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Combined MALDI–TOF MS and NMR characterization of copoly(arylen ether sulphone)s

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Abstract

The synthesis and the chemical characterization of some novel random copolyethersulphones of the type P(ESES-co-EES) (Polyethersulphone-ethersulphone:Polyetherethersulphone), is reported. The ESES:EES molar ratio was varied from 80:20 to 20:80 and all the copolymers were terminated with reactive amino groups, and then were fully characterized through (^{1}H and ^{13}C)-NMR and MALDI–TOF MS analysis to confirm their chemical structures and chemical compositions. End chains were revealed by these techniques. Contrary to chlorine-ended copolymers, oligomers terminated with hydroxyl groups were revealed in the amine-ended copolymers, indicating that transetherification reactions occur during the capping reaction with *m*-aminophenol. Cycles were also revealed by MALDI–TOF MS, that revealed also some unexpected end chains may be formed for the impurities in the feed. The glass transition temperatures of the copolymers have been determined by differential scanning calorimetry (DSC).

Keywords: Copolysulphones; MALDI; NMR

1. Introduction

Polyethersulphones (PES's) are a useful engineering polymers which have found wide application as adhesives for metal-to-metal bonds [1], membranes for separating gases and solids from solution [2], matrices for fiber reinforced composite and as toughening agents for thermosetting resins [3]. The key properties of these thermoplastics are their thermal stability, good mechanical properties and easy processability in the melt state or in solution. The latter property is of particular interest for composite processing because, being the polymer solvent soluble, it can be easily prepregged from low cost solvents.

Previous researches were focused on the systematic study of the synthesis and the thermal stability of some aromatic thermoplastics containing ether, ketone and sulphone groups [4–10]. In particular it was showed [4] that the substitution of the ketone group with the sulphone group lead to an increase of the apparent activation energy and of the glass transition temperature. The introduction of an ether group lead to a decrease of the apparent activation energy and of the glass transition temperature. The effect of the copolymer's end groups and of the molecular weight on the thermomechanical properties of some epoxy blends, were also studied [10]. The end groups showed to have a profound effect on the fracture resistance of the blends and on the rheological and morphological behavior. In particular the amine groups were proved to give the highest increases of toughness and to avoid the cure reaction delay which, instead, was observed with hydroxyl and chlorine groups [10].

It has been reported [11] that the chemical structure of the toughening agent, as for liquid rubbers, can influence the phase separation phenomena and therefore the mechanical performances of the blends. However, there are not detailed studies on the effect of thermoplastic copolymer structure on the thermomechanical properties of epoxy blends.

The aim of present paper is to report a study on the synthesis and the chemical characterization of a series of some random copolyethersulphones. The copolymers were synthesized with a PES/PEES molar ratio varying from 80:20 to 20:80 with step increases of 10 of the PEES content and with similar molecular weights. All the copolymers were functionalized with reactive

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amine end groups so that they could be used as toughening agents for epoxy blends. These copolymers can thus be useful to investigate the effect of copolymer structure on the blend properties.

All the polymers were characterized through NMR (^{1}H and ^{13}C) and MALDI–TOF mass spectrometry (MALDI–TOF MS) analysis to ensure that the macromolecular chain had the expected composition from stoichiometric calculation. The molar composition of the copolymers were calculated applying the appropriate statistical model at the NMR and MALDI–TOF MS spectra. The copolymers were also characterized through differential scanning calorimetry (DSC) to asses their glass transition temperatures.

2. Experimental

2.1. Materials

4,4′-dichlorodiphenylsulphone (DCDPS) (98% of purity grade), dihydroxydiphenylsulphone (DHDPS) (98% of purity grade) hydroquinone (HQ) (99% of purity grade), 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. Syntheses

2.2.1. Chlorine-ended copolymer synthesis

Chlorine-ended copolymers with different molar composition in ESES (ether sulphone ether sulphone, referred as A) and EES (ether ether sulphone, referred as B) units were synthesized via nucleophilic condensation of DCDPS with DHDPS and HQ, as reported in Scheme 1. The molar ratio of DHDPS and HQ monomers was varied in order to prepare copolymer samples with different molar composition.

A typical example of solution polymerization of a chlorine ended copolymer is as follows: to a 250 ml three-neck flask, equipped with an overhead stirrer and a nitrogen inlet were added DCDPS (6.5 g, 2.2×10^{-2} mol), DHDPS (2.17 g, 8.7×10^{-3} mol), HQ (1.43 g, 1.3×10^{-2} mol), in 25 ml of sulfolane. 3.22 g (2.33×10^{-2}—3% excess) of potassium carbonate were then added to the mixture and the temperature increased to 180 °C under a nitrogen flow. The mixture was allowed to react for 30 min at this temperature, for one hour at 205 °C and for 4 h at 225 °C.

The solution obtained was then precipitated in methanol. The product was washed several times with water and with methanol and finally dried under vacuum at 80 °C overnight.

According to such Scheme 1 the repeats units of the copolymers formed are of ESES (A) and EES (B) type, thus, in the following, we will refer to the copoly(aryl-ethersulphones) as P(ESES-co-EES) copolymers. However it has to be noted that such kind of copolymers are named also, for commercial purposes, as PES/PEES or PES (see for example RADEL A100 from Solvay) [12].

In Table 1 are reported the molar ratios of the HQ/DHDPS monomers in the feed and the code of the synthetised copolymers.

2.2.2. Amine ended copolymer synthesis

Chlorine-ended copolymers were end capped by nucleophilic reaction with *m*-aminophenol (Scheme 2) at 205 °C using sulfolane as a solvent.

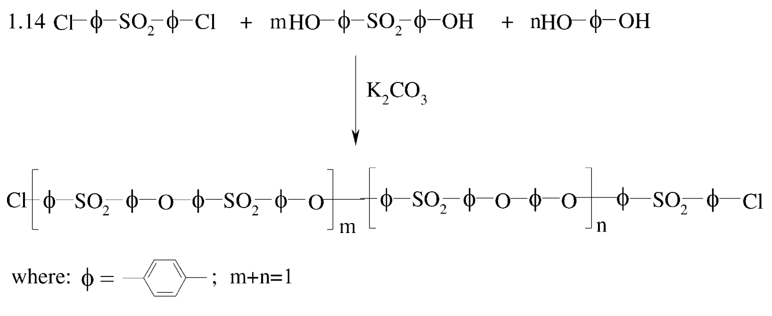
In a typical procedure, 0.12 g of *m*-aminophenol (1.10×10^{-3} mol) and 0.15 g potassium carbonate (1.14×10^{-3} mol) were added to a stirred solution of 5 g of a chlorine-ended copolymer in 12 ml of sulfolane. The solution was then allowed to stir for one hour at 205 °C and precipitated in methanol and washed several times with water and methanol. The product was dried in a vacuum oven at 80 °C overnight.

2.3. Measurements

2.3.1. NMR spectroscopy

^{1}H NMR spectra were recorded using a Brucker 200 MHz. The samples were dissolved in d^6-DMSO without any internal standard at 60 °C. 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. Similar results were obtained when spectra were recorded with a Varian 500 MHz at room temperature and also at 50 °C.

^{13}C NMR spectra were obtained at 50 MHz with a Bruker A-CF 200 spectrometer at 35 °C, using deuterated DMSO at 60 °C, and a polymer concentration of about 30 mg/ml.



Scheme 1. Polymerization reaction.

Table 1
Molar ratios of the DCDPS, HQ and DHDPS monomers in the feed of the copolymers synthesised

Sample code	Molar feed ratio		
	DCDPS	HQ	DHDPS
RLS72	1.14	0.8	0.2
RLS63	1.14	0.7	0.3
RLS79	1.14	0.6	0.4
RLS83	1.14	0.5	0.5
RLS78	1.14	0.5	0.5
RLS85	1.14	0.4	0.6
RLS86	1.14	0.3	0.7
RLS88	1.14	0.2	0.8
RLS80	1.14	0.6	0.4

The acquisition parameters were optimized in order to obtain for similar carbon types present similar relaxation rates, and therefore reliable quantification of ^{13}C NMR is possible. 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.

The chemical shift resonances were accurately assigned to the specific proton and carbon atoms, using the data reported in literature [13–15]. In particular the signals due the chain ends were assigned according to the chemical shifts assignments published by Maes et al. [13].

2.3.2. MALDI–TOF mass spectrometry

The 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, 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 prepared as follows. 10 μl of polymer solution (3–4 mg/ml in $CHCl_3$), were mixed with 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 better MALDI mass spectra were obtained in reflectron mode.

2.3.3. DSC (differential scanning calorimetry)

The glass transition (T_g) temperatures were determined by a Mettler DSC 20 calorimeter coupled with a Mettler TC 10A processor as control and evaluation unit. Both heat flow and temperature calibrations of calorimeter were performed following the procedures suggested by the supplier and reported in the operating instructions of the equipment. The reported T_g values were taken at the midpoint of the glass transition in all DSC thermograms. Samples of about 6.0×10^{-2} g, held in sealed aluminium crucibles, the scanning rate of 10 °C·min^{-1} and a static air atmosphere were used for determinations.

