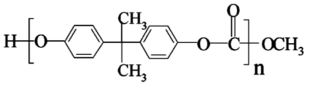
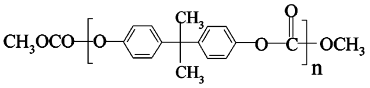
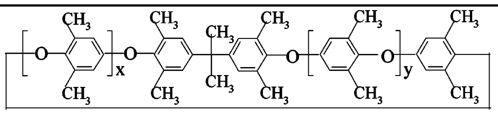
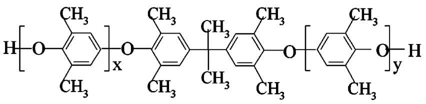
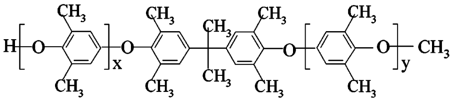
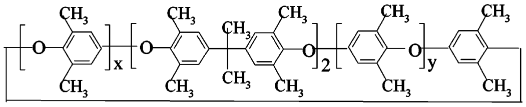
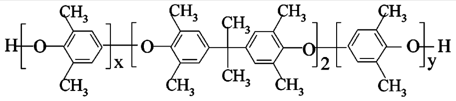
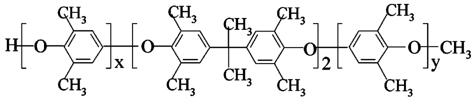
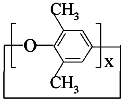
$$M_n = X_n \times 254.2 \qquad (2)$$

Looking at the data in Table 2, the fact emerges that there is a relatively good agreement between the M_n molar mass averages calculated from both SEC−MALS−DV and NMR analyses.

3.2. Synthesis and Characterization of PPO-2OH Homopolymer. As well as the PC-2OH sample, either the MMD and the chemical structures of low molar mass PPO-2OH samples synthesized was characterized by FT-IR, SEC−MALS−DV, NMR, and MALDI−TOF analysis. The FT-IR spectra of the PPO-2OH homopolymer was reported previously.[1] Four low molar mass PPO-2OH samples, having a few units of tetramethyl bisphenol A units (TMBPA) in the chains, were synthesized. Apart from the higher molar mass PPO-2OH (3) sample, the M_w values range from 6100 to 9400 g/mol, the polydispersity index D was about 1.5, and $[\eta]$ ranges from 0.13 to 0.15 dL/g (see Table 2 for details).

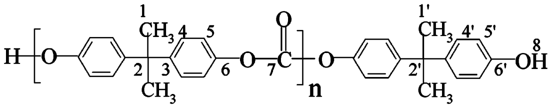
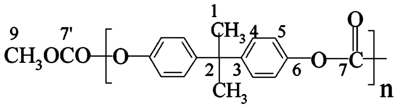
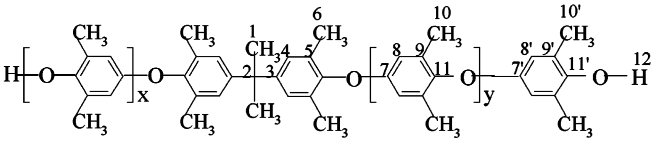
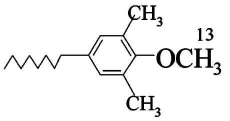
The MALDI−TOF mass spectrum of a PPO-2OH (4) sample reported in Figure 2 shows a series of peaks from 600 up to

Table 3. Structural Assignments of Peaks Displayed in the MALDI−TOF Mass Spectra of the Polymers Reported in Figures 1, 2, and 7

SPECIES	Structures	Masses
PC OLIGOMERS $[M+Na]^+$ (n)[a]		
α		1522.2 (5); 1776.4 (6); 2030.6 (7); 2284.8 (8); 2793.2 (10); 3810 (14); 4572.6 (17); 5335.2 (20)
β		1326 (5); 1580.2 (6); 1834.4 (7); 2088.6 (8); 2342.8 (9); 2851.2 (11); 3868 (15); 4630.6 (18); 5393.2 (21)
χ		1384 (5); 1638.2 (6); 1892.4 (7); 2146.6 (8); 2400.8 (9); 2909.2 (11); 3926 (15); 4688.6 (18); 5451.2 (21)
PPO OLIGOMERS $[M+H]^+$ (n)[a]		
δ		867.7 (4); 1005.8 (6); 1125.9 (7); 1246 (8)
ε		885.7 (5); 1005.8 (6); 1125.9 (7); 1246(8); 1366.1 (9); 1486.2 (10): 1606.3 (11); 1726.4 (12); 1846.5 (13)
φ		899.7 (5); 1019.8 (6); 1139.9 (7); 1260 (8)
γ		909.6 (2); 1029.7 (3); 1149.8 (4)
λ		927.3(3); 1047.8(4); 1167.9(5)
μ		941.7 (3); 1061.8 (4); 1181.9 (5)
ν		961.8 (8); 1081.9 (9); 1202 (10)

