

## The influence of chain rigidity on the thermal properties of some novel random copolyethersulfones

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### ABSTRACT

Some random low molar mass ( $M_n \approx 9000 \text{ g mol}^{-1}$ ) poly(ethersulfoneethersulfone)/poly(ethersulfoneethersulfonebiphenylsulfone) P(ESES)/P(ESESBS) copolymers, with various (25%, 50% and 75%) ESESBS units contents, were synthesized to obtain compounds with higher chain rigidity than PES. The thermal characterization of the prepared copolymers, as well as that of corresponding P(ESES) and P(ESESBS) homopolymers, was performed, and all investigated parameters showed strong dependence on polymer composition.

The glass transition temperature ( $T_g$ ) was calorimetrically determined by DSC technique, and the obtained values increased linearly as function of ESESBS units percentage, thus indicating an increasing chain rigidity.

Degradations were carried out in dynamic heating conditions, from 35 °C to 700 °C, in both flowing nitrogen and static air atmosphere, and the characteristic parameters of degradation were determined in order to draw useful information about the overall thermal stability of the studied compounds. The apparent activation energy of degradation ( $E_a$ ) was obtained by the Kissinger method, and the values found increased linearly as a function of ESESBS content, while the temperature values at 5% mass loss ( $T_{5\%}$ ) showed an opposite linear trend. The results are discussed and interpreted.

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### 1. Introduction

Aromatic thermoplastic poly(ether-sulfone)s (PESs) are engineered materials of great scientific and industrial interest owing to their very good mechanical, chemical and thermal properties [1–3], which allow their application in various fields, for instance, as adhesives for metal-to-metal bonds [2], as membranes to separate gas or solid from solutions [3], as matrices for fibre reinforced composite [4,5] and in the preparation of membranes for fuel cells [6].

PESs can be also used as toughening agents of epoxy resins employed as matrices for advanced composites in the aerospace field [4,7]. Moreover, they can create an advantage over traditional tougheners (i.e. rubbers) owing to the resulting thermoplastic/thermoset blends do not show decrement of mechanical and thermal properties if compared with unmodified resins. In addition, if reactive PESs are used as modifiers, interpenetrating networks (IPNs) can be formed, so giving rise to blends showing enhanced mechanical and thermal properties [8].

It is well known in literature that PES copolymers with a wide spectrum of thermal and mechanical properties can be obtained by varying the type and the quantity of co-monomer as well as the ratio between the ether, sulfone and/or other groups [4]. Moreover, since in the past some miscibility problems were encountered by using high molecular mass PESs for the purpose as toughening agents [9,10], low molecular mass PES copolymers have been considered for this use [9,11–13].

Since our group is interested in synthesizing new polymers which could be used as toughening agents for epoxy resins, and/or for manufacturing membranes, in this work we investigated some novel low molar mass ( $M_n \approx 9000 \text{ g mol}^{-1}$ ), amino-ended, random copolyethersulfones, prepared with various percentages of LCDC (Long Chain DiChloride) as comonomer:



where Ar = 1,4-phenylene.

The studied compounds were:

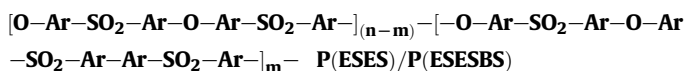


where P(ESES) = poly(ethersulfoneethersulfone)



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where P(ESESBS) = poly(ethersulfoneethersulfonebiphenylsulfone) and some P(ESES)/P(ESESBS) copolymers at various ESES/ESESBS ratios:



The various copolymers will be indicated in the text by the percentages of ESES and ESESBS repeating units, respectively. Thus, for instance, the symbol **25:75** represents the copolymer with 25% of ESES and 75% ESESBS repeating units.

We selected LCDC owing to the presence of the rigid biphenyl group, aiming to obtain copolymers with higher  $T_g$  than PES. In order to verify this hypothesis, and, also, to check if and how much the introduction of ESESBS units into copolymers chain affects the comprehensive thermal stability, in this work we determined the glass transition temperature ( $T_g$ ), the temperature at 5% mass loss ( $T_{5\%}$ ) and the apparent activation energy of degradation ( $E_a$ ) of the studied compounds.

## 2. Experimental

### 2.1. Materials

Commercial Aldrich 4,4'-dichlorodiphenylsulfone (DCDPS) (98% of purity grade), di-hydroxydiphenylsulfone (DHDPS) (98% of purity grade), 4,4'-bis[(4-chlorophenyl)sulphonyl]-1,1'-biphenyl (long chain di-chloride LCDC) (99% of purity grade), m-aminophenol, potassium carbonate (anhydrous grade) and tetramethylenesulfone (sulfolane) were used for syntheses. DCDPS was crystallized twice from toluene; sulfolane was distilled under vacuum and stored under nitrogen until use; potassium carbonate was dried at 150 °C under reduced pressure, while all other products were used without any further purification.