Pertinent data were reported in Table 4.

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. Measures values are reported in Table 4.

2.3.5. NMR calculations

Experimental number average molar mass ($\bar{M}_n$) of each copolymer was calculated from integrated area of the peaks due to chain ends via comparison with peaks due aromatic protons in ortho position to the ether-oxygen groups in the backbone (protons I_f, I_g and I_h in Table 2), using the following Eqs. (1–5).

$$C_A = \frac{I_f + 1/2I_g}{(I_f + I_g + I_h)} \tag{1}$$

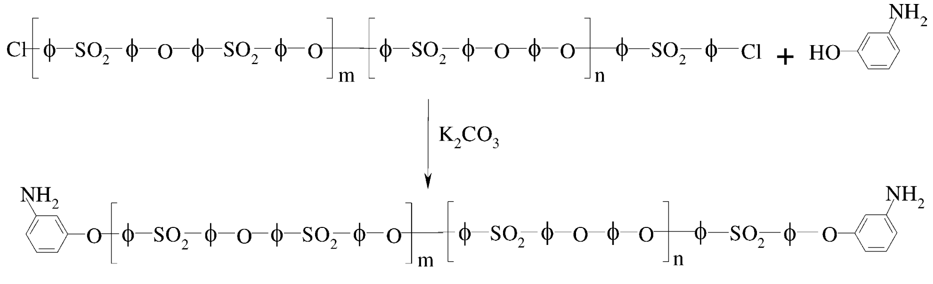
$$C_B = \frac{I_h + 1/2I_g}{(I_f + I_g + I_h)} \tag{2}$$

$$C_A + C_B = 1 \tag{3}$$

$$\bar{X}_{AB} = \frac{(I_h + I_g + I_h)/8}{(I_q + I_l)/4} \tag{4}$$

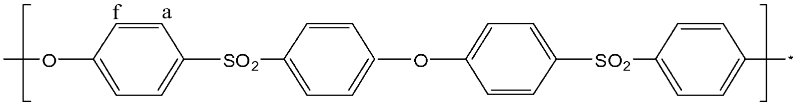
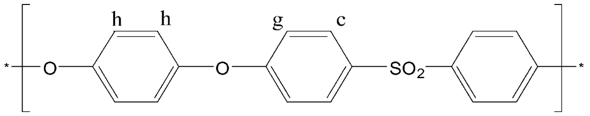
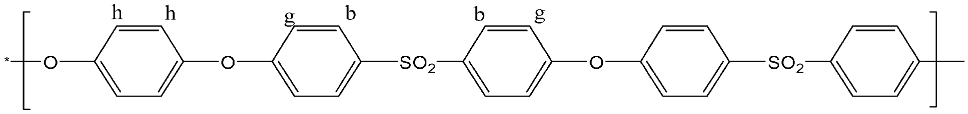
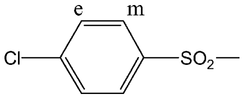
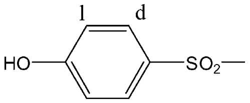
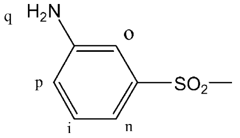
$$\bar{M}n = \bar{X}_{AB}(C_A M_A + C_B M_B) \tag{5}$$

where C_A and C_B indicate the molar composition of ESES (A) and EES (B) units, respectively; $\bar{X}_{AB}$ the degree average of



Scheme 2. End capping.

Table 2
Assignments of the repeat units and of the end groups present in the P(ESES-co-EES) copolymers, as observed in their ^{1}H-NMR spectra

Structures	Proton	Chemical shift (ppm)
	a f	7.99 7.24–7.28
	c g	7.91 7.13
	b h	7.94 7.19
	e m	7.68 6.59
	d l	7.79 7.05
	i n o p q	7.08 6.43 6.27 6.21 5.16

polymerization of the copolymer, whereas I_q and I_l indicate the intensity of the protons of the amine terminal groups and of the aromatic protons in ortho with respect to the HO–phenol terminal chains (see Table 2 for their assignments). M_A and M_B are the molecular mass of the ESES (464.5 Da) and of the EES (324.3 Da) repeat units.

The molar composition, the sequence distribution, the average sequence length of the AA (<A–A>) and BB (<B–B>) dyads, and the degree of randomness (β) of the P(ESES-co-EES) copolymers were calculated from ^{13}C NMR spectra applying an appropriate statistical model that we have developed (Eqs. (6–9)). The intensities (I) of the quaternary carbons linked the oxygen of the ether groups (Carbons marked as: 1, 18, 7 and 11, in Table 3), and belonging to the sequences ESES, EESES. EES and EESES, respectively, were used.

$$C_A = \frac{(I_1 + I_{18})}{I_{TOT}}; \qquad C_B = \frac{(I_7 + I_{11})}{I_{TOT}} \tag{6}$$

$$F_{AA} = \frac{I_1}{I_{TOT}}; \qquad F_{AB} = \frac{I_{18}}{I_{TOT}}; \qquad F_{BA} = \frac{I_{11}}{I_{TOT}}; \qquad F_{BB} = \frac{I_7}{I_{TOT}} \tag{7}$$

$$<A-A> = \frac{C_A}{F_{AB}}; \qquad <B-B> = \frac{C_B}{F_{BA}} \tag{8}$$

$$\beta = \frac{F_{AB}}{C_A} + \frac{F_{BA}}{C_B} \tag{9}$$

where $I_{TOT} = I_1 + I_{18} + I_7 + I_{11}$

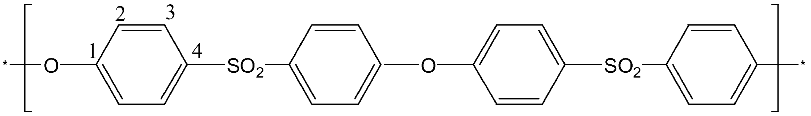
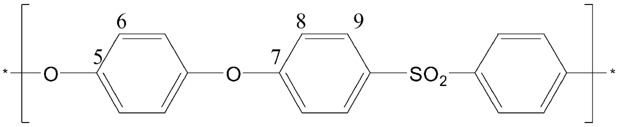
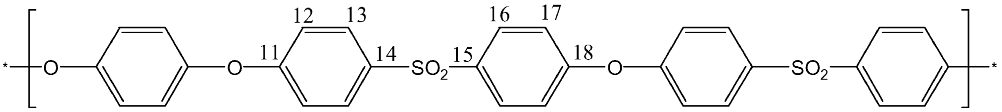
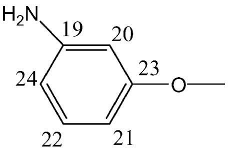
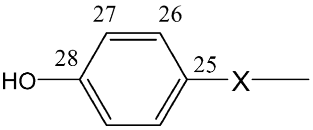
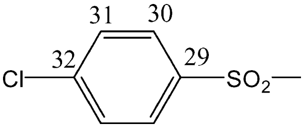
In these equations, CA and CB indicate the molar concentration of the component A (ESES) and of the component B (EES), respectively, in the copolyarylenesulphones; F_{AA}, F_{AB}, F_{BA} and F_{BB} indicate the molar fractions of the AA, AB, BA and BB dyads, respectively; I_1, I_7, I_{11} and I_{18} indicate the intensity of their corresponding quaternary carbon peaks in the ^{13}C NMR spectra.

2.3.6. MALDI calculation

MALDI is, a soft ionization techniques and was demonstrated that did not cleave the polymeric chains, so that only preformed oligomers are essentially desorbed and detected in MALDI analysis [16–18]. The structure of the co-oligomers thus detected therefore reflects the co-monomer distributions along the copolymer chains, and this assumption formed the basis for the calculation of the molar composition by MALDI analysis. Since, the peak displayed by the mass spectra of copolymers contain direct information about the relative abundance of comonomers, a copolymer composition estimate can be directly extracted from the analysis of the mass spectra without making any hypothesis on the distribution of the comonomers units along the copolymer chains [19,20]. In the case of a two component copolymer AB, as well the P(ESES-co-EES) samples here studied, it is possible to make an estimate of the copolymer composition (C_A and C_B) from a knowledge of the x-mer peak intensities $I_{A_mB_n}$, where $m+n=x$, using the formulas (10)–(12).

$$C_A + C_B = 1 \tag{10}$$

Table 3
Assignments of the repeat units present in the P(ESES-co-EES) copolymer, as observed in their ^{13}C NMR spectra