[a] $n = (x + y)$ for PPO oligomers.

Table 4. Assignments of the Chemical Shifts Due to the Carbons and Hydrogens Present in the Backbone and in the End Chains of the PC-2OH and of PPO-2OH Samples, As Observed in Their ^{1}H and ^{13}C NMR Spectra

Samples	Structures	Chemical shifts			
		H	(ppm)	C	(ppm)
PC-2OH	 	1 1' 4 4' 5 5' 8 9	(1.68) (1.64) (7.13-7.18) (6.70-6.74) (7.23-7.28) (7.06-7.10) 4.82 3.91	1 1' 2 2' 3 4 4' 4'' 5 5' 6 6' 7 7' 9	(30.92) (30.98) (42.56) (41.10) (148.85) (120.33) (114.78) (120.17) (127.81) (127.40) (148.05) (148.75) (152.19) (153.47) (55.37)
PPO-2OH	 	1 4 6 8 8' 10 12 13	1.7 6.96 2.04 6.47 6.36 2.09 4.78 3.85	1 2 3 4 5 6 7 7' 8 8' 9 9' 10 10' 11 11' 13	(30.90) (41.90) (149.18) (124.20) (128.96) (16.50) (154.70) (154.41) (114.28) (114.00) (132.60) (131.50) (17.00) (16.27) (145.48) (146.33) (56.70)

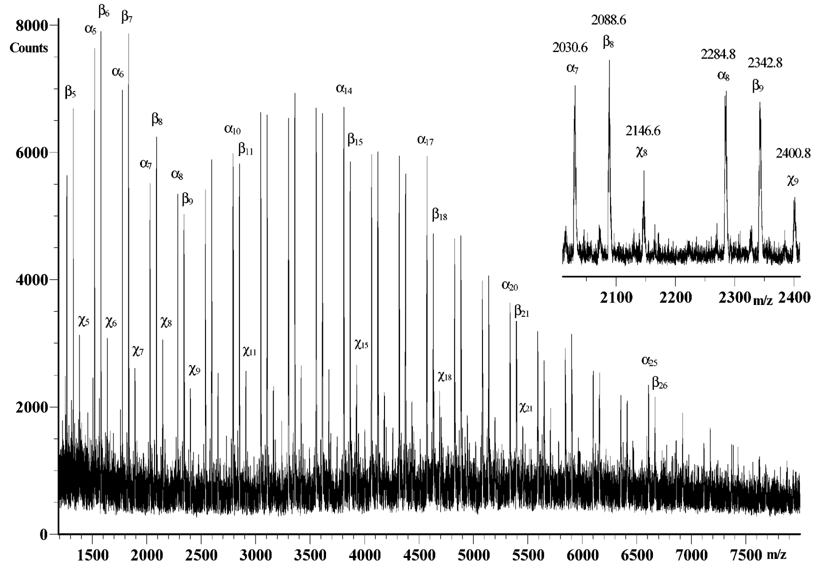


Figure 1. MALDI−TOF mass spectrum of the PC-2OH homopolymer.

3500 g/mol, corresponding to the seven different ending PPO oligomers depicted in Table 3, which appear as protonated ions.

