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Amino terminated copoly(ethersulphone)s bearing biphenylenic units in the backbone: Synthesis and characterization

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ABSTRACT

The present project is based on the synthesis of new essentially amino-ended copoly(ether sulphone)s which are characterized by the presence of rigid biphenyl units in the main chain. All the compounds have been fully characterized by (^{1}H and ^{13}C) NMR, FTIR, and MALDI-TOF MS techniques. Complete assignments of the ^{1}H and ^{13}C NMR spectra have been accomplished by comparison with model compounds and literature data. The thermal properties of the copolymers were studied by differential scanning calorimetry (DSC). The glass transition temperature of the copolymers increases as increasing the molar composition of ethere sulphone units containing biphenyl moiety. The copolymers synthesized might find application as reactive toughening agents for multifunctional epoxy resins when high thermal properties are a requirement.

1. Introduction

Poly(ether-sulfones)s (PES)s have a great scientific and industrial interest owing to their good mechanical, chemical and thermal stabilities [1–4]. Those features are due to the structure of these polymers. A great advantage of polyethersulfones is the possibility to obtain copolymers with various co-monomers containing special in-chain or pendent groups without substantial changes to the synthetic routes. This feature can be advantageously used to control and enhance the final properties of the copolymers itself or of its blends with other polymers [5–8].

Among the different uses of polyethersulfones their exploitation as toughening agents has encountered a great success in the last years [9–15]. Nowadays all the most important epoxy-based resin matrices for aerospace composites devoted to primary structures are obtained blending polyethersulfones with mixture of difunctional and multifunctional epoxy resins [16–20]. The thermal behavior (ie. glass transition temperatures and thermal stability) of such blends is clearly the result of the contribution of both the thermoset and thermoplastic contribution. In the recent years the need for high glass transition epoxy matrices for pre-preg systems devoted to advanced aerospace applications for the next generation of planes has lead to consistent research aimed to increase the thermal properties of all the components of a resin systems. In a preview work, we have synthesized and characterized a series of nominally amino-ended poly (ether-sulphone-ether-sulphone-co-ether-ether-sulphone) P(ESES-co-EES) random copolymers with a different ESES/EES molar ratio [21], which has Tg ranging from 180 °C up to 215 °C. In order to prepare PESs with more high Tg, in this work we have performed the synthesis and chemical characterization of essentially amino-ended random copolyethersulfone bearing ESES (ether-sulphone-ether-sulphone) and ESESBS (ether-sulphone-ether-sulphone-biphenyl-sulphone) units in the chain The copolymers were prepared by nucleophilic aromatic substitution polycondensation of 4,4′-dihydroxydiphenylsulphone (DHDPS) with different molar ratio of 4,4′-dichlorodiphenylsulphone (DCDPS) and 4,4′-bis[(4-chlorophenyl) sulphonyl]-1,1′-biphenyl (Long Chain DiChloride: LCDC) (See Scheme 1). LCDC has been selected due to the conformational stability of biphenyl group which can improve the thermal and chemical stabilities of the copolymers. The copolymers were synthesized varying the amount of LCDC in the chain and the effect of such variation on thermal properties has been studied in detail.

2. Experimental

2.1. Materials

4,4′-Dichlorodiphenylsulphone (DCDPS) (98% of purity grade), 4,4′-dihydroxydiphenylsulphone (DHDPS) (98% of purity grade),

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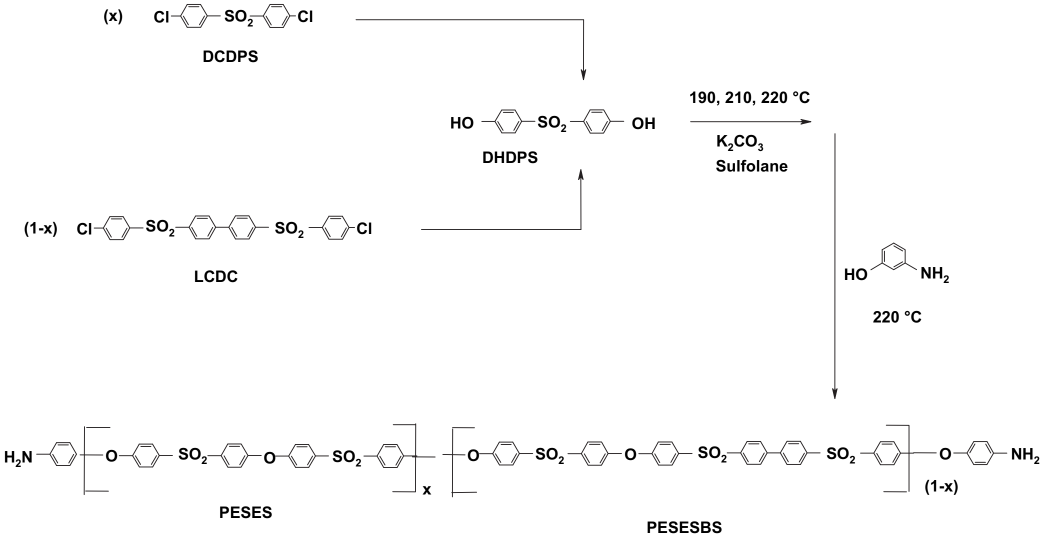


Scheme 1.

4,4′-bis[(4-chlorophenyl)sulphonyl]-1,1′-biphenyl (long chain dichloride LCDC) (99% of purity grade), *m*-aminophenol (*m*-AP), potassium carbonate and tetramethylenesulphone (sulfolane) were purchased from Aldrich Chemical Co. (Italy). All reagents used in these experiments were obtained from commercial sources and utilized without any special purification. Potassium carbonate [K_2CO_3 anhydrous grade] was dried at 150 °C under reduced pressure. Tetramethylenesulphone was distilled under reduced pressure and stored under nitrogen until used.

2.2. Synthesis

2.2.1. Amino-ended copolymer synthesis

A one pot synthesis was used to obtain amino-ended polymers with different molar composition in ESES (ether-sulphone-ether-sulphone) and ESESBS (ether-sulphone-ether-sulphone-biphenyl-sulphone) units, via nucleophilic condensation of DHDPS with DCDPS and/or LCDC, followed by a end capping nucleophilic reaction with *m*-AP, as reported in Scheme 1.

The molar ratio of DCDPS and LCDC monomers was varied in order to prepare copolymer samples with different molar composition.

A typical example of polymerization of an amino ended random copolymer with a molar composition 50/50 is as follows: to a 500 ml three necked flask, equipped with an overhead stirrer and a nitrogen inlet were added DCDPS (4.0 g, 13.9 mmol), DHDPS (6.6 g, 26.4 mmol), and LCDC (7.0 g, 13.9 mmol), in 200 ml of sulfolane. Potassium carbonate (4.0 g, 29.0 mmol) was then added and the temperature increased to 180 °C under a nitrogen flow.

The mixture was allowed to react for 30 min at this temperature, for 3 h at 200 °C and finally for 3 h at 220 °C. Then *m*-AP (0.3 g, 2.73 mmol) was added and the mixture was allowed to stir for 4 h at 220 °C. After cooling at room temperature, the mixture was poured into 400 mL of methanol to get, after stirring, filtration, methanol/water washings, and vacuum drying (80 °C, overnight), 12.5 g of copolymer (**3**) as off-white powder. Table 1 shows the mols of monomers used such as the expected composition of the synthesized polymers. Copolymers formed are of ESES and ESESBS type, thus, in the following, we will refer to the copoly(aryl-ethersulphones) as P (ESES-co-ESESBS) copolymers.

2.3. Measurements

2.3.1. NMR spectroscopy

Proton and carbon NMR spectra of all samples were performed in deuterated dimethylsulfoxide (DMSO-d_6) with a Varian INOVA 500 instrument at room temperature without any internal standard at a concentration of 30 mg/ml. ^{13}C NMR spectra were collected by using the Attached Proton Transfer (APT) technique in order to distinguish between quaternary (up signals) and tertiary (down signals) carbons. The acquisition parameters were optimized in order to obtain, for similar carbon types present, similar relaxation rates. The spectra were recorded with the following acquisition parameters: sweep width: 10,000 Hz; 65,536 data points, giving a digital resolution of 0.305 Hz per point and an acquisition time of 2755 s. A pulse width of 4 ms and delay of 4 s were used for about 10,000 accumulations. All chemical shifts are reported in ppm with respect to the signal references corresponding to the DMSO: at 2.5 ppm for protons and at 39.5 ppm for carbons.