Structure	Carbon	Chemical shift (ppm)
	1	159.20
	2	119.63
	3	129.86
	4	136.59
	5	151.25
	6	117.69
	7	161.22
	8	121.88
	9	129.57
	10	135.30
	11	161.34
	12	121.88
	13	129.72
	14	134.98
	15	136.92
	16	129.72
	17	119.63
	18	159.06
	19	150.56
	20	104.90
	21	106.71
	22	130.34
	23	155.30
	24	110.78
 $X = (SO_2, O)$	25	134.40
	26	129.45
	27	105.80
	28	162.12
	29	130.29
	30	129.77
	31	116.11
	32	162.10

$$C_x^{\mathrm{A}} = \frac{1}{x\theta_x}\left\{\sum_{m=0}^{x} m[\delta_{x,n+m} I_{\mathrm{A}m\mathrm{B}n}]\right\} \tag{11}$$

where θ_x is the sum of x-mer intensities and δ is the Kronecker symbol defined by $\delta_{ij}=1$ if $i=j$ and $\delta_{ij}=0$ if $i\neq j$; i.e. explicating the Eq. (11) for a two component copolymer and for $x=5$ we obtain:

$$C_5^{\mathrm{A}} = \frac{1}{5}\,\frac{[(5I_{\mathrm{A}_5} + 4I_{\mathrm{A}_4\mathrm{B}_4} + 3I_{\mathrm{A}_3\mathrm{B}_2} + 2I_{\mathrm{A}_2\mathrm{B}_3} + I_{\mathrm{AB}_4})]}{[(I_{\mathrm{A}_5} + I_{\mathrm{A}_4\mathrm{B}_4} + I_{\mathrm{A}_3\mathrm{B}_2} + I_{\mathrm{A}_2\mathrm{B}_3} + I_{\mathrm{AB}_4} + I_{\mathrm{B}_5})]} \tag{12}$$

Eqs. (11) and (12) implies that each oligomer groups (i.e. tetramers, pentamers, examers, eptamers, etc.) provides an independent estimate of the copolymer composition. The molar compositions of the P(ESES-co-EES) copolymers reported in Table 1 were calculated using the MALDI-MS intensities of

Table 4
Molar composition, average numeric molar mass of the series of synthesised amine capped PESES/PEES copolymers calculated from ^{1}H NMR and MALDI spectra and the corresponding T_g values obtained from DSC

Sample code	Copolymer composition			$\bar{M}_n$ (^{1}H-NMR)	η_{inh} (dL/g)	T_g (°C)
	^{1}H NMR	^{13}C NMR	MALDI			
RLS72	26/74	24/76	26/74	8000	0.23	180.00
RLS63	33/67	32/68	32/68	8300	0.25	187.20
RLS79	44/56	44/56	44/56	10000	0.30	196.00
RLS83	54/46	53/47	53/47	5000	0.20	202.00
RLS78	54/46	55/45	52/48	9000	0.28	202.00
RLS85	60/40	60/40	58/42	9000	0.28	206.00
RLS86	68/32	68/32	67/33	8800	0.28	210.00
RLS88	75/25	77/23	73/28	8200	0.24	214.75

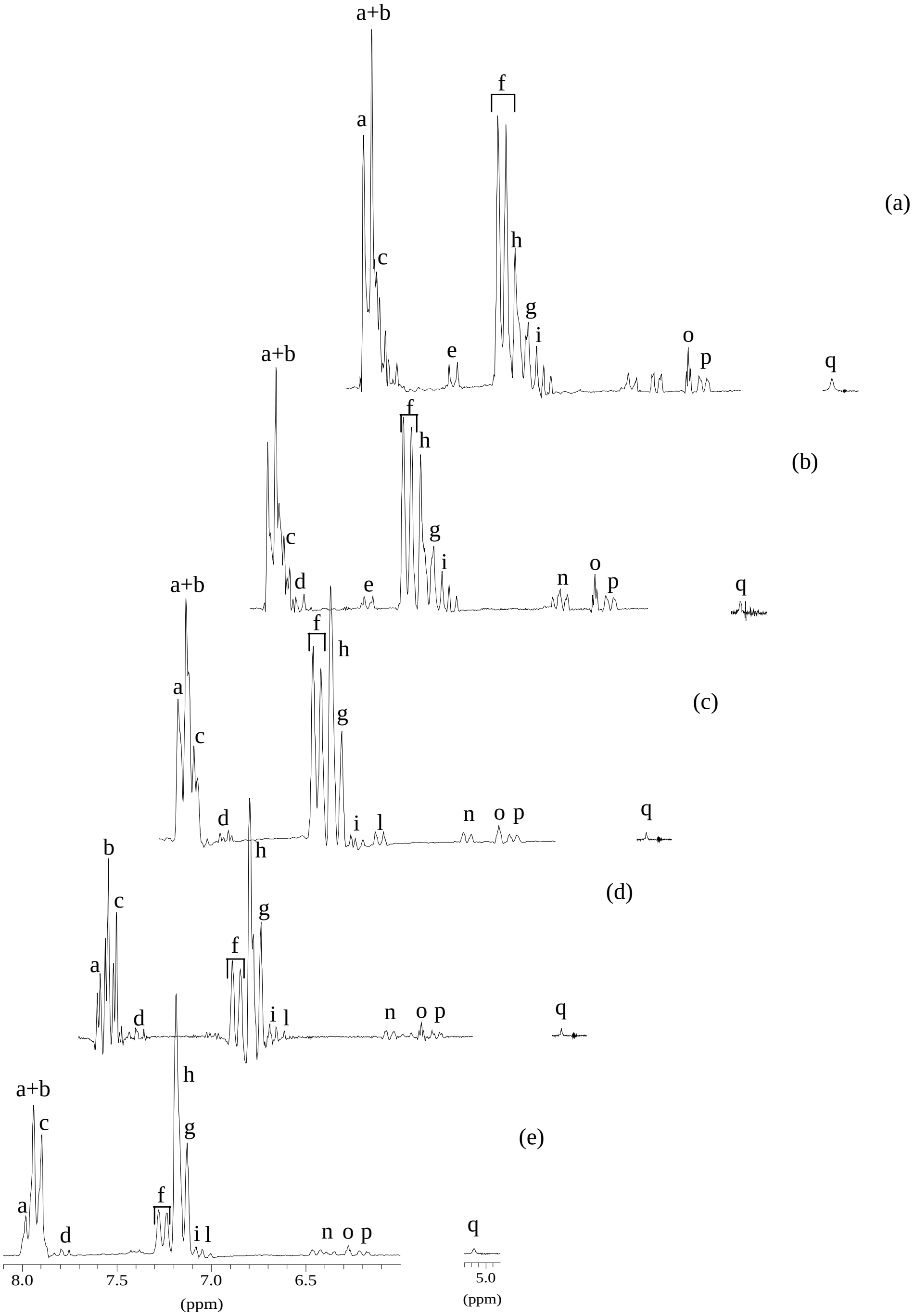
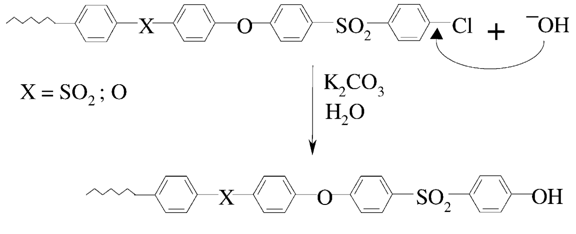


Fig. 1. ^{1}H NMR spectra in the region 8,1–4,9 ppm of the PESES-PEES copolymers: (a) RLS88, (b) RLS86, (c) RLS83, (d) RLS63 and (e) RLS 72.

the peaks belonging to the pentamers, examers, eptamers, octamers and nonamers, and the calculated average values are reported in Table 4.

The molar composition of the copolymers from MALDI spectra can be also calculated using the chain statistic model and assuming an a appropriate distribution model (i.e. Bernoullian or Markoffian) of the repetitive units along the copolymer chains. By the chain statistical one has the possibility to build a theoretical mass spectrum for any given copolymer sequence and for different molar composition of the



Scheme 3.