The presence of seven mass peak series stands out from the inset in Figure 2. As expected on the base of the synthesis

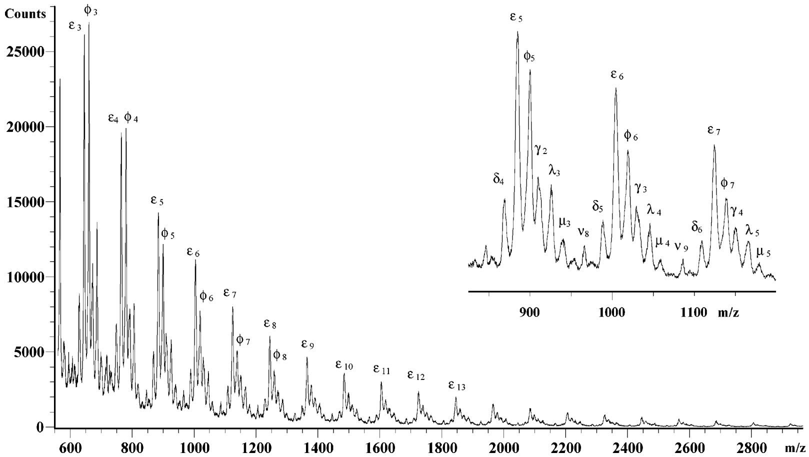
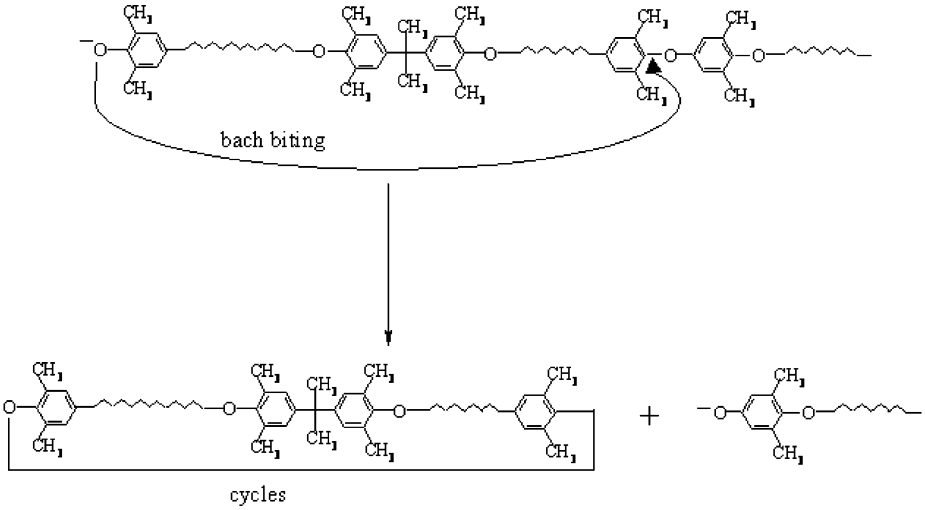


Figure 2. MALDI−TOF mass spectrum of the PPO−OH (4) homopolymer.

Scheme 3



procedure,[1] the most intense peaks correspond to the PPO chains terminated with phenol groups at both ends and having one TMBPA unit in the backbone (species ϵ in Figure 2 and in Table 3). These peaks are accompanied by intense peaks labeled with the symbol ϕ, having a difference of 14 g/mol more than that of peaks ϵ and corresponding to the linear PPO oligomers with the same structure but bearing a methyl ether groups (species ϕ in Table 3). These species may be formed by reaction of phenoxy end groups of PPO chains and methanol during the precipitation of the PPO-2OH sample from $CHCl_3$ solution. Low, intense peaks belonging to the linear PPO oligomers with the same end groups of species ϵ and ϕ but with two tetramethyl BPA units in the backbone are also present in the MALDI−TOF spectrum of the PPO-2OH (4) sample (species λ and μ in Figure 2 and in Table 3). Very low intense peaks of PPO chains without tetramethyl BPA unit, were also observed (species ν in Figure 2 and in Table 3). Finally, cyclic oligomers (species δ and γ in Figure 2 and in Table 3), may be formed by the back-biting reaction depicted in Scheme 3, were also observed in the MALDI spectrum. Very similar MALDI mass spectra were recorded for the other PPO-2OH samples analyzed.

The structures and the end groups of the four PPO-2OH samples were also confirmed by (^{1}H and ^{13}C) NMR analyses, and the pertinent assignments of the protons and carbons resonance signals are reported in Table 4. The intensities of the signals belonging to the aromatic protons of the PPO units, which resonate at 6.47 and 6.36 ppm (protons 8 and 8′ in Table 4), were used to calculate the average degree of polymerization (X_n) by the eq 3. The M_n average were determined by eq 4, where 120.1 is the mass of the PPO repeat unit. The results are reported in Table 2.

$$X_n = \frac{I(6.47)}{I(6.36)} \tag{3}$$

$$M_n = X_n \times 120.1 \tag{4}$$

As well the PC-2OH sample, also for PPO-2OH samples there is a quite good agreement between the M_n molar mass averages calculated from SEC−MALS−DV and NMR data.