The Cl-ended derivatives were first synthesized, by a polycondensation reaction of DHDPS with DCDPS and/or LCDC, as follows: reactants, in various molar ratios according to the compound to be prepared, were dissolved in sulfolane in the presence of potassium carbonate, and the mixture was then heated step by step up to 220 °C according to a precise temperature profile. The amino-ended derivatives were then obtained by nucleophilic reaction of Cl-derivatives with m-aminophenol, in the presence of potassium carbonate. The precipitated amino-ended copolymers were washed several times with water and methanol, and then dried under vacuum at 80 °C overnight. All details of syntheses are elsewhere reported [14].

### 2.2. $^1\text{H}$ NMR measurements

A Varian Unity Inova 500 MHz spectrometer was used for  $^1\text{H}$  NMR measurements. Spectra were performed at 25 °C, without internal standard and by using deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) as solvent. A literature method [1] was used for the determination of both the number average molar mass ( $M_n$ ) and the ESES/ESESBS molar ratio of the investigated polymers. In particular: the number average molar masses were determined by the integration of chain end peaks, via the comparison with the peaks due to the aromatic protons in *ortho* position to the ether-oxygen groups in the backbone. For all compounds studied the number average molar mass was included in the 8800 ÷ 9300 g mol<sup>-1</sup> range. The percentages of ESES and ESESBS repeating units were determined through the evaluation of the peaks assigned to the protons in *ortho* position in respect to sulfone and biphenyl groups, respectively; the experimental values from  $^1\text{H}$  NMR spectra [14] were in very good agreement with the theoretical ones calculated on the basis of reactant mixtures, and

confirmed the copolymers compositions as in the Tables here reported.

### 2.3. TG and DTG measurements

Thermal degradations were carried out in a Mettler TA 3000 thermobalance, coupled with a Mettler TC 10A processor as control and evaluation unit. The temperature of furnace was calibrated following the procedure reported in the user's manual of equipment [15], based on the change of the magnetic properties of three metal samples (Isatherm, Nickel and Trafoperm) at their Curie points (142.5, 357.0 and 749.0 °C, respectively). The temperature calibration was repeated every month.

Degradations were carried out under flowing nitrogen (0.02 L min<sup>-1</sup>) and in a static air atmosphere, in dynamic heating conditions, in the temperature range 35–700 °C, at various selected heating rates ( $\phi = 2, 5, 7.5, 10, 12.5, 15, 17.5$  and 20 °C min<sup>-1</sup>). Samples of  $4 \times 10^{-3}$  to  $6 \times 10^{-3}$  g, held in alumina open crucibles, were used for degradations, and their weights as a function of temperature were stored in the list of data of the appropriate built-in program of processor. The experimental data at various temperatures were elaborated by the TC 10A processor at end of each experiment and the corresponding TG and DTG curves were immediately printed. The same data were thus transferred to a PC, and then used to plot the percentage of undegraded polymer (1 -  $D$ )% as a function of temperature, where  $D = (W_o - W)/W_o$ , and  $W_o$  and  $W$  were the weights of sample at the starting point and during scanning.

### 2.4. DSC measurements

A Mettler DSC 20 differential scanning calorimeter, coupled with the same Mettler TC 10A processor used for TG experiments, was employed for the determination of glass transition temperature. Both heat flow and temperature of calorimeter were calibrated following the procedure suggested by Mettler and reported in the operating instructions of equipment [15]. Samples of about  $6.0 \times 10^{-3}$  g, held in sealed aluminium crucibles, a heating rate of 10 °C min<sup>-1</sup> and a static air atmosphere were used for measurements.

## 3. Results and discussion

In the scanned temperature range all studied polymers degraded, in both used environments, in a single stage, with complete mass loss in air and the formation of a stable residue in flowing nitrogen. The TG curves at 10 °C min<sup>-1</sup> in both inert and oxidative atmospheres are reported as an example in Figs. 1 and 2, respectively.

The apparent activation energies of degradation were obtained through the classical Kissinger equation [16],

$$\ln\left(\frac{\phi}{T_m^2}\right) = \ln\left(n\text{RAW}_m^{n-1}/E_a\right) - E_a/RT_m$$

where  $\phi$  is the heating rate and  $T_m$  is the temperature at the maximum rate of weight loss. We used as  $T_m$  values the temperatures of DTG peaks. At least three runs were carried out at each selected scanning rate. The average  $T_m$  values (Tables 1 and 2) were smoothed according to the Kissinger equation, and the apparent activation energies of degradation were determined through the slopes of the linear equations obtained (Tables 3 and 4).

Since it was difficult to single out exactly the initial decomposition temperatures ( $T_i$ ) owing to the irregularity of the initial part of TG curves in oxidative atmosphere, the temperatures at 5% mass loss, which are roughly correlated with  $T_i$  [17], were determined at the various selected heating rates, by using the degradation data stored in the TC 10A processor. Since the experimental conditions, and the scanning rate in particular, largely influence the shape of TG

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