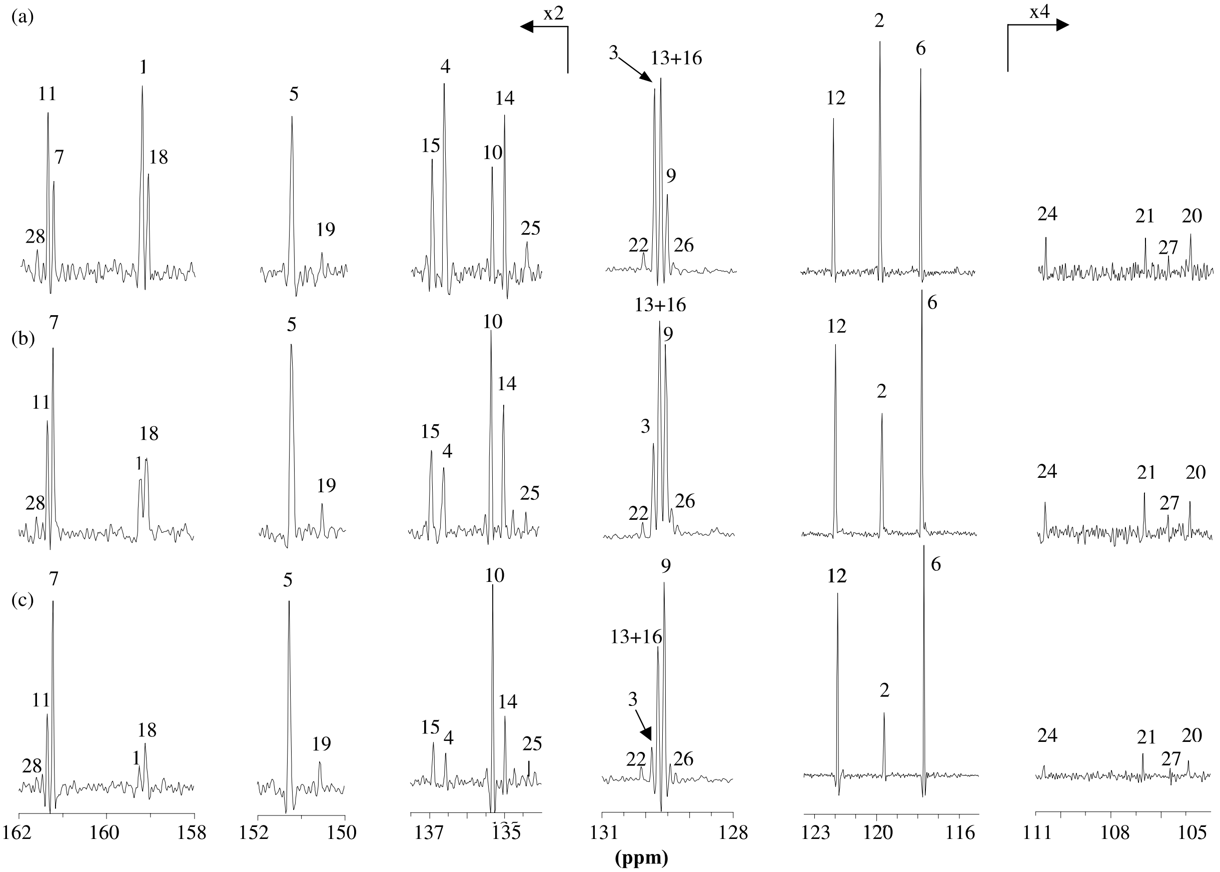


Fig. 2. ^{13}C NMR spectra of the P(ESES-co-EES) copolymers: (a) RLS83, (b) RLS63 and (c) RLS 72.

components. Fitting the experimental mass spectra with those theoretically calculated, the composition of the copolymer investigated can be determined [16,19,20]. In the present work the copolymer composition was determined applying the Bernoullian model, which describe a random distribution of monomer units, and calculating the intensity of the mass peaks due to A_mB_n co-oligomers by well-known Newton formula (Eq. (13)) [18]:

$$I_{A_mB_n} = [(m+n)!m!n!](C_A)^m(C_B)^n \tag{13}$$

3. Results and discussion

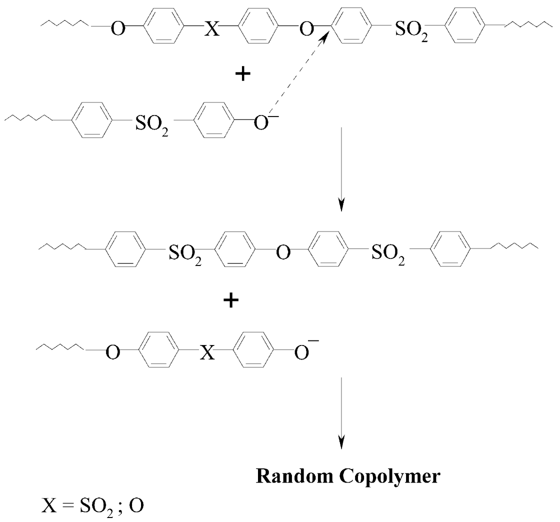
A series of amine- terminated P(ESES-co-EES) copolymers with different molar composition in ESES and EES units, and with very similar average molar masses (Table 4), were synthesized and characterized by means of NMR (^{1}H and ^{13}C) MALDI–TOF MS and DSC methods. These copolymers were prepared by end functionalization of the corresponding chlorine- terminated copolymers (Scheme 2). The latter were synthesized by nucleophilic condensation polymerization of dichlorodiphenyl sulphone with diphenols (DHDPS and HQ),

Table 5
Copolymer composition, molar fraction of dyads, average sequence lengths (<A–A> and <B–B>, and degree of randomness (β) of the P(ESES-co-EES) copolymers, calculated from their ^{13}C NMR spectra, using Eqs. (6)–(9)

Code	Copolymer composition C_A/C_B[a]	Molar fractions				Average sequence lengths		β
		F_{AA}	F_{AB}	F_{BA}	F_{BB}	<A–A>	<B–B>	
RLS72	24/76	0.09	0.15	0.23	0.53	1.6	3.4	0.94
RLS63	32/68	0.14	0.18	0.26	0.42	1.8	2.6	0.95
RLS79	44/56	0.25	0.19	0.30	0.26	2.3	1.9	0.96
RLS83	53/47	0.34	0.19	0.29	0.18	2.8	1.6	0.98
RLS78	55/45	0.32	0.23	0.26	0.19	2.4	1.7	0.99
RLS85	60/40	0.42	0.18	0.25	0.15	3.3	1.6	0.93
RLS86	68/32	0.51	0.17	0.21	0.11	4.1	1.5	0.92
RLS88	77/23	0.62	0.15	0.16	0.06	5.2	1.4	0.92
RLS80[b]	43/57	0.31	0.12	0.21	0.36	3.6	2.7	0.65

[a] A indicates the ESES units whereas B indicates the EES units in the copolyarylenesulphones.

[b] Chlorine ended copolymer.



Scheme 4.

as depicted in Scheme 1. The molar ratio of DHDPS and HQ monomers was varied to prepare the chlorine- terminated copolymers which were then functionalized according to Scheme 2.

3.1. NMR characterization

A complete NMR characterization was made on the samples studied and the chemical shift resonances were accurately assigned to the specific protons and carbons, according to the published data obtained using appropriate model compounds [13–15]. The specific assignments of protons and carbon atoms present in the P(ESES-co-EES) copolymers analysed are reported in Tables 2 and 3, respectively.

Fig. 1 reports the ^{1}H NMR spectra of five P(ESES-co-EES) copolymers with different molar composition: namely RLS88, RLS86, RLS83, RLS73 and RLS72 in Table 1. The figure reports also the assignments of all peaks according to the chemical shifts assignments reported in Table 2. In all cases, the spectra were found to be consistent with the expected structure. Aromatic protons in ortho to the ether-oxygen linkage (protons f, h, and g in Table 2) show resonance signals in the range 7.0–7.3 ppm, while those in ortho to the sulphone groups (protons a, b and c in Table 2) give resonance signals in the range 7.8–8.1 ppm, because the sulphone group causes a downfield shift.

From the relative areas of the ^{1}H NMR resonance peaks of the aromatic protons f, h, and g in Fig. 1, assigned to the sequences EESES, EES and EESES, respectively (see Table 2), using the Eqs. (1)–(3) described in Section 2 were calculated the copolymer compositions of the sample studied, and the results are reported in Table 4. The resonance peak of the aromatic protons fin the ESES sequences (Table 2) is constituted by a doublet in the range 7.24–7.28 ppm, whereas the aromatic protons h in the EES sequences (Table 2) is constituted by a large singlet at 7.19 as well as the protons g at 7.13 ppm due to the EESES sequences (Table 2) in the copolymers. The data, summarized in Table 4, show that in all cases the final polymer composition is close to that of the feed (Table 1). The end-chains of all copolymers, as reported in Fig. 1, were also characterized by ^{1}H NMR analysis, and their chemical shifts are reported in Table 2. In Fig. 1, peaks q, p, o, n, i that resonate at 5.16, 6.21, 6.27, 6.43 and 7.08 ppm