3.3. Synthesis and Characterization of PPO-*b*-PC Copolymers. More important macromolecular properties of the PPO-*b*-PC copolymers synthesized from SEC−MALS−DV, NMR, and MALDI−TOF are summarized in Table 2. According to the synthesis procedure (see Scheme 1 and ref 1) the synthesized PPO-*b*-PC copolymers have average molar mass higher than of the initial PPO-2OH and PC-2OH homopolymers used for their synthesis. It should be noticed that respect to the starting homopolymers, PPO-*b*-PC copolymers with higher molar mass were obtained if a PPO-2OH homopolymer having $M_n < 10\,000$ g/mol is employed.

The comparison of the differential MMD of the starting PC-2OH and PPO-2OH (1) homopolymers and of the final PPO-*b*-PC (1) block copolymer is shown in Figure 3. For each of the four PPO-*b*-PC copolymers synthesized a meaningful increasing of the molar mass and of the intrinsic viscosity it is

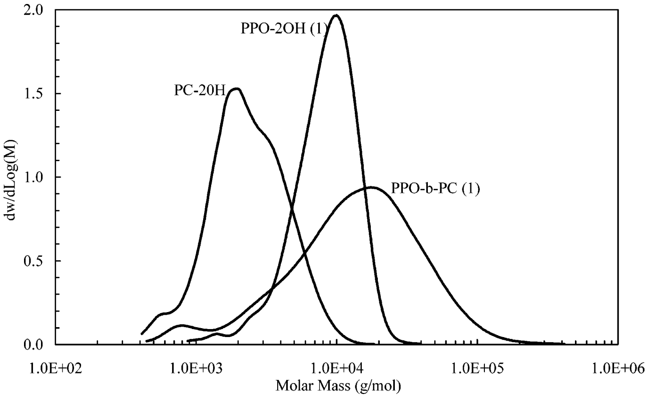


Figure 3. Comparison of the differential MMD of the starting PC-2OH and PPO-2OH (1) homopolymers and of the final PPO-*b*-PC (1) copolymer.

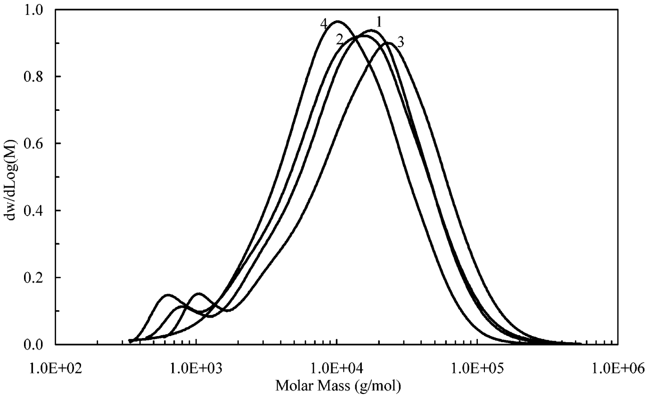


Figure 4. Comparison of the differential MMD of four PPO-*b*-PC copolymers.

evident (see Table 2). The comparison of the differential MMD of the four different PPO-*b*-PC copolymers synthesized is shown in Figure 4. The molar mass data of PPO-*b*-PC copolymers reported in Table 2 and in Figures 3 and 4 were obtained using an on-line light scattering (MALS) detector. It is well-known that for a copolymer with chemical drift along the macromolecular chain the molar mass from a light scattering detector is not absolute but apparent because the d*n*/d*c* parameter is not a constant. Fortunately the difference in d*n*/d*c* between the two different blocks, PC and PPO, is not high (less than 10%, see Table 2). Considering the agreement between the M_n molar mass average from NMR and SEC-MALS, MALDI−TOF data and the congruence between the M_w molar mass average from SEC-MALS and $[\eta]$ values from viscometry, that does not depend from the chemical composition, we can state that the molar mass data from SEC-MALS method also for the PPO-*b*-PC copolymers reported in Table 2 are substantially correct.