2.3.2. MALDI-TOF mass spectrometry

The MALDI-TOF mass spectra were recorded in linear mode, 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, 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 threshold. Samples used for the MALDI analyses were

Table 1
Mols of DHDPS, DCDPS and LCDC monomers in the feed, and expected molar composition of the polymers synthesized.

Sample Code	Mols (mmol) of monomers in the feed			Molar composition (C_A/C_B)[a]
	DHDPS	DCDPS	LCDC	
(**1**)	26.40	27.80	-	100/0
(**2**)	26.40	20.85	6.95	75/25
(**3**)	26.40	13.90	13.90	50/50
(**4**)	26.40	6.95	20.85	25/75
(**5**)	26.40	-	27.80	0/100

[a] C_A and C_B indicate the molar composition of the ESES and ESESBS units, respectively, in the polymer chains (indicate also with x and $1 - x$ in Scheme 1)

prepared as follows: 10 µl of polymer solution (3–4 mg/ml in CHCl3), were mixed with 10 or 30 µl of HABA solution (0.1 M in $CHCl_3$/THF 90/10 v/v). This solution was added to 1 µl of a 0.01 M solution of CF_3COONa salt as cationizating agent, in THF solvent. Then 1 µl of each analyte/matrix/salt mixture was spotted on the MALDI sample holder and slowly dried to allow analyte/matrix co-crystallization.

The best MALDI spectra reported here present a mass resolution of 1000–1200 FWHM and were recorded using a (matrix solution)/(polymer solution) ratio of 3/1. The mass peaks corresponding to the macromolecular species were measured with an accuracy of ±0.4 Da. The spectra were calibrated using external calibration file made by MALDI analysis of a Ny6 sample terminated with only amino groups and having a Mn of about 6000 Da, appropriately synthesized.

2.3.3. Differential scanning calorimetry (DSC)

The Tg values of the polymer samples were determined in nitrogen atmosphere by TA Instrument Q100 Differential Scanning Calorimetry (DSC), calibrated with melt purity indium standard (156.6 °C and 28.45 J/g) following the procedures suggested by the supplier. Before any experiment, the baseline is recorded using empty aluminium pan (reference and sample). The Tg values were taken at the midpoint of the glass transition in all DSC thermograms. Generally, samples of about 5 ± 1 mg, held in aluminium crucibles, were analyzed under nitrogen flow (50 ml min^{-1}). Each sample was analyzed following the same runs: (i) heating at 10 °C/min two from 0 °C up to 300 °C; (ii) quenching at 100 °C/min from 300 °C to −50 °C; and (iii) heating at 10 °C/min from 0 °C up to 300 °C. Three repeated scans were performed to verify the reproducibility of thermal transitions. The Tg values measured in the second heating were reported in Table 2.

2.3.4. Viscosimetry

The intrinsic viscosity was determined by viscosimetry using a Ubbelohde suspended-level viscometer in dimethylformamide (DMF) as solvent at 25 °C. Measured values are reported in Table 2.

2.3.5. IR spectroscopy

The Fourier Transform Infrared (FTIR) absorption spectra were recorded on a Perkin Elmer model Spectrum 100 using a universal ATR sampling accessory.

3. Results and discussion

3.1. Polymer synthesis

The one pot synthesis of essentially amino ended PESES and PESESBS homopolymers such as of P(ESES-co-ESESBS) copolymers was performed in two steps, according to Scheme 1, improving (by a careful choice of experimental parameters) the method reported in the literature [21].

Table 2

Molar composition (calculated from ^{1}H NMR and MALDI-MS data), average numeric molar mass, intrinsic viscosity, TGA and thermal properties of the homopolymers (PESES, PESESBS) and P(ESES-co-ESESBS) copolymers synthesized.

Polymer	Molar composition (C_A/C_B)[a]		M_n[b] (g/mol)	η_{intr} (dL/g)	Tg (°C)		
	^{1}H NMR	MALDI			Exp.	By Fox Eq. from	
						MALDI	^{1}H NMR
(**1**)	100/0	100/0	8900	0.180	205	–	–
(**2**)	75/25	70/30	9300	0.180	218	219	217
(**3**)	49/51	52/48	8800	0.180	225	227	229
(**4**)	24/76	22/78	8800	0.181	245	243	241
(**5**)	0/100	0/100	9000	0.182	252	–	–

[a] C_A and C_B indicate the molar composition of the ESES and ESESBS units, respectively, in the copolymer chains (indicate also with x and $1 - x$ in Scheme 1).

[b] M_n values in Dalton (Da), calculated from ^{1}H NMR spectra by using published equations in Ref. [21].

The preparation of the amino-ended polymers foresees the initial synthesis of macromolecules chloro-ended (first step), followed by conversion to amino-ended polymers (end capping). The chloro-ended pre-polymers were synthesized by nucleophilic condensation polymerization of DHDPS with DCDPS or LCDC as precursors for homopolymers (**1**) and (**5**), respectively (see Scheme 1 and Table 1). Furthermore Table 1 shows the mols of the DHDPS, DCDPS and LCDC monomers used in order to get the precursor for copolymers (**2**), (**3**), and (**4**), such as the code and expected molar composition of the polymer samples based on DCDPS/LCDC molar ratio in the feed. All monomers were dissolved in sulfolane by using a precise excess of the chlorinated monomer in order to get chains terminated with chloro functions at both ends.

Three gradients of temperature have been used and precisely: (i) the mixture has been stirred under flowing nitrogen and heated to 180 °C for 30 min, (ii) then at 200 °C for 1 h and (iii) to 220 °C for 3 h. During the first gradient of temperature K_2CO_3 powder was added slowly. At the end of the third gradient *m*-Ap, was added by portion in order to get, *via* nucleophilic condensation and ether bridge formation, the capping with amino groups maintaining the temperature to 220 °C for other 4 h. Once completing the reaction, the mixture was allowed to cool to room temperature and then poured into methanol to give a off-white powder that after filtration and several methanol–water washings was dried at 80 °C under vacuum overnight.

It is worth to note that in a preliminary study, in order to increase the kinetic of the end capping reaction, at the end of the third temperature gradient, the *m*-Ap was added along with a second amount of K_2CO_3 (10% mol). But as a result we got a lowering of the average molar mass due to the trans-etherification reaction that occur in the presence of excess of alkaline sample (see Scheme 4).

All copolymers were characterized by NMR (^{1}H and ^{13}C), FTIR, DSC, and MALDI-TOF mass spectrometry. A complete list of their chemical and physical properties is reported in Table 2.

3.2. NMR characterization

The ^{1}H NMR spectroscopy technique proved to be a useful tool to check the composition of the synthesized polymers. By taking advantage of ^{1}H NMR work on model compounds [21,22], we were able to make by comparison the overall proton assignments for our polymers. The chemical shift resonances of PESES and PESESBS homopolymers such as of P(ESES-co-ESESBS) copolymers are reported in Table 3.

The ^{1}H NMR spectra of the synthesized polymers show the same trend in the region 5.0–8.5 ppm and in Fig. 1a–e were reported the enlarged sections of the ^{1}H NMR spectra of the five amine terminated synthesized polymers (**1**)–(**5**), respectively. The figure reports also the assignments of all peaks according to the chemical shift assignments reported in Table 3. In all cases, the spectra were found to be consistent with the expected structures. As an example, the ^{1}H NMR spectrum of the P(ESESBS) homopolymer (**5**) (Fig. 1e) shows the expected pattern of (i) poly(arylen ether sulphone containing biphenylene moieties) *i.e.* three *AA′XX′* systems (five doublets at 8.05, 8.02, 7.98, 7.93 and 7.27 ppm), diagnostic of *p*-disubstituted benzene rings that are easily recognized because of their symmetry and apparent simplicity, (ii) the amine end groups (two double doublets, and a broad singlet in the range 6.41–6.18 ppm and a triplet at 7.04) (iii) two couples of doublets diagnostic of *p*-disubstituted benzene rings at 7.79, 6.90, and at

Table 3
Chemical shifts assignments[i] of the repeat units and of the end groups present in the PESES (**1**) and PESESBS (**5**) homopolymers such as in the P(ESES-co-ESESBS) copolymers (**2**–**4**), as observed in their ^1H NMR spectra.