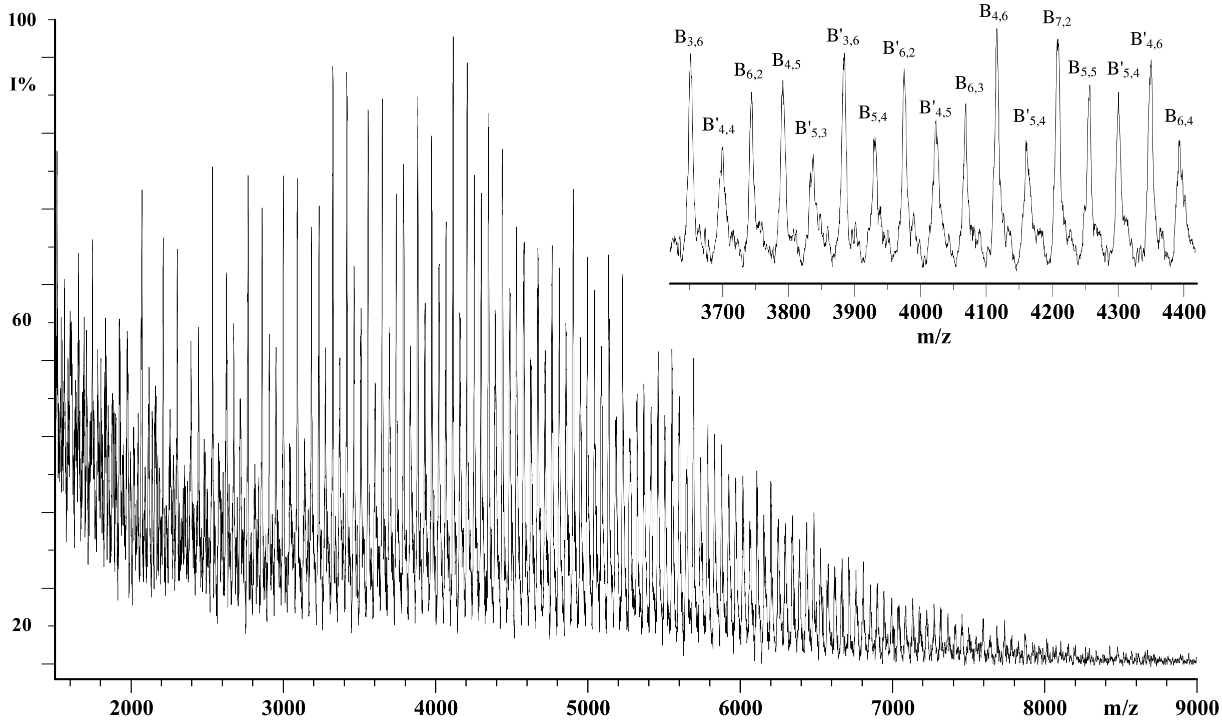


Fig. 3. MALDI–TOF MS spectrum of the chlorine-ended copolymer RLS80.

(Table 2) were assigned to the expected m-amino phenol end-chains, whereas peaks at 7.79 and 7.05 ppm were assigned to the aromatic protons d and l, respectively, belonging to the phenol end-chains (Table 2). In the case of the RLS88 (Fig. 1a) and RLS86 (Fig. 1b) samples, two unexpected doublet peaks at 7.68 (protons e) and at 6.59 ppm (protons m) due to the protons in ortho and in meta to the chlorine ends were also observed. This indicate an incomplete amine-functionalization of the corresponding chlorine-ended 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 transetherification reaction occurs during the amino-functionalization at 205 °C, as well before observed Maes et al [13]. However the mechanism of this supposed transetherification process has not been demonstrated [13]. We believe that, owing to the trace of the water present in the *m*-aminophenol sample, the hydroxyl ions give a nucleophylic substitution of chlorine ends leading to the formation of P(ESES-co-EES) chains terminated with phenol groups (Scheme 3).

From ^{1}H-NMR spectra the $\bar{X}n$ and the $\bar{M}_n$ were also calculated applying the Eqs. (4)–(5), using the integrate of peaks due to the amine at 5,16 (protons q) and those at 7,05 ppm due to the protons in ortho with respect to OH-phenols end groups (protons 1), and those of peaks in the range 7.1–7.3 ppm corresponding to the aromatic protons in ortho with respect to the ether-oxygen linkage (protons f, g and h in Table 2 and in Fig. 1). The calculated values reported in Table 4, indicate that all copolymers have a similar $\bar{M}_n$ (8000–10000 Da).

The end groups detected by ^{1}H-NMR of all the P(ESES-co-EES) samples, were also confirmed by ^{13}C-NMR analysis. Fig. 2 reports the ^{13}C-NMR spectra of three copolymers: RLS83, RLS63 and RLS72, respectively. In Fig. 2, the small peaks labelled with the numbers 19, 20, 21, 22 and 24 (see Table 3 for assignments) are due to the amino-phenol end-chains, whereas carbon peaks 25, 26, 27 and 28 were assigned to the phenol ends (Table 3). In the case of the chlorine-terminated copolymers were observed only the carbon resonance signals due to the p-chloro phenyl sulphone ends (carbons 29, 30, 31 and 32 in Table 3).

The ^{13}C-NMR spectra in Fig. 2 show relevant changes in the relative intensity of the four signals due to the quaternary carbons 11, 7, 1, 18 (Table 3) linked with to the ether-oxygen, which resonate in the range 161–159 ppm, as well the quaternary carbons linked to the sulphone group (carbons 15, 4, 10, 14 in Table 3) which give four carbon peaks in the range 134.5–139 ppm. In fact, at higher percentages of ESES units, the quaternary carbons in ortho position to the ether group (signal at 159.2 ppm) shows an increase in the intensity, while at higher percentages of EES units the peak at 161.2 ppm due to the quaternary carbon next to the ether group in these units increase its intensity. Fig. 2 reports the ^{13}C NMR spectra of all the copolymers studied. The good resolution of the peaks has permitted their assignments to the arylene ether sulphone sequences present along the copolymers chains. In fact, carbon signals 1 and 4 were unequivocally assigned to the homo-sequences ESES, those labelled 7 and 10 were assigned to the homo-sequences ESES, those labelled 7 and 10 were assigned at the homo-sequences EES and finally the carbon signals 11, 14, 15 and 18 were assigned to the co-sequences EESES (Table 3). The tertiary carbons in ortho to the sulphone groups (carbons 3, 13, 16, 9 in Table 3) give three resolved peaks in the range 129.5–129.9 ppm. The signals at 129.57 ppm were assigned to the carbon 9 of the EES sequences, those at 129.72 ppm were assigned to the carbons 13 and 16 of the EESES sequences, and those at 129.86 ppm were assigned to the carbons 3 of the ESES sequences. From the ^{13}C-NMR spectra emerge that the tertiary and quaternary carbon resonance signals of the P(ESES-co-EES) copolymers are sensitive to changes in the sequence distribution, and that the relative intensities of the corresponding resonance signals change as a function of the ESES/EES molar ratio in the copolymers.

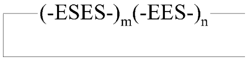
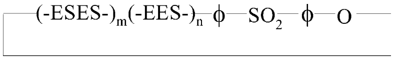
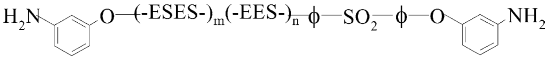
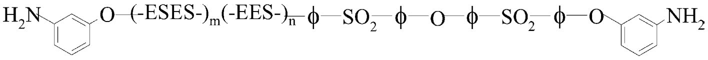
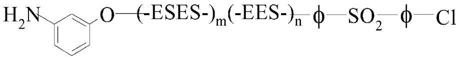
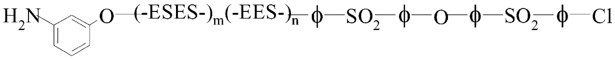
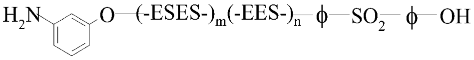
It is well known that the final properties of the copolymers depend on their composition and on the block or random or alternate distribution of the sequences in the copolymer chains. Information on the molar composition, the molar sequence distribution of dyads (AA, AB, BA and BB), the number-average sequence lengths of AA and BB dyads, and the degree of randomness of the P(ESES-co-EES) copolymers studied, were obtained from their ^{13}C NMR spectra. These copolymer parameters have been calculated applying the Eqs. (6–9) (see Section 2), using the relative intensities of the aromatic quaternary carbon linked with the ether-oxygen (peaks 1, 11 and 18 in Fig. 2 and in Table 3), which resonate in the range 159–161.5 ppm. The results are reported in Table 5. Very similar results were obtained using the intensity of the aromatic quaternary carbons linked with the sulphone groups (peaks 4, 10, 14 and 15 in Fig. 2 and in Table 3), which appear well resolved in the carbon spectra of all copolymers.

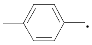
Looking the data in Tables 4 and 5, is evident that the molar compositions determined by ^{13}C NMR data are close to those calculated by ^{1}H-NMR, and that the distribution of the dyads is random for the all amine-ended copolymers. In fact, these copolymers have a degree of randomness values (β) near to 1, contrary to the corresponding chlorine terminated copolymers with the same molar composition which have an β values around 0.6–0.7, as well the RLS80 sample reported in Table 5. The last data indicate that segmented copolymers were obtained in the syntheses of chlorine-terminated samples, and that their amine-functionalization reaction leads to essentially random copolymers owing to the *trans*-etherification reactions (Scheme 4) which occur at the temperature used (205 °C).