Figure 5 shows the comparison of the Mark−Houwink−Sakurada (MHS) plot, $[\eta] = kM^a$, of the initial PC-2OH and PPO-2OH (1) homopolymers (blocks) and of the final PPO-*b*-PC (1) block copolymer. The MHS parameters, slope *a* and intercept *k*, for PC-2OH and PPO-2OH homopolymers and PPO-*b*-PC copolymer are reported in Table 5. The slope $a = 0.54$ is congruent for a PC sample with low molar mass ($M_w \approx 3000$ g/mol) in chloroform solvent. It is important to note that the MHS plot of the PPO-*b*-PC block copolymer is substantially similar to the initial PPO block (see Figure 5 and Table 5 data). In other words, from a conformational point of view PPO blocks are dominant in the PPO-*b*-PC multiblock copolymer.

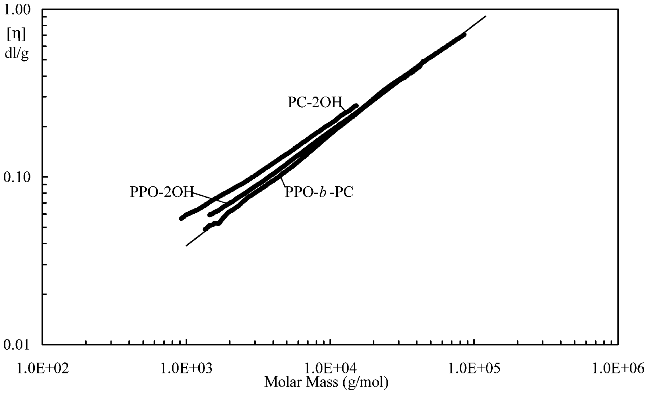


Figure 5. Comparison of the MHS plot of the starting PC-2OH and PPO-2OH (1) homopolymers and of the final PPO-*b*-PC (1) copolymer.

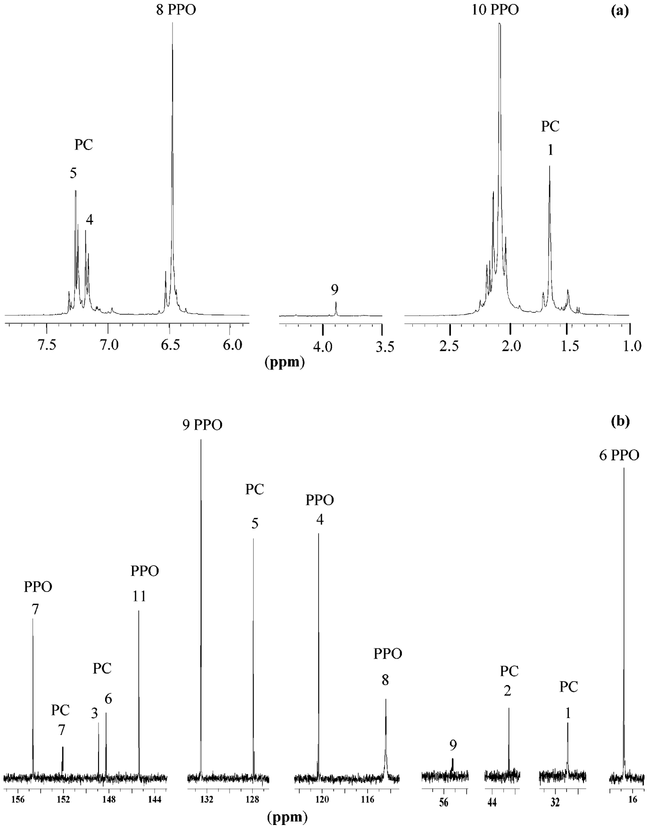


Figure 6. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of the PPO-*b*-PC (2) copolymer.

Table 5. MKS Parameters for PC-2OH and PPO-2OH Homopolymers and PPO-*b*-PC Copolymer from SEC-DV

sample	**k** (dL/g)	**a**
PC-2OH	1.44×10^{-3}	0.54
PPO-2OH	5.56×10^{-4}	0.63
PPO-*b*-PC	4.13×10^{-4}	0.66

Typical ^{1}H NMR and ^{13}C NMR spectra of PPO-*b*-PC (2) copolymer are reported in Figure 6. The assigned of the proton and carbon signals were performed according to the chemical shifts in Table 4. The peaks at 6.47 and 1.68 ppm due to the aromatic PPO hydrogen and isopropylidene methyl groups of the PC blocks, respectively, and the M_n data of starting oligomers obtained by SEC−MALS−DV, were used to evaluate the PPO block fraction in the copolymer. As reported in Table 2, the PPO block molar fraction of all the synthesized PPO-*b*-PC materials ranges from 0.39 to 0.56. The average molar composition of the PPO-*b*-PC copolymers was also calculated using the integrated area of the peaks at 2.04 and 1.68 ppm due to methyl protons belonging to the PPO (protons 6 in Table