Protons[j]	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
H^A	7.27 d $J = 7.5$ *100*	7.27 d $J = 8.0$ *100*	7.26 d $J = 8.0$ *100*	7.27 d $J = 7.5$ *100*	7.27 bd *100*
H^B	7.98 d $J = 7.5$ *100*	7.98 d $J = 8.0$ *86.12*	7.98 d $J = 8.0$ 75.0	7.98 d $J = 7.5$ *62.51*	7.98 d $J = 8.0$ *50.20*
$H^{B'}$	–	8.02 bd *12.65*	8.02 bd *25.0*	8.02 bd *37.41*	8.02 bd *49.28*
H^C	–	7.93 bd *16.53*	7.93 bd 30.16	7.93 bd *43.85*	7.93 bd *52.78*
H^D	–	8.04 d $J = 8.0$ *16.72*	8.04 d $J = 8.5$ *30.16*	8.04 d $J = 8.0$ *42.77*	8.05 d $J = 8.5$ *51.76*
H^a	6.25 bs *0.70*	6.25 bs *0.74*	6.24 bs 1.10	6.24 bs *0.81*	6.24 bs *0.88*
H^b	6.18 d $J = 7.5$ *0.67*	6.19 d $J = 7.5$ *0.70*	6.19 d $J = 7.5$ *1.06*	6.18 d $J = 7.5$ *0.88*	6.18 d $J = 7.5$ *1.08*
H^c	7.03t $J = 7.0$ *0.78*	7.04t $J = 7.5$ *0.56*	7.04t $J = 7.5$ *1.19*	7.04t $J = 7.0$ *0.97*	7.04t $J = 7.0$ *0.78*
H^d	6.43 dd $J = 7.5; 1.5$ *0.61*	6.43 dd $J = 8.0; 1.5$ *0.72*	6.42 dd $J = 8.0; 1.5$ *1.23*	6.43 dd $J = 8.0; 1.5$ *0.76*	6.41 dd $J = 8.0; 1.5$ *0.93*
H^e	7.75 d $J = 8.0$ *0.56*	7.76 d $J = 9.0$ *0.76*	7.86m *0.43*	7.83 d $J = 8.5$ *0.65*	7.69m *1.32*
H^f	6.93 d $J = 8.0$ *0.58*	6.92 d $J = 9.0$ *0.62*	6.90m *0.47*	6.94 d $J = 8.0$ *0.67*	6.90 d $J = 8.5$ *1.02*
H^g	7.08 d $J = 7.5$ *0.74*	7.08 d J = 8.0 *1.07*	7.09 d $J = 7.5$ *0.84*	7.09 d $J = 7.5$ *1.50*	7.09 d $J = 7.0$ *0.93*
H^h	7.69 d $J = 7.5$ *0.70*	7.68 d $J = 8.5$ *1.01*	7.69m *0.78*	7.70 d $J = 8.0$ *1.44*	7.62m *0.86*
NH_2	5.33 s *1.33*	5.34 s *1.16*	5.31 s 2.00	5.31 s *1.45*	5.30 s *1.90*

[i] The spectra were obtained in DMSO-d_6, chemical shift in ppm, coupling constant in Hz. Intensity values are reported in italics. Abbreviations used: bs = broad singlet, s = singlet, bd = broad doublet, d = doublet, dd = double doublet, t = triplet, m = multiplet.

[j] Numbering pattern as shown in Scheme 2.

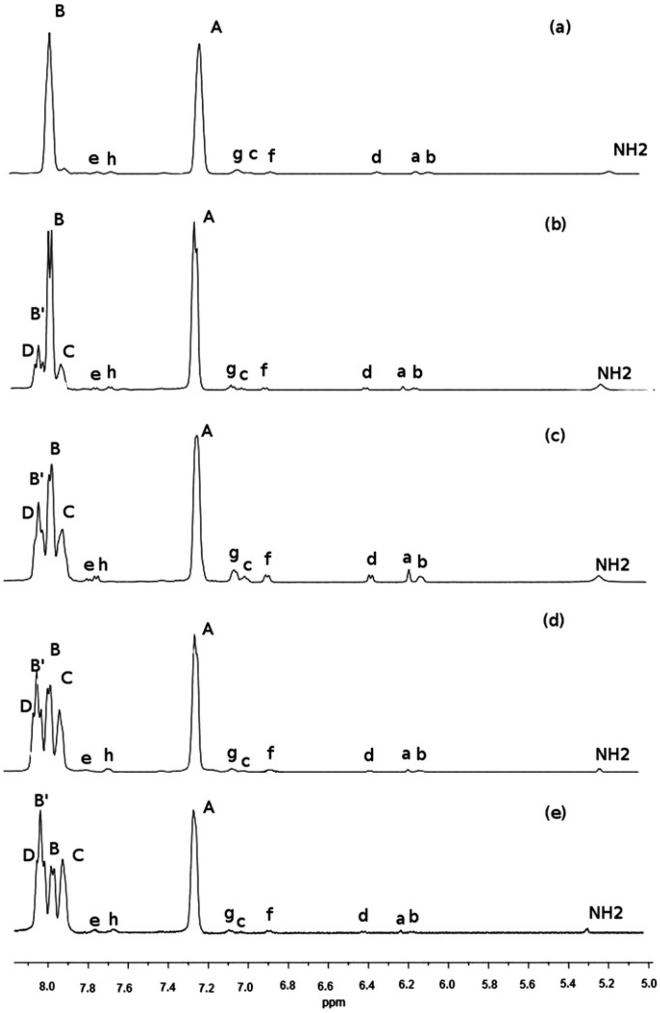


Fig. 1. ^1H NMR Spectra in the region 8.20–5.20 ppm of (a) PESES homopolymer (**1**); (b–d) P(ESES-co-ESESBS) copolymers (**2**–**4**), respectively; and (e) PESESBS homopolymer (**5**).

7.09, 7.69 indicating the presence of hydroxyl and chloro chain ended moieties, respectively.

The presence of chlorine-ended copolymers indicates an incomplete amine-functionalization of the corresponding copolymers. Since all the initial chlorine-ended copolymers present only chlorine end chains, the presence of phenol groups in the corresponding amine terminated samples can be explained assuming that trans-etherification reaction occurs during the amino-functionalization, as well before observed by Maes et al. [22].

Aromatic protons in *ortho* to the ether–oxygen linkage (protons A in Scheme 2) show resonance signals in the range 7.26–7.28 ppm, while those in *ortho* to the sulphone groups (protons H^B in Scheme 2) give resonance signals in the range 7.98–7.99 ppm, because the sulphone group causes a downfield shift.