3.2. MALDI characterization

In order to obtain detailed information about the chemical structure of the P(ESES-co-EES) copolymers, we have also recorded their MALDI–TOF mass spectra, that is able to look at the mass of individual molecules in a mixture of homologues permitting thus the structural identification of the single macromolecules. In literature is published that MALDI–TOF MS technique provides mass-resolved spectra up to 50–70 kDa, allowing to the identification of the repeat units,

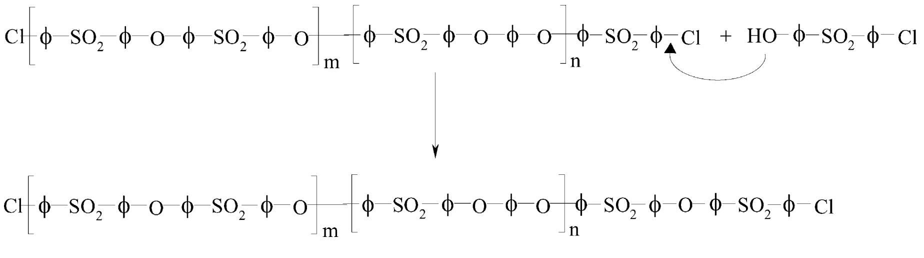
Table 6
Structural assignments of peaks displayed in the MALDI–TOF mass spectra of the P(ESES-co-EES) copolymers reported in Figs. 3–6

Species	Structures[a]	$[M+Na]^+$ (m,n)
$A_{m,n}$		1644.5 (0,5); 1784.7 (1,4); 1924.9 (2,3); 2065.1 (3,2); 2109 (1,5); 2249.2 (2,4); 2389.4 (3,3); 2433.3 (1,6); 2573.5 (2,5)
$A'_{m,n}$		1692.6 (1,3); 1832.8 (2,2); 1973 (3,1); 1876.7 (0,5); 2016.9 (1,4); 2157.1 (2,3) 2297.3 (3,2); 2201 (0,6); 2341.2 (1,5); 2481.4 (2,4); 2621.6 (3,3); 2761.8 (4,2); 2665.5 (1,6)
$B_{m,n}$	$Cl-(\text{-ESES-})_m(\text{-EES-})_n-\phi-SO_2-\phi-Cl$	1747.5 (1,3); 1887.7 (2,2); 2027.9 (3,1); 1931.6 (0,5); 2071.8 (1,4); 2212 (2,3); 2352.2 (3,2); 2492.4 (4,1); 2396.1 (1,5); 3649.4 (3,6); 3745.7 (6,2); 3789.6 (4,5); 3929.8 (5,4); 4070 (6,3); 4210.2 (7,2); 4254.1 (5,5); 4394.3 (6,4); 4114 (4,6)
$B'_{m,n}$	$Cl-(\text{-ESES-})_m(\text{-EES-})_n-\phi-SO_2-\phi-O-\phi-SO_2-\phi-Cl$	1655.4 (1,2); 1839.5 (0,4); 1979.7 (1,3); 2120 (2,2); 2260 (3,1); 2163.8 (0,5); 2304 (1,4); 24.44 (2,3); 3697.5 (4,4); 3837.7 (5,3); 3978 (6,2); 3881.6 (3,6); 4021.8 (4,5); 4162 (5,4); 4302.2 (6,3); 4346 (4,6)
$C_{m,n}$	$Cl-(\text{-ESES-})_m(\text{-EES-})_n-H$	1917.5 (4,0); 1961.4 (2,3); 2101.6 (3,2); 2241.8 (4,1); 2382 (5.0); 2145.5 (1,5); 2285.7 (2,4); 2426 (3,3); 2566 (4,2); 2706.3 (5,1); 2750.3 (3,4)
$C'_{m,n}$	$Cl-(\text{-ESES-})_m(\text{-EES-})_n-\phi-SO_2-\phi-OH$	1729.1 (1,3); 1869.3 (2,2); 2009.5 (3,1); 2149.7 (4,0); 2053.4 (1,4); 2193.6 (2,3); 2474 (4,1); 2614.2 (5,0); 2377.7 (1,5); 2518 (2,4); 2798.3 (4,2);
$D_{m,n}$	$HO-(\text{-ESES-})_m(\text{-EES-})_n-H$	1758.8 (3,1); 1802.7 (1,4); 1942.9 (2,3); 2083.1 (3,2); 2223.3 (4,1); 2127 (1,5); 2267.2 (2,4); 2407.4 (3,3); 2547.6 (4,2); 2687.8 (5,1)
$D'_{m,n}$	$HO-(\text{-ESES-})_m(\text{-EES-})_n-\phi-SO_2-\phi-OH$	1710.6 (1,3); 1991 (3,1); 2315.3 1 (3,2)
$E_{m,n}$		1893.1 (1,3); 2217.4 (1,4); 2357.6 (2,3); 2682 (2,4); 2822 (1,5)
$E'_{m,n}$		1801 (1,2); 1941 (2,1); 2125.2 (1,3); 2265.4 (2,2); 2405.6 (3,1); 2309.3 (0,5); 2449.5 (1,4); 2589.7 (2,3); 2730 (3,2); 2773.8 (1,5)
$F_{m,n}$		1820.2 (1,3); 2144.5 (1,4); 2284.7 (2,3); 2425 (3,2); 2565 (4,1); 2468.8 (1,5); 2609 (2,4); 2749.2 (3,3)
$F'_{m,n}$		1868.3 (2,1); 2192.6 (2,2); 1912.2 (0,4); 2332.8 (3,1); 2376.7 (1,4); 2517 (2,3); 2701 (1,5)
$G_{m,n}$		1709.7 (2,2); 1850 (3,1); 2034 (2,3); 2174.2 (3,2); 2314.4 (4,1); 2454.6 (5,0); 2358.3 (2,4); 2498.5 (3,3); 2638.7 (4,2); 2779 (5,1)
$G'_{m,n}$		1801.7 (1,3); 1942 (2,2); 2082 (3,1); 2222,3 (4,0); 2126 (1,4); 2406.4 (3,2); 2546.6 (4,1); 2686.8 (5,0)

[a] where: $(\text{–ESES–}) = -\phi-SO_2-\phi-O-\phi-SO_2-\phi-O-$; $(\text{–EES–}) = -\phi-SO_2-\phi-O-\phi-O-$; $\phi =$ .

the end chains, cyclic oligomers and also of species present in minor amount [16,17]. In the case of copolymer samples MALDI–TOF MS analysis has been applied for the determination also of the chemical composition, average sequence length and degree of randomness [16,20]. To the best of our knowledge, no data has ever been reported by literature on the characterization of poly(arylene ether sulphone) copolymers by MALDI–TOF MS analysis. Here we report the MALDI–TOF mass spectra of the P(ESES-co-EES) copolymers, recorded in reflectron mode using HABA as a matrix and CF_3COONa ad cationizing agent.

A MALDI–TOF mass spectrum of a chlorine ended copolymer referred as RLS80, taken before the end-capping with *m*-amino phenol is shown in Fig. 3, and mass assignments



Scheme 5.

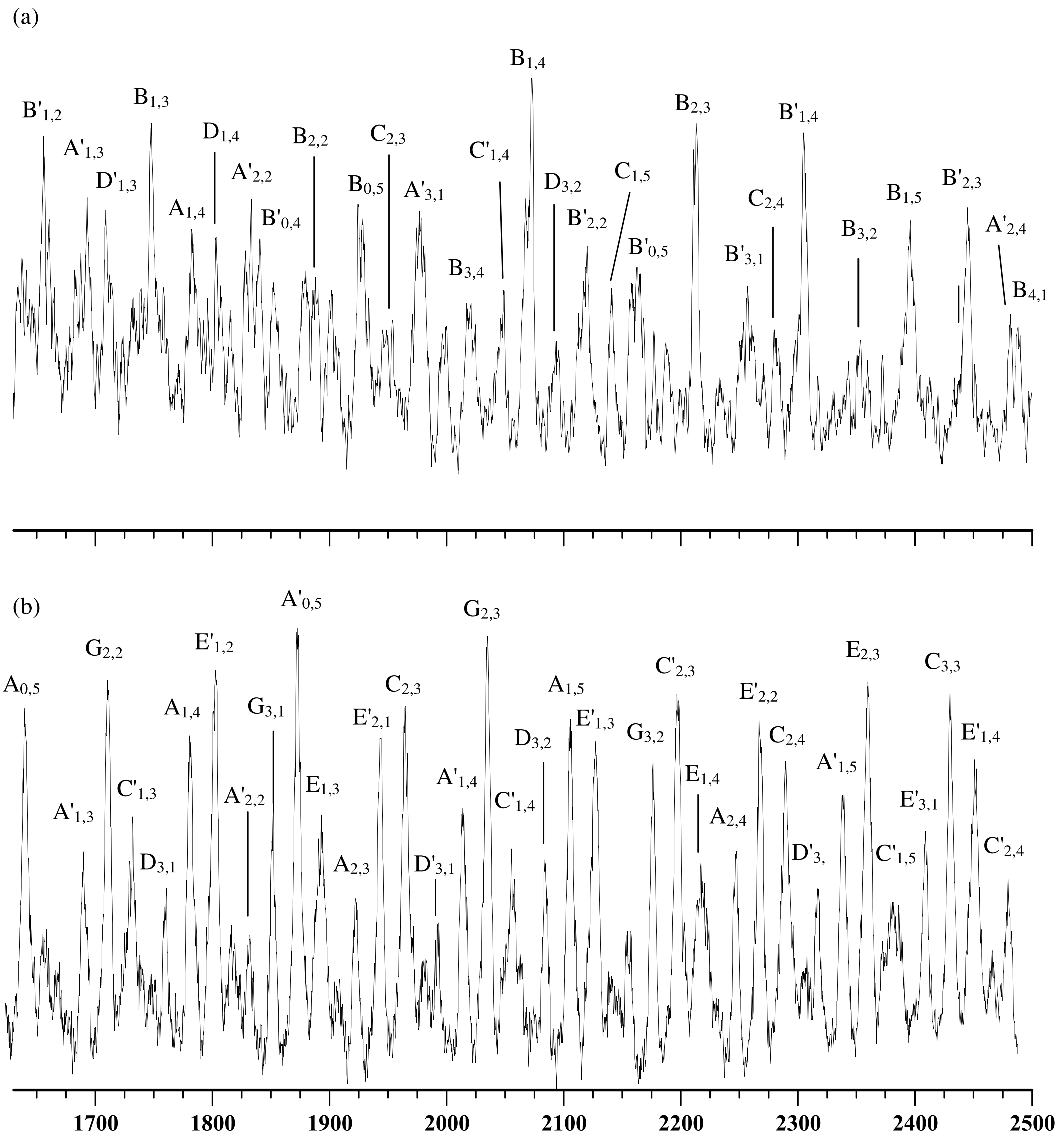
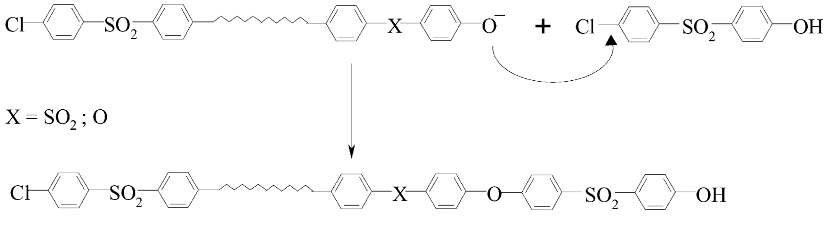