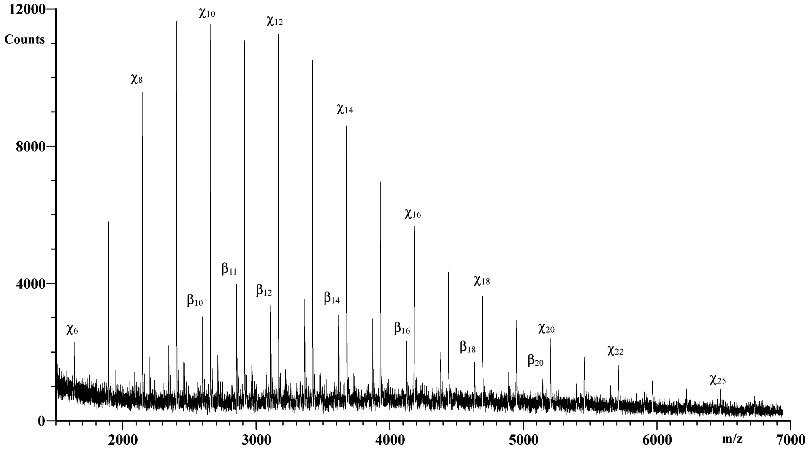


Figure 7. Positive ions MALDI−TOF mass spectra of the SEC fraction F42, eluted at 20.30 min, of the PPO-*b*-PC (4) copolymer.

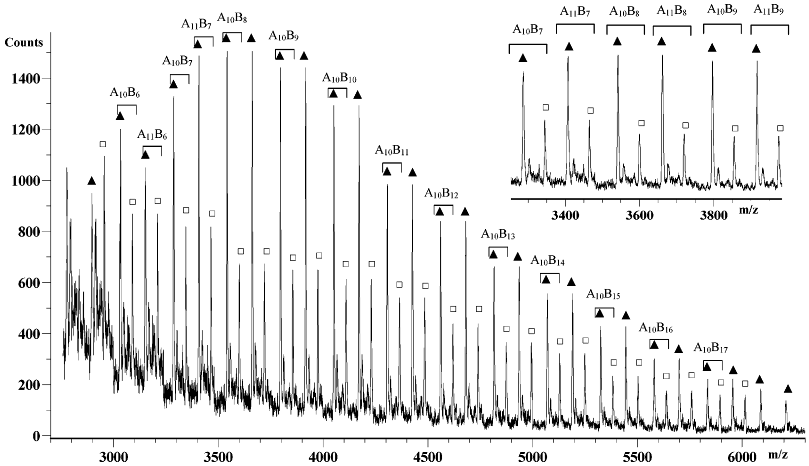


Figure 8. Positive ions MALDI−TOF mass spectra of the SEC fraction F22, eluted at 17.60 min, of the PPO-*b*-PC (4) copolymer.

4) and PC (protons 1 in Table 4) repeat units, respectively. The results are reported in Table 2, which shows that the copolymers have a PPO/PC molar composition ranging from 80/20 up to 85/15. In the carbon spectra, besides the peaks due to the carbons belonging to the PPO and PC blocks (Figure 6), a weak peak appears at 151.8 ppm that we have assigned at the carbonyl of the carbonate groups linking the PPO and PPC blocks in the copolymers. Using the relative intensity of the last new peak with respect to the carbonyl of the PC block (peak 7 at 152.19 ppm in Figure 6 and in Table 4), we have calculated the average block lengths of the PC chains (L_{PC}) in the copolymers by eq 5

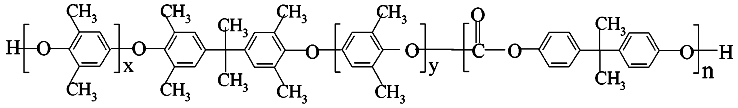
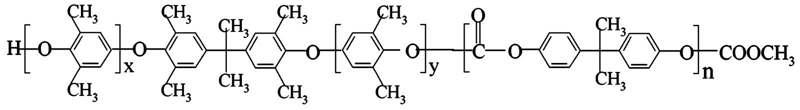
$$L_{PC} = I_{(152.19)}/I_{(151.8)} \qquad (5)$$

The calculated L_{PC} values range from 7.2 up to 8 for the four copolymers *a* values, and because these data are close to the average degree of polymerization ($X_n = 7.7$) of the initial PC-2OH polymer, we believe that chain extension of the last polymer does not occur during the copolymerization reaction (Scheme 1) of the PPO−PC copolymers studied.