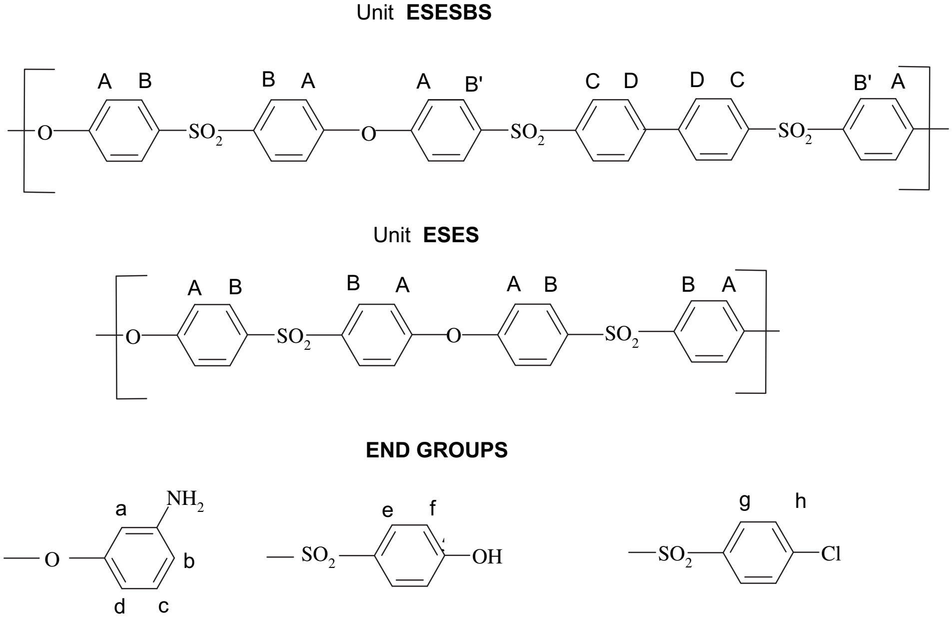
As shown in Table 3 and Fig. 1a, the PESES homopolymer (**1**) do not show any resonance for protons H^C, H^D and $H^{B'}$ that are diagnostic for the presence of biphenylene units while these resonances, as expected, are present in the other synthesized polymers (see Fig. 1b–e). It is worth to note that the presence of the biphenylene moiety produces also the appearance of a new doublet at 8.02 ppm ($H^{B'}$) belonging to B protons linked by a sulphone bridge directly to biphenylene units that, as a consequence, experience a larger downfield effect, moving from 7.98 to 8.02 ppm, of $\Delta\delta = 0.04$ ppm. By looking into Fig. 1a–e it is easy to note also that, by moving from the spectrum of copolymer (**2**) of Fig. 1b to the spectrum of homopolymer (**5**) of Fig. 1e, as expected, the intensity of $H^{B'}$ increase.

The intensity of the signals $H^{B'}$ (referred as $I_{B'}$) reflect the copolymer composition, in fact indicating with C_A and C_B the molar composition of ESES and ESESBS units, respectively, and being $C_A + C_B = 1$ we desumed the following equations:

$$C_B = 2 \cdot I_B \tag{1}$$

$$C_A = 1 - C_B \tag{2}$$

From the relative areas of the ^1H NMR resonance peaks of the aromatic protons H^A, H^B, and $H^{B'}$, assigned to the sequences ESES, and ESESB, respectively (see Table 3), using the Eqs. (1) and (2) we calculated the copolymer compositions of the samples studied, and the results are reported in Table 2. The data, summarized in Table 2, show that in all cases the final polymer composition is close to that of the feed. The number average molar mass (Mn) of PES samples (**1**)–(**5**) were also calculated from the relative integrations of the ^1H NMR resonance peaks of the aromatic H^A (assigned to the sequences ESES, and ESESBS) via comparison with the integrated



Scheme 2.

peaks due to the chain ends, using the equations described elsewhere [21].

As pointed before, also if the Scheme 1 shows two synthetic steps, we used the one pot synthesis methodology in order to minimize the deleterious effect of the trans-etherification side reactions and, as a consequence, to improve the average Mn values of the final amino-ended P(ESES-co-ESESBS) copolymers. To confirm our idea we parallelized, for example, the one pot synthesis of copolymer (**3**) with the old literature method [21], namely by isolating the dichloro-oligomer intermediate (**3a**) and then by reacting it with *m*-aminophenol, to get the amino end capping copolymer (**3b**).

By ^{1}H NMR studies (deuterated DMSO) of (**3a**) and (**3b**), assuming an integration value of 100 for H^A, we got for the protons H^e the integration values of 0.12 and 1.59, while for the protons H^h the integration values were 4.94 and 0.76, respectively. The integration value of proton H^a, present only in the copolymer (**3b**), was 1.87. By using the previous integration values we calculated that, for copolymer (**3a**), the percentages of −OH and −Cl end groups were 2.5 and 97.5, respectively, while for (**3b**) copolymer the new percentages of −OH, −Cl, and amino end groups were 26.0, 12.5, and 61.5, respectively.

Namely, taking into account the residual −OH groups and assuming a theoretical conversion of 100% of the polymer reaction when they are not present, going from the dichloro-oligomer intermediate (**3a**) to the end capping copolymer (**3b**), we note an increase of 23.5 percentage points of the −OH groups or, in other words, a decrease of the conversion from 97.5% (**3a**) to 74.0% (**3b**). Obviously, going from (**3a**) to (**3b**), the significant decrease of the conversion is also reflected on the average M_n values that we calculated at about 17.0 percentage points. Finally, by using the integration data shown in Table 2 it was easy to calculate the percentage of the end groups for each copolymer and, as a consequence, the percentage conversion that, for example, for copolymer (**3**) resulted 87.9%. Therefore by comparing the conversion data of copolymer (**3b**) = 74.0% with respect to copolymer (**3**) = 87.9%, our idea to use the *one pot synthesis methodology* was a winner.

It is important to point out, however, that these spectral data alone afforded little assistance in the structural assignment of the products regarding, especially, the presence of end groups. Since ^{13}C NMR spectroscopy provides a powerful tool for distinguishing between substitution on oxygen and/or on chlorine, we deemed essential the acquisition of the ^{13}C NMR spectra of all the synthesized polymers. The ^{13}C NMR (DMSO-d_6) spectra assignments of synthesized polymers are gathered in Table 4, carbon signals were tentatively assigned by comparison with literature data [21,22].

Fig. 2 reports the ^{13}C NMR spectrum, recorded using the APT technique, of the homopolymer (**1**) showing, as main signals, two quaternary carbons (labeled as 9 and 12) at 159.26 and 136.50 ppm linked to oxygen and sulphone groups, respectively, and two tertiary carbons (labeled as 10 and 11) at 119.80 and 130.04 ppm for the phenyl rings. The small peaks labeled with the numbers 13, 14, 15, 16, 17, 18, 9″ and 10″ (see Table 4 for assignments) are due to the amine chain ends, carbon peaks 19, 20, 21 and 22 were assigned to the hydroxyl chain ends (Table 4), whereas carbon peaks 23, 24, 25, 26, 11″ and 12″ indicate the presence of chlorine chain ends.

From Scheme 3, it is possible to realize that the difference between the ESES and ESESBS moieties is due to the presence in the latter of a biphenylene group in the backbone.

As a consequence, the ^{13}C NMR spectrum of PESESBS homopolymer (**5**) (see Fig. 3), is a quite complex with respect to PESES homopolymer (**1**) (see Fig. 2). As a matter of fact, we noted the appearance of 8 new signals, namely: four signals due to the quaternary carbons 1, 4, 5, and 8, as well as four signals due to tertiary carbons 2, 3, 6, and 7 (see Table 4). The signals 1, 2, 3, and 4 were easily assigned to the carbon atoms of biphenylene moiety while the remaining new four signals (5, 6, 7, 8) belonging to the phenyl rings linked, by a sulphone group, to the biphenylene units experience, as a consequence, mesomeric and/or inductive effects. Namely carbons 5 and 7 (*meta*) experience, with respect to carbons 12 and 10, a upfield shift, while the behavior of carbons 6 and 8 (*ortho* and *para*), with respect to carbons 11 and 9, is oppositive experiencing a downfield effect. As pointed out by Maes et al., the appearance of doublets in the ^{13}C NMR is diagnostic of trans-etherification side reactions [22] (see Scheme 4).

All peaks present in the ^{13}C NMR spectra of P(ESES-ESESBS) copolymers (**2**)–(**4**) have assigned also by matching with those of the homopolymers (**1**) and (**5**) reported in Figs. 2 and 3, respectively.

Table 4
Chemical shifts assignments[a] of the repeat units and of the end groups present in the PESES (**1**) and PESESBS (**5**) homopolymers such as in the P(ESES-ESESBS) copolymers (**2**–**4**), as observed in their ^{13}C NMR spectra.