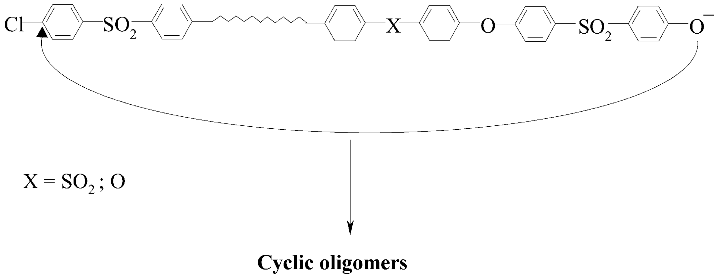
Fig. 4. Enlarged sections of the MALDI spectra of the P(ESES-co-EES) copolymers: (a) RLS 80 and (b) RLS79.

are reported in Table 6. It show a lot of mass-resolved peaks from 1000 to 9000 Da, as well as the spectra of all copolymers analysed. According to the synthesis procedure, in the spectrum of the RLS80 sample were observed only peaks due to the co-oligomers terminated with chlorine atoms at both side of the chains (species B in Table 6). This result emerge looking the inset in Fig. 3, that reports the spectra in the region 3650–4440 Da. Another series of co-oligomers terminated with chlorine atoms at both ends and having one more *p*-chloro diphenylsulphone unit with respect to those expected on the base of polycondensation mechanism (Scheme 1), were also observed (species B′ in Fig. 3 and in Table 6). These unexpected series of co-oligomers could be produced by the reaction of chlorine-ended copolymer chains with 4hydroxy,4′chloro diphenylsulphone, present as impurity in the used commercial 4,4′dichloro diphenylsulphone sample (Scheme 5).

Looking at Fig. 4a that reports a portions of the MALDI spectrum of chlorine-ended RLS80 sample, in the regions from 1650 to 2500 Da, besides the two mass series of peaks



Scheme 6.



Scheme 7.

belonging to the only chlorine terminated chains (species B and B′), low intense peaks due to the cyclic co-oligomers (species A and A′, in Table 5) and Cl/OH (species C and C′, in Table 6) are also observed. These open and cyclic co-oligomers were not revealed by NMR analysis may be because of their negligible concentration. The unexpected co-oligomers terminated with chlorine at one side and with hydroxyl group at the other side (species C and C′) could be formed by nucleophilic reaction of chlorine-ended chains with the 4hydroxy,4′chlorodiphenylsulphone, present as impurities in the feed (Scheme 6). The co-oligomers belonging to the species C and C′, then can be generate cyclic co-oligomers (Scheme 7). Cyclic oligomers and linear Cl/OH terminated co-oligomers were also observed in the MALDI–TOF mass spectrum of the corresponding amine-ended copolymer (RLS 79 sample in Table 4). The mass spectrum in the range 1650–2500 Da of the RLS 79 sample is reported in Fig. 4b. It shows intense peaks due expected amine-ended co-oligomers (species E, E′, G and G′, in Table 6). However, it shows also intense peaks due to the oligomers terminated with phenol groups at both side (species D and D′), which arise from the nucleophilic substitution reaction of hydroxyl ions with chlorine end chains (Scheme 3), which occurs during the capping of chlorine-ended copolymers with *m*-aminophenol. The same oligomer species were also observed in the MALDI-TOF mass spectra of all nominally amine-ended copolymers. Fig. 5 reports the mass spectra of three copolymers, namely RLS86, RLS83 and RLS63, in the mass region from 1800 to 2800 Da. Peaks belonging to the co-oligomers terminated with *m*-aminophenol at one side and chlorine at the other side (species F and F′ in Fig. 5 and in Table 6), were also observed in the mass spectra of these copolymers indicating the incomplete capping of *p*-chlorophenyl ends. Analysing the MALDI spectra in Fig. 5, is evident that the relative intensity of the peaks belonging of the same family of oligomers (i.e. $C_{2,3}$ and $C_{3,2}$, $G_{3,2}$ and $G_{2,3}$) changes with the molar composition of the ESES and EES units

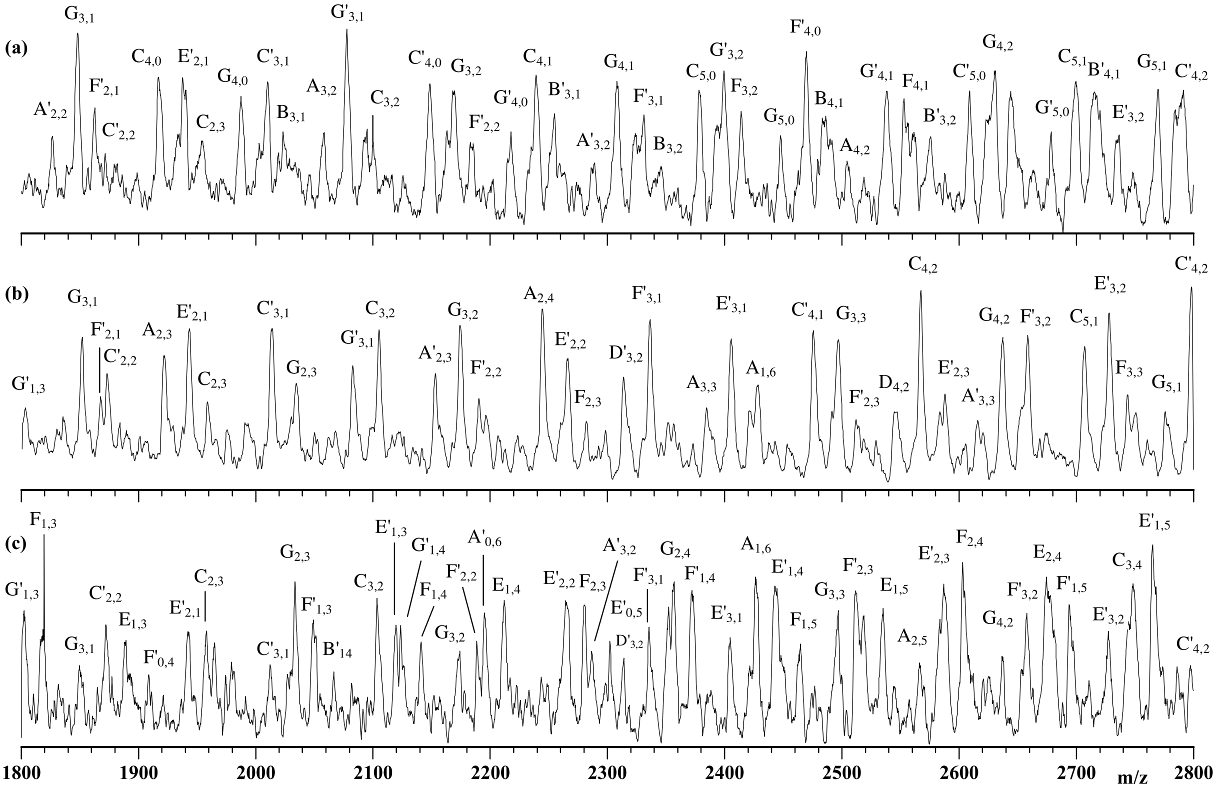


Fig. 5. MALDI spectra in the region 1800–2800 Da of the P(ESES-co-EES) copolymers: (a) RLS86, (b) RLS83 and (c) RLS63.