MALDI−TOF mass spectra of all unfractionated PPO-*b*-PC copolymers show intense peaks due to only the unreacted PC oligomers terminated with BPA and methyl carbonate (species β in Table 3) and with methyl carbonate at both ends (species χ in Table 3), whereas the expected mass peaks due to the copolymer chains appear with very low intensity. This surprising result suggests that PC might have a better ionization and desorbing efficiency with respect to either the PPO-*b*-PC or PPO macromolecules, under our experimental MALDI−TOF MS conditions. This behavior, observed also in other polymer systems,[10,11,18] was confirmed by MALDI−TOF analysis of PPO-2OH/PC-2OH mixtures with different weight/weight (w/w) ratios, using different matrices (namely HABA, IAA, DHB, and dithranol). MALDI−TOF spectra of these mixtures give mass peaks due to the PPO-2OH oligomers only when the PC-2OH amount was lower than 5 wt %. To overcome this problem, the PPO-*b*-PC copolymers were fractionated by a conventional SEC system using only an on-line DRI concentration detector, and several SEC fractions were collected and then analyzed off-line by MALDI−TOF. The chromatogram of the conventional SEC system used for collecting the narrow MMD fractions presented a maximum of the elution volume (*V*) around 18 min while the maximum of the *V* for the corresponding PPO-2OH (4) homopolymer was at 18.60 min, confirming that the coupling reaction of PPO-2OH sample with PC-2OH polymers (Scheme 1) allows to the formation of PPO-*b*-PC block copolymers with average molar mass higher with respect to those of initial homopolymers. In Figures 7 and 8 are reported the MALDI−TOF mass spectra of the SEC fractions eluted at 20.30 and 17.60 min, referred to as F42 and F22, respectively.

MALDI−TOF mass spectrum of the copolymer SEC fractions F42 (Figure 7), as well as the mass spectrum of the unfractionated copolymer, shows two families of peaks corresponding to the unreacted PC oligomers terminated with methyl carbonate units (species β and χ in Figure 7 and in Table 3). The same results were obtained analyzing the SEC fractions eluted at times higher than 19.60 min. Mass peaks belonging to the PC oligomers and PPO-*b*-PC copolymer were observed in the SEC

Table 6. Structural Assignments of Peaks Displayed in the MALDI−TOF Mass Spectrum of the Copolymer F22 SEC Fraction Reported in Figure 8

Symbol	Structures	$[M+Na]^+$ (AmBn)[a]
▲		3033.4 (10,6); 3153.5 (11,6); 3287.6 (10,7); 3407.7 (11,7); 3541.8 (10,8); 3661.9 (11,8); 3796 (10,9); 3916.1 (11,9); 4050.2 (10,10); 4304.4 (10,11); 4558.6 (10,12); 4812.8(10,13); 5067 (10,14); 5321.2 (10,15); 5575.4 (10,16); 5829.6 (10,17)
□		3091.4 (10,6); 3211.5 (11,6); 3345.6 (10,7); 3465.7 (11,7); 3599.8 (10,8); 3719.9 (11,8); 3854 (10,9); 3974.1 (11,9); 4108.2 (10,10); 4362.4 (10,11); 4616.6 (10,12); 4870.8(10,13); 5125 (10,14); 5379.2 (10,15); 5633.4 (10,16); 5887.6 (10,17)

[a] $m = (x + y)$ for PPO blocks.