Carbons[b]	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
C_1	–	143.06	143.072	143.06	143.06
C_2	–	127.94	127.95	127.93	127.95
C_3	–	128.53	128.54	128.52	128.53
C_4	–	140.93	140.94	140.93	140.94
C_5	–	136.18	136.18	136.20	136.21
				136.17	136.18
C_6	–	130.20	130.21	130.19	130.21
C_7	–	119.78	119.80	119.79	119.80
C_8	–	159.34	159.41	159.40	159.41
				159.36	159.36
C_9	159.26	159.24	159.25	159.24	159.24
			159.21	159.20	159.20
C_{10}	119,80	119.85	119.85	119.84	119.85
C_{11}	130.04	130.03	130.04	130.03	130.03
C_{12}	136.50	136.50	136.51	136.50	136.53
C_{13}	155.23	155.41	155.24	153.66	155.22
C_{14}	104.88	104.90	104.90	104.89	104.90
C_{15}	150.77	150.67	150.75	150.70	150.75
C_{16}	110.71	110.72	110.72	110.72	110.72
C_{17}	129.83	129.83	129.83	129.88	129.84
C_{18}	106.73	106.57	106.76	106.77	106.77
$C_{9''}$	161.73	161.70	161.72	161.41	161.72
$C_{10''}$	117.63	117.63	117.64	117.62	117.66
C_{19}	134.20	134.44	134.22	134.23	134.21
C_{20}	129.65	129.72	129.68	129.72	129.71
C_{21}	116.33	116.28	116.15	116.32	116.55
C_{22}	162.33	162.41	161.86	161.83	161.85
C_{23}	138.70	138.70	138.71	138.76	138.78
C_{24}	129.77	129.52	129.33	129.32	129.36
C_{25}	129.41	129.45	129.52	129.48	129.33
C_{26}	137.00	137.69	137.96	137.69	137.79
$C_{11''}$	128.14	127.70	127.76	128.07	127.94
$C_{12''}$	139.90	140.11	139.90	140.15	140.39

[a] The spectra were obtained in DMSO-d_6, chemical shift in ppm.
[b] Numbering pattern as shown in Scheme 3.

3.3. MALDI-TOF mass spectrometry

The chemical composition and the end groups of the PES samples (**1**)–(**5**) and of the corresponding chlorine-ended-prepolymer were also characterized by MALDI-TOF MS [22–25]. MALDI spectra confirm the NMR data indicating that all essentially amino-ended samples (**1**)–(**5**) have a heterogeneous distribution in end groups.

As an example, in Fig. 4 is shown the MALDI-TOF mass spectrum of a chlorine-ended P(ESES-ESESBS) copolymer with a molar composition 50/50, taken before the end capping with *m*-amino phenol. The mass spectrum shows a series of mass-resolved peaks from 1000 up to 9000 Da, and very similar mass spectra were recorded for all intermediate homo and copolymers samples, essentially terminated chlorine groups. The pertinent mass assignments of the homologous families of peaks are reported in Table 5. According to the synthesis procedure, in the spectrum of the Cl-ended P(ESES-ESESBS) copolymer (50/50) are present intense peaks due to the co-oligomers terminated with chlorine atoms at both side of the chains (species $A_{m,n}$, $B_{m,n}$ and $B'_{m,n}$ in Table 5 and in Fig. 4).

However, looking the inset in Fig. 4 that reports a section of the spectrum in the region 2950–3560 Da, we can observe the presence of other series of peaks belonging both to the copolymer chains terminated with chlorine and phenol groups (species $C_{m,n}$ in Table 5 and in Fig. 4) and to the copolymers terminated with phenol groups at both ends (species $D_{m,n}$ in Table 5 and in Fig. 4).

Low intense peaks due to cyclic co-oligomers were also observed in the mass region 1000–2500 Da. Applying the composition estimate model and using the intensities of the peaks corresponding to the trimers, tetramers, pentamers, examers and eptamers co-oligomers, and assuming a random distributions of the ESES and ESESBS units, we have calculated a ESES/ESESBS molar composition of 52/48, that is in accord with the molar ratio of the monomers LCDC and DCDPS (see Scheme 1 and Table 2) in the feed [21].

All MALDI mass spectra of the P(ESES- ESESBS) copolymers analyzed appear very complex owing to the presence of mass series bearing different end groups and showing a lot of peaks in the mass regions 800–7000 Da as shown in Fig. 5a–c where is reported an enlarged sections of the mass spectra of the copolymers (**2**), (**3**), and (**4**), respectively. Intense peaks belonging to the copolymer chains terminated with amine and phenol groups (species G, G′ and G″ in Table 5) and peaks corresponding to the co-oligomers terminated with amine and diphenlsulphone groups were also observed (species G″ in Table 5). The presence of diphenyl sulphone ends was also observed in the mass spectra of the corresponding chlorine-

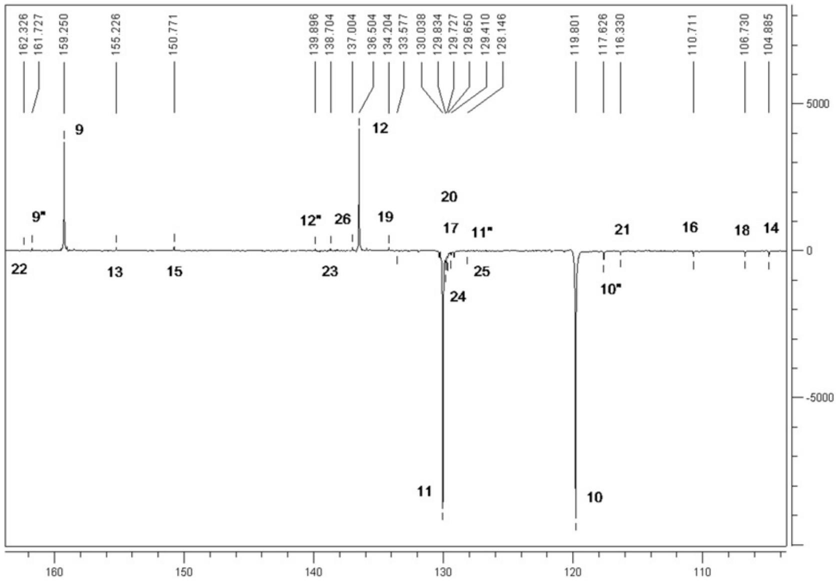
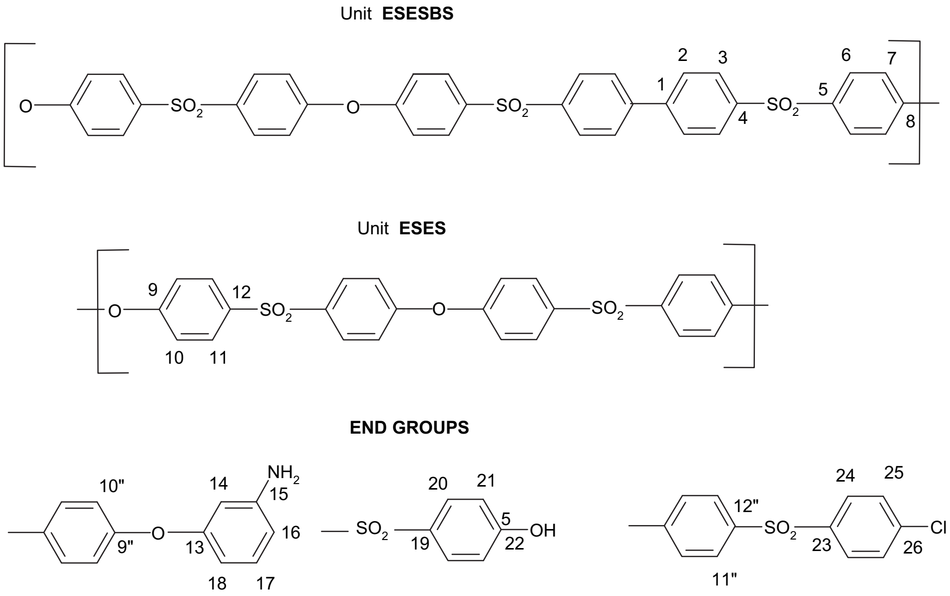


Fig. 2. ^{13}C NMR Spectrum in the region 104.0–164.0 ppm of homopolymer (**1**).



Scheme 3.

ended copolymers. The species G″ may be formed by reaction of chlorine-ended chains with 4-hydroxy diphenylsulphone present as impurity in the used 4-4′ hydroxy diphenylsulphone monomer. Peaks belonging to the co-oligomers terminated with *m*-aminophenol at one side and chlorine at the other side (species F, F′ and F″ in Table 5), were also observed in the mass spectra of the copolymers (**3**) and (**4**), indicating the incomplete capping of *p*-chlorophenyl ends in these copolymers. These results also suggest that the end capping nucleophilic reaction with *m*-AP occur with a less kinetic as increasing the molar amount of ESESBS units in the copolymers, and therefore raises the probability that they are terminated with chlorine atoms belonging to the LCDC units. This behavior was also confirmed by analyzing the MALDI spectra of homopolymers P(ESES) (**1**) and P(ESESBS) (**5**), the latter showing more peaks corresponding to macromolecular species terminated with *m*-aminophenol at one side and chlorine at the other side (species F in Table 5).