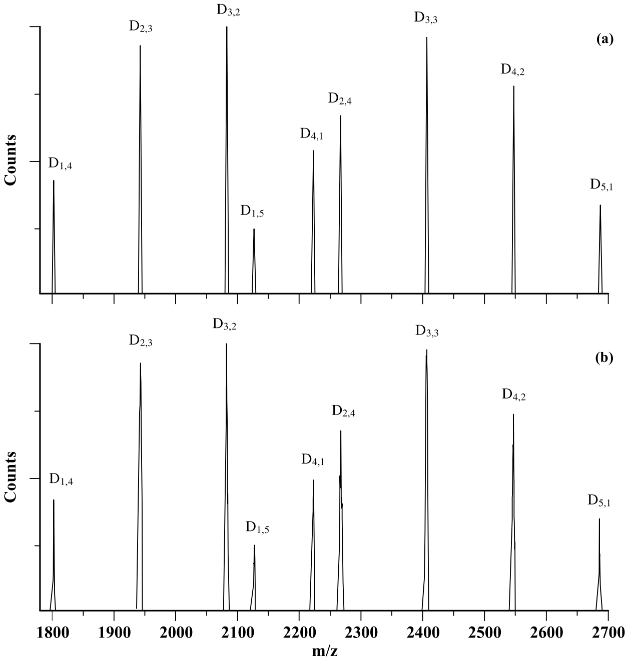


Fig. 6. Mass spectra for peaks corresponding to the pentamers and examers co-oligomers terminated with phenol groups at both side (mass series D in Table 5) present in the copolymer RLS85: (a) calculated mass spectrum using Eq. (13); (b) experimental MALDI mass spectrum.

in the copolymers. Applying the composition estimate model (Eqs. (11) and (12)), and using the intensities of the peaks corresponding to the pentamers, examers and eptamers co-oligomers, and assuming a random distributions of the ESES and EES units, we have calculated the molar composition of all the copolymers analysed. The results reported in Table 5 are in accord with those calculated by ^{1}H and ^{13}C NMR tools, and confirm that random copolymers were obtained by reaction of chlorine-ended P(ESES-co-EES) copolymers with *m*-aminophenol at 205 °C, owing of transetherification side reactions (Scheme 4).

The molar composition of the copoly(arylene ether sulphone)s was also determined by applying the chain statistic analysis, and matching the experimental intensity of the mass peaks belonging to one series of co-oligomers with that calculated using the well-known Newton formula (Eq. (13)). All MALDI mass spectra of the P(ESES-co-EES) copolymers analyzed appear very complex owing to the presence of mass series bearing different end groups. However, by selecting a single mass series, one obtain an experimental spectrum immediately comparable to the theoretical one. Fig. 6b reports the normalized intensities of mass peaks corresponding to the pentamers and examers belonging to the oligomers terminated with phenols groups at both side (mass series D in Table 6), present in the MALDI mass spectrum of the RLS78 sample. It matches very well with the theoretical mass spectrum (Fig. 6a) generated for a random copolymer containing 52 mol% of ESES (A) and 0.48 mol% of EES (B), considering the same families of oligomers. Therefore, we can conclude that the copolymer RLS78 have a random distribution of ESES and EES units and a molar composition of 52/48, according with NMR (^{1}H and ^{13}C) data and the value calculated applying the estimate composition method at the MALDI mass spectrum of this sample (Table 5).

3.3. DSC analysis

All copolymers were also characterized by DSC, and the glass transition temperatures (T_g) determined are reported in Table 4. In the case of random copolymers single T_g values, intermediate between those of the two homopolymers, are expected according to the Fox [21] equation: $1/T_{gAB} = (W_A/T_{gA} + W_B/T_{gB})$ were W_A and W_B indicate weight % of components A and B, and T_{gA} and T_{gB} indicate the glass transition of the two corresponding homopolymers, respectively. The data can also be fitted with Gordon-Taylor [22] or Kwei [23] theories, Eqs. (14) and (15), respectively.

$$T_g = \frac{T_{gA}W_A + kT_{gB}W_B}{W_A + kW_B} \tag{14}$$

$$T_g = \frac{T_{gA}W_A + kT_{gB}W_B}{W_A + kW_B} + qW_AW_B \tag{15}$$

Fig. 7 shows the results of the least square analysis on the experimental data using the equations reported above. The best fitting ($R^2 = 0.99$) was obtained with Kwei model (Eq. (15)) and the values of k and q were 1.6 and 64.6, respectively. The k parameter is an adjustable variable whereas q is an interaction parameter which can be correlated with the intermolecular forces originating in copolymer structure. The high value of q obtained indicates strong specific interactions which, in our case, could be due explained in terms of hydrogen bonding. The data (Table 4) show a linear increase of the glass transition temperature on increasing of the ESES mol% unit content. This behaviour can be interpreted on the basis of the Carlier concept [24] of the Percentage Rigid Chain Length (PRCL) and then of the chain rigidity resulting from the presence of various sulphone and ether groups. In fact, the strong electronegative characteristics of sulphone group lead to the delocalisation of

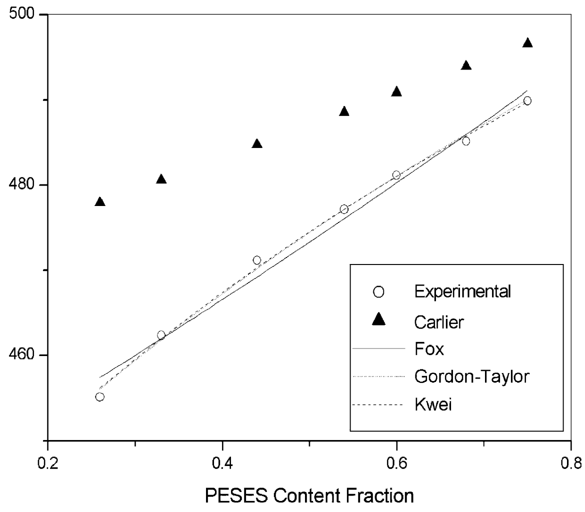


Fig. 7. Comparison of experimental T_g data with values predicted by Carlier's approach and fitting by Fox, Gordon Taylor and Kwei models.

π-electrons from the aromatic rings, with an increase of double-bond character of the S–C bonds on both sides of SO_2 group (100% rigidity) in comparison with that of the C–O links on both sides of ether group (0% rigidity). Then the increasing of the number of sulphone groups increases the chain rigidity, with an increase of T_g. According to the Carlier concept the PRCL values for the ESES (A) and EES (B) units are 76.07 and 67.77%, respectively. Thus the T_g values for the copolymers could be calculated with the following Eq. (16) proposed by Carlier [24]:

$$T_g = -115.15 + 4.575 PRCL_{tot} \tag{16}$$

Where $PRCL_{tot}$ is the total PRCL of the copolymers calculated with respect to the composition of the copolymers according to formula (17):

$$PRCL_{tot} = PRCL_{PESES} C_{PESES} + PRCL_{PEES} C_{PEES} \tag{17}$$

Fig. 7 reports the comparison between the values predicted with Eq. (16), if molar compositions calculated by ^{1}H NMR are considered, and the experimental T_g's. The predicted values are always higher than the experimental data and the differences are greater for the copolymers RLS72 and RLS63 which have lower $\bar{M}_n$. The difference between predicted and experimental values can be ascribed to the presence of two factors which the Carlier approach does not account for: the molecular mass and the end groups [24]. The influence of molecular mass on T_g can be approximately described by an equation of the type (Fox and Flory (1950) [25]):

$$T_g = T_{g\infty} - \frac{A}{\bar{M}_n} \tag{18}$$

where $T_{g\infty}$ is the glass transition for a very high molecular mass and A is a constant. Thus, according to Eq. (16), the molecular mass of the copolymer of the present study is lower than the critical value of $\bar{M}_n$ after which T_g is independent from molecular mass. The end groups of the copolymer chains, revealed by MALDI–TOF MS analysis, have size that could decrease the possibilities for dense packing of the chains, thus the glass transition temperatures can be reduced with respect to the same copolymers with higher molar mass and lower amount of end chains.

4. Conclusions

Combining NMR (^{1}H and ^{13}C) and MALDI–TOF MS analysis, a reliable characterization of the end-chains, the molar composition and the sequence distribution of the P(ESES-co-EES) copolymers is possible. ^{13}C NMR and MALDI–TOF MS data confirm the occurrence of transetherification side reaction during the synthesis of amine-terminated P(ESES-co-EES) copolymers, leading to a random copolymers. The MALDI–TOF analysis revealed also the formation of cycles due to the thransetherification reaction occurring at the temperature (205 °C) used for the reaction of chlorine-ended copolymers with *m*-aminophenol. Unexpected end groups, formed for the presence of impurities in the feed, were also detected by MALDI-TOF MS. The work presented has proved the feasibility of the proposed synthesis as a useful mean to obtain controlled structure for the P(ESES-co-EES) copolymers. These copolymers could be particularly useful to study the effect of the macromolecular structure on the morphology and thermomechanical behaviours of epoxy/thermoplastic blends.

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