fractions eluted between 18.20 and 19.60 min. MALDI spectra of the SEC fractions eluted between 15.30 and 18.20 min shown well resolved peaks corresponding only to PPO-*b*-PC chains. Figure 8 reports the mass spectrum of the fraction eluted at 17.60 min (F22) (maximum of the SEC curve). It shows two families of peaks corresponding to the PPO-*b*-PC copolymer chains, one terminated with hydroxy groups at both ends (species labeled with symbol ▲ in Figure 8 and in Table 6) and the other terminated with hydroxy and methyl carbonate groups (species labeled with the symbol □ in Figure 8 and in Table 6). These families of co-oligomers were indicated as A_mB_n, where A_m indicated *m* PPO units and B_n *n* PC units (see Table 6) in the copolymer chains. Looking at Figure 8, we can observe that the SEC fraction is composed of copolymers having the same units of PPO and different PC units. In fact the mass spectrum in Figure 8 shows intense peaks corresponding to the copolymer chains AB having 10 or 11 PPO units (A) and PC units (B) ranging from 5 up to 20. The same behavior was observed in the well resolved mass spectra of the SEC fractions eluted at lower elution time (between 15.00 and 18.20 min), as can be observed in Figure 1S that reports the MALDI−TOF mass spectrum of the SEC fraction F24 eluted at eluted at 17.9 min. In this case, the mass spectrum shows intense peaks corresponding to the copolymer chains AB having 6 or 7 PPO units and different PC units ranging from 3 up to 20.

These results suggest that in this case the elution time in the SEC runs depend on the average lengths of the PPO blocks in the copolymers, as confirmed also by the MALDI−TOF mass spectra of the SEC fractions obtained by fractionation of the other PPO−PC block copolymers synthesized.

3.4. Aminolysis of PPO-*b*-PC Copolymers. To determine the average length of the PPO blocks in the PPO-*b*-PC copolymers, we have performed an exhaustive and selective aminolysis of the carbonate groups by reaction with a large excess of piperidine. This because it is known that the polycarbonates are easily degraded by reaction with this amine.[16] The residues obtained by precipitation in ethyl alcohol of the aminolyzed reaction mixtures, were analyzed by ^{1}H NMR, MALDI−TOF, and viscosimetric methods. The NMR and MALDI−TOF spectra indicate that the residues contain only PPO chains with a chemical structure close to those of the initial PPO-2OH samples. Since the viscosimetric values of these aminolyzed residues were similar to those of the PPO-2OH initial polymers, we deduce that the degree of polymerization of the PPO blocks does not change during the synthesis of the copolymer samples, and therefore using the M_n data of the PPO-2OH polymers determined from their ^{1}H NMR spectra, we have calculated the average lengths of the PPO blocks in the corresponding copolymers. On the basis of these data and considering either the M_n values of the copolymers and those of the corresponding initial homopolymers (Table 2), we believe that each PPO-*b*-PC copolymer synthesized contains a rough average of two PPO blocks and two PC blocks along the macromolecular chain.

4. Conclusions

A new class of homogeneous multiblock copolymers containing PPO and PC segments having single T_g, good processability, lower dynamic viscosity compared to similar PPO homopolymer and thermal stability was synthesized by a chain extension reaction between low molar mass PPO and PC diol-terminated blocks. An accurate full characterization of PC and PPO homopolymers and of some PPO-*b*-PC multiblock copolymers by SEC−MALS−DV, MALDI−TOF, and NMR techniques was performed. More important finding of this study were the following.

- MMD, [η], and MHS parameters of PC-2OH and PPO-2OH homopolymers and of four different PPO-*b*-PC block copolymers were obtained by a multidetector (light scattering and viscometry) SEC system.
- MALDI−TOF of the PC-2OH homopolymer reveals three different families of oligomers terminated with different end groups: (1) PC terminated with BPA groups at both end chains; (2) PC terminated with BPA group at one end and methyl carbonate group at the other end; (3) PC terminated with methyl carbonate groups at both ends.
- MALDI−TOF of PPO-2OH homopolymer reveals a series of peaks from 600 g/mol to 3500 Da corresponding to seven different ending PPO oligomers.
- MALDI−TOF analysis showed that the final PPO-*b*-PC copolymers synthesized were constituted of multiblock PPO-*b*-PC chains and also of some no-reacted PC oligomers terminated with methyl carbonate groups.
- The PPO molar fraction in the four different PPO-*b*-PC block copolymers synthesized ranges from 0.39 to 0.56.
- Each PPO-*b*-PC copolymer synthesized contains a rough average of two PPO blocks and two PC blocks along the macromolecular chain.

Supporting Information Available: Figure 1S, positive ion MALDI-TOF mass spectra of the SEC fraction 24 of the PPO−PC copolymer eluted at 17.9 min. This material is available free of charge via the Internet at http://pubs.acs.org.

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