The mass spectrum of the copolymer (**3**) also (Fig. 5b) shows peaks due to the co-oligomers terminated with amine groups at both ends (species E in Table 5), and peaks belonging to the co-oligomers terminated with phenol groups at both side (species D and D′ in Table 5), which arise during the capping of chlorine-ended copolymers with *m*-aminophenol according to nucleophilic substitution reaction of hydroxyl ions with chlorine end chains (Route A) and/or by trans-etherification reaction (Route B) as shown in Scheme 4.

However, as discussed before for Cl-ended pre-copolymer (50/50), the molar composition of the copolymer (**2**), (**3**), and (**4**) was calculated from their mass spectra by making use of the intensities

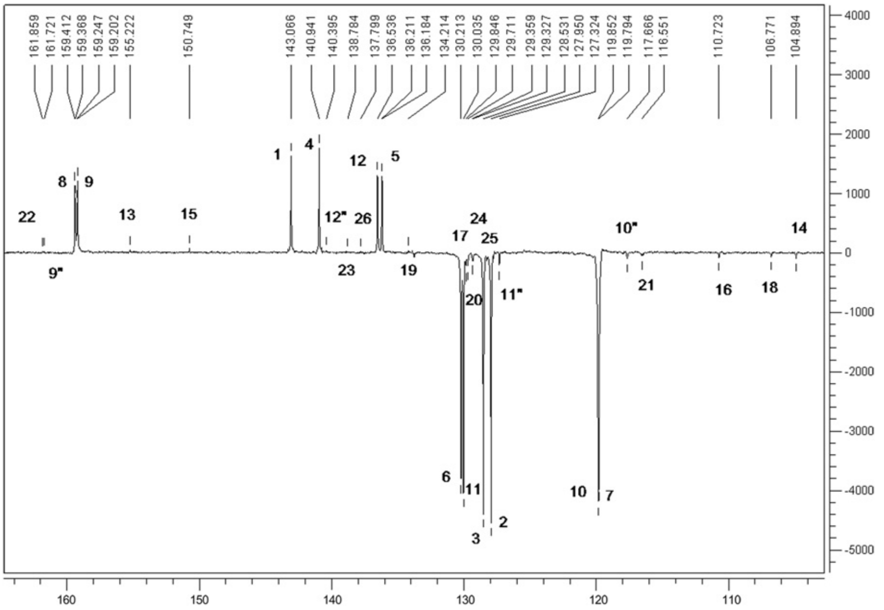
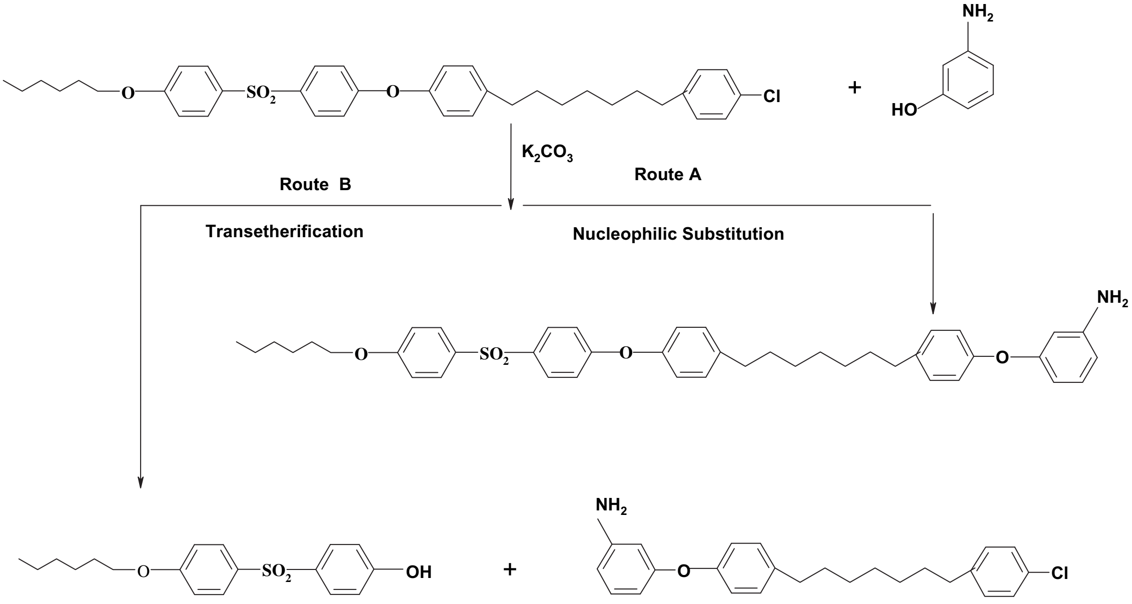


Fig. 3. ^{13}C NMR Spectrum in the region 104.0–164.0 ppm of homopolymer (**5**).



Scheme 4.

of peaks corresponding to the tetramers, pentamers, examers, eptamers, octamers and nonamers co-oligomers according to literature data [21]. The calculated values are summarized in Table 2, and as can be observed they are in accord with those determined from ^{1}H NMR spectra.

3.4. FTIR characterization

The FTIR spectra of the synthesized compounds show common features. As an example, Fig. 6 show the FTIR spectrum of the copolymer (**3**) that is characterized, by (i) prominent aromatic C–H and C–C ring stretching bands at 3100–2900 and at 1586–1460 cm^{-1} , respectively; (ii) two bands at 1394 and 1145 cm^{-1} associated to the asymmetric and symmetric SO$_2$ stretching, respectively; (iii) a band at 1323–1303 diagnostic for the presence of biphenylene moieties due to central –C–C– stretching mode; (iv) bands ranging between 1261 and 1147 cm^{-1} associated to the ether C–O–C moiety, (iv) well resolved absorption bands at lower frequencies, which can be ascribed to the in-plane and out-of-plane ring deformation. As a matter of fact are also present bands that are diagnostic for the presence of the chain-ended groups, *i.e:* (i) three bands at 3407, 3295 and 1585 cm^{-1} associated at asymmetrical, symmetrical, and bending N–H moiety, respectively; (ii) C–Cl stretching bands at 1087–1070 cm^{-1} and (iii) a band at 3360 cm^{-1} associated to the phenolic OH stretching.

3.5. DSC analysis

The thermal properties of all polymer samples (**1**)–(**5**) were also characterized by DSC, and the glass transition temperatures (Tg)

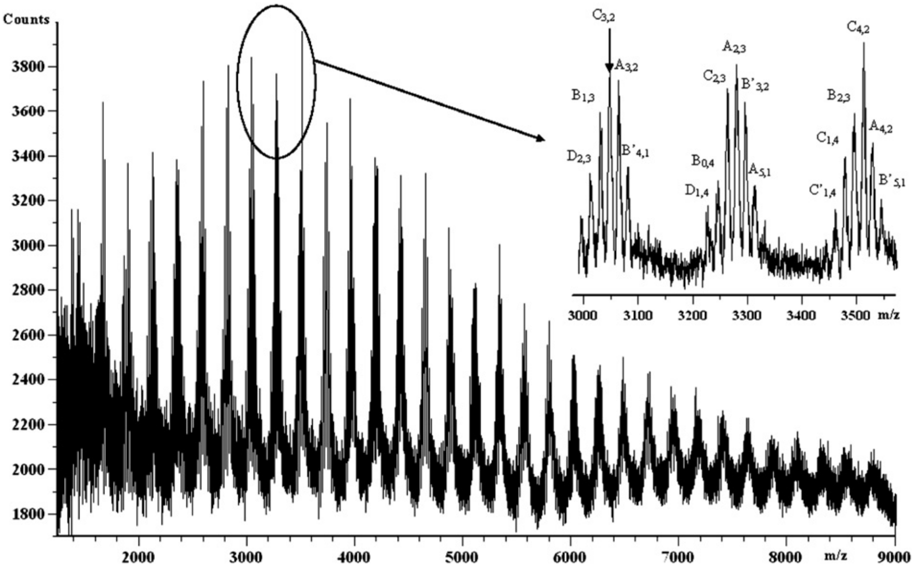


Fig. 4. MALDI-TOF mass spectrum of the intermediate chloro-ended copolymer (**3**) (50/50). The inst shows a section of the spectrum.

Table 5
Structural assignments of peaks displayed in the MALDI-TOF mass spectra of PES samples (**1**–**5**) shown in Figs. 4 and 5

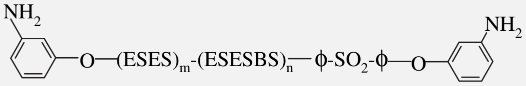
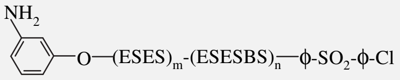
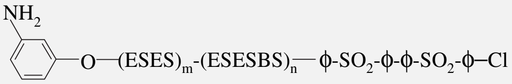
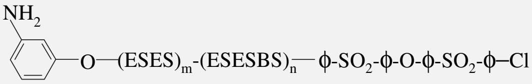
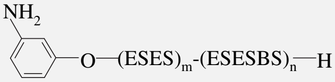
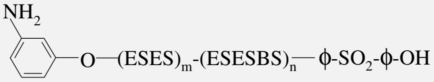
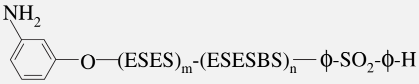
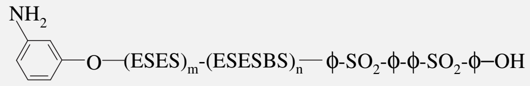
Species	Structures[a]	m, n	$[\mathrm{M} + \mathrm{Na}^+]$[b]
$\mathrm{A}_{m,n}$	Cl–(ESES)$_m$–(ESESBS)$_n$–φ–SO$_2$–φ–Cl $M_{\mathrm{A}m,n} = m\ 464.4 + n\ 580.6 + 286.2$	3, 2	3063.4
		2, 3	3279.5
		5, 1	3311.7
		4, 2	3527.8
$\mathrm{B}_{m,n}$	Cl–(ESES)$_m$–(ESESBS)$_n$–φ–SO$_2$–φ–φ–SO$_2$–φ–Cl $M_{\mathrm{B}m,n} = m\ 464.4 + n\ 580.6 + 502.4$	1, 3	3031.3
		0, 4	3247.4
		3, 2	3279.6
		2, 3	3495.7
$\mathrm{B}'_{m,n}$	Cl–(ESES)$_m$–(ESESBS)$_n$–φ–SO$_2$–φ–O–φ–SO$_2$–φ–Cl $M_{\mathrm{B}'m,n} = m\ + n\ 580.6 + 518.4$	1, 3	3047.3
		4, 1	3079.5
		6, 0	3095.6
		0, 4	3263.4
		3, 2	3295.6
		5, 1	3543.9
$\mathrm{C}_{m,n}$	Cl–(ESES)$_m$–(ESESBS)$_n$–φ–SO$_2$–φ–OH $M_{\mathrm{C}m,n} = m\ 464.4 + n\ 580.6 + 268.2$	2, 3	3261.5
		3, 2	3045.4
		1, 4	3477.6
		4, 2	3509.8
$\mathrm{C}'_{m,n}$	Cl–(ESES)$_m$–(ESESBS)$_n$–φ–SO$_2$–φ–H $M_{\mathrm{C}'m,n} = m\ 464.4 + n\ 580.6 + 252.2$	1, 4	3461.6
$\mathrm{D}_{m,n}$	HO–(ESES)$_m$–(ESESBS)$_n$–H $M_{\mathrm{D}m,n} = m\ 464.4 + n\ 580.6 + 18$	1, 4	3227.4
		2, 3	3011.3
		3, 3	3475.7
$\mathrm{D}'_{m,n}$	HO–(ESES)$_m$–(ESESBS)$_n$–φ–SO$_2$–φ–OH $M_{\mathrm{D}'m,n} = m\ 464.4 + n\ 580.6 + 250.2$	1, 4	3443.5
		2, 3	3243.5
		4, 2	3491.8
$\mathrm{E}_{m,n}$	 $M_{\mathrm{E}m,n} = m\ 464.4 + n\ 580.6 + 432.4$	3, 2	3209.6
		2, 3	3425.7
		5, 1	3457.9
$\mathrm{F}_{m,n}$	 $M_{\mathrm{F}m,n} = m\ 464.4 + n\ 580.6 + 359.3$	3, 2	3136.5
		2, 3	3352.6
		5, 1	3384.8
		1, 4	3568.7
		4, 2	3600.9
$\mathrm{F}'_{m,n}$	 $M_{\mathrm{F}'m,n} = m\ 464.4 + n\ 580.6 + 575.4$	2, 2	2888.2
		1, 3	3104.3
		4, 1	3136.5
		3, 2	3352.6
$\mathrm{F}'_{m,n}$	 $M_{\mathrm{F}'m,n} = m\ 464.4 + n\ 580.6 + 591.4$	2, 2	2904.2
		4, 1	3152.8
		3, 2	3368.6
		2, 3	3584.7
		5, 1	3616.9
$\mathrm{G}_{m,n}$	 $M_{\mathrm{G}m,n} = m\ 464.4 + n\ 580.6 + 109$	1, 4	3318.4
$\mathrm{G}'_{m,n}$	 $M_{\mathrm{G}'m,n} = m\ 464.4 + n\ 580.6 + 341.2$	1, 3	2870.1
		0, 4	3086.2
		3, 2	3118.4
		2, 3	3334.5
		5, 1	3366.7
		1, 4	3550.6
		4, 2	3582.8
$\mathrm{G}'_{m,n}$	 $M_{\mathrm{G}'m,n} = m\ 464.4 + n\ 580.6 + 325.2$	1, 3	2854.1
		2, 2	3070.2
		3, 2	3102.4
		2, 3	3318.5
		5, 1	3350.7
		1, 4	3534.6
		4, 2	3566.8

Table 5 (*continued*)

Species	Structures[a]	m, n	$[M+Na^+]$[b]
$G''_{m,n}$	 $M_{G''m,n} = m\ 464.4 + n\ 580.6 + 557.4$	0, 4	3302.4

[a] For each structure is also reported the respective pertinent equation to calculate the corresponding molecular mass (*M*), considering that the molar mass of ESES and ESESBS repetitive units are 464.4 and 580.6 Da, respectively.

[b] The mass accuracy was better than $\Delta m = \pm 0.4$ Da.

determined are reported in Table 2. As expected on the base of the glass transition temperatures (Tg) of the homopolymers P(ESES) and P(ESESBS) (see Table 2), the Tg of the random copolymers (**2**), (**3**) and (**4**) increase as increasing the molar amount of ESESBS units in the chains. This is due to the increased rigidity of the chains with increasing amount of diphenylene sulphone units along the chains. Fig. 7 reports the experimental and calculated Tg values vs. the molar composition of ESESBS units (C_B) calculated by MALDI-TOF MS analysis. It shows that for synthesized P(ESES-co-ESESBS)s copolymers experimental Tg values fit very well with those calculated using the Fox Eq. (3), valid for random copolymer [26].

$$1/\mathrm{Tg}_{AB} = (W_A/\mathrm{Tg}_A + W_B/\mathrm{Tg}_B) \tag{3}$$

where Tg_A and Tg_B indicate the glass transition of the two homopolymers P(ESES) and P(ESESBS), respectively. The weight % of components ESES and ESESBS units (A and B, respectively) in each copolymer, have been calculated using the corresponding molar composition calculated from their MALDI spectra, and respective

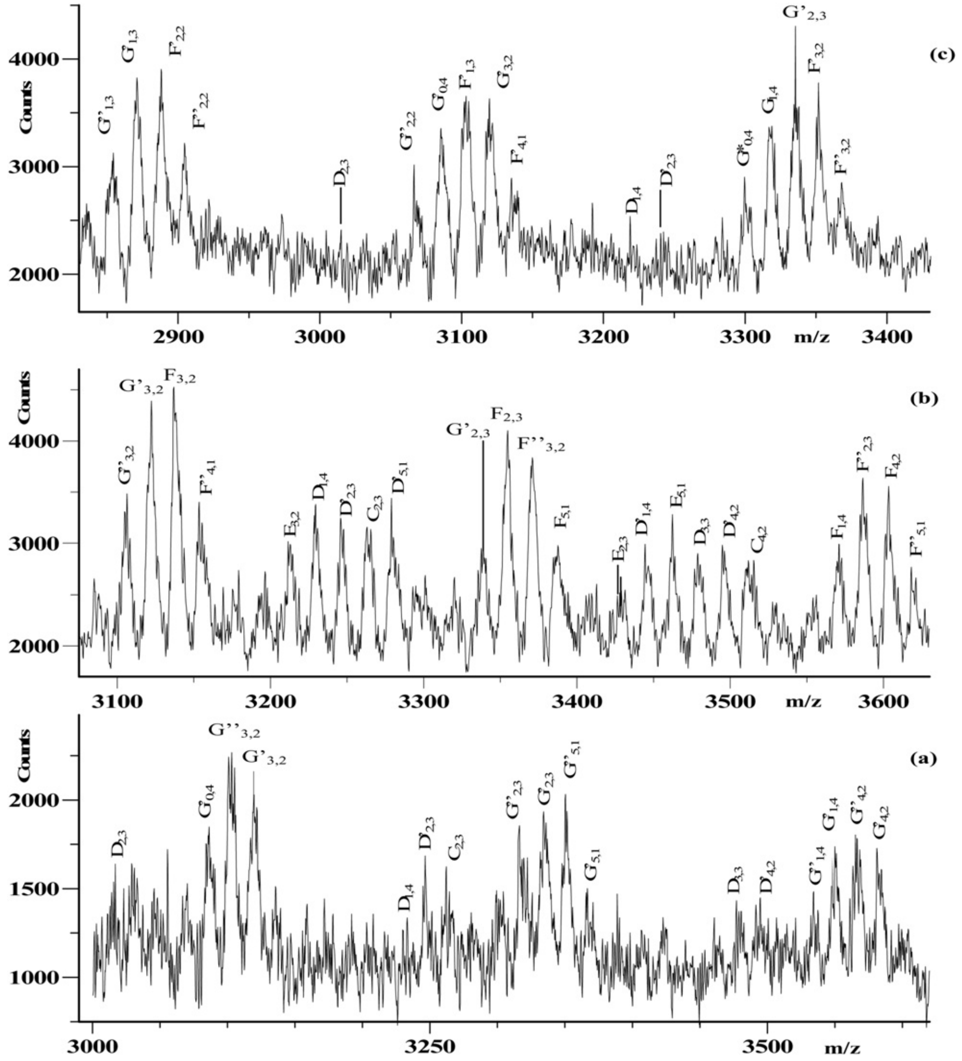


Fig. 5. Enlarged section of the MALDI-TOF mass spectra of the copolymer **2** (a), **3** (b) and **4** (c), mentioned in Table 1.

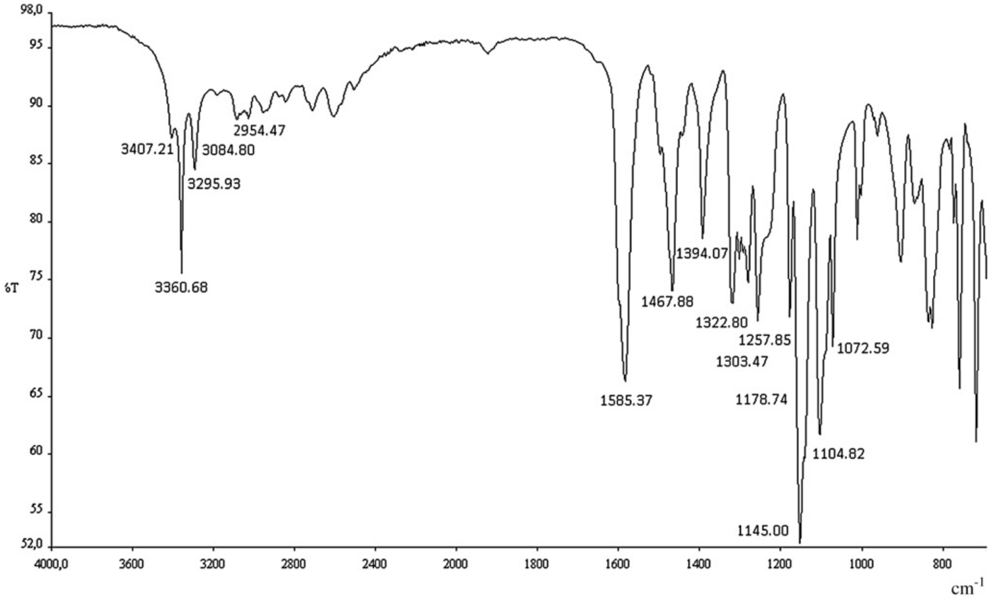


Fig. 6. FTIR spectrum of the P(ESES co ESESBS) copolymer (**3**).

repetitive mass units (464.4 Da and 580.5 Da for ESES and ESESBS units, respectively).

Tg values for the copolymers (**2**)–(**4**) were also calculated by Fox equations using the molar composition calculated by ^{1}H NMR analysis, and the results are summarized in Table 2. Tg data in Table 2 and Fig. 7, confirm the reliability of copolymers' molar compositions calculated by MALDI-MS method. Thermal stability of polymers (**1**)–(**5**) will be published in the future.

3.6. *Viscosity*

Intrinsic viscosities of samples were measured in order to obtain any relationship between the hydrodynamic volumes of these macromolecules and percentage of biphenyl groups in the chains. Being the viscosity a function of molar mass, terminal groups, and rigidity of the chains; the fact that intrinsic viscosity values are very similar for each sample show that chain rigidity don't influence solution behavior of this class of polymers and confirm the values of average molecular mass calculated.

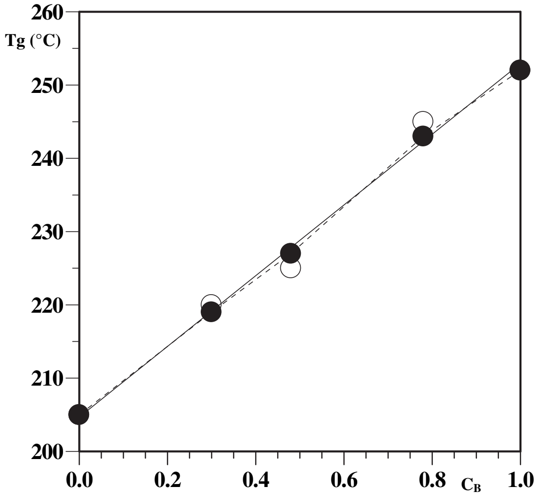


Fig. 7. Experimental (●) and calculated (○) Tg values of PES samples (**1**–**5**), vs. the molar composition of ESESBS unit (C_B) obtained by MALDI-TOF MS analysis.

4. Conclusions

The NMR, MALDI-TOF, and FTIR analyses such as viscosity data provide positive evidence that we have successfully synthesized copoly(aryl-ethersulphones) as P(ESES-co-ESESBS) copolymers such as hypothesized in the pre-synthesis calculations. From the study about the intensities of the signals corresponding to a unit in the chain and end groups has been possible to calculate average values of various samples of M_n and the values fall within a range that goes from 8500 to 9500 atomic mass units. All the above techniques have also enabled the confirmation of the structure and composition of the polymers synthesized such as have confirmed the presence of different chain ends. The study of the thermograms obtained by DSC instead highlights an increasing trend of Tg values for the percentage of biphenylene units in the chain confirming the contribution in the conformational stability conferred by the LCDC monomer on the polymeric system structure. As mentioned in Section 1, one objective of these syntheses is the use of this new/high Tg polyether sulphone as an additive for advanced epoxy matrices. But it is worth to note that, till now, preliminary data show that copolymers with more than 75% of biphenyl units in the chain exhibit low miscibility in some epoxy matrix tested.

Acknowledgments

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