Mechanical and macromolecular changes during thermal degradation of polyphenylsulfone

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ABSTRACT

Polyphenylsulfone was thermally aged at temperatures corresponding to its processing and was mainly shown to undergo crosslinking as observed by measurements of average molar mass, rheometry and changes in glass transition temperature. Those experiments were completed by mechanical testing thin sample films at 250 and 280 °C. The same degradation mechanisms were observed and result in a strong decrease of ultimate strain accompanied by a slight decrease in elastic modulus and yield stress. Overall results were discussed using well know structure-properties relationships.

1. Introduction

Polysulfones form a wide family of thermoplastic polymers obtained by condensation of a diphenolate with a dihalogenated monomer [1]. These amorphous polymers belong to the high performances polymer familiy. The presence of aromatic ring induces relatively high glass transition temperature (typically around 200 °C) [2] together with a high stability towards irradiations in comparison with aliphatic polymers [3]. In the same time, they benefit from a sub-glassy relaxation at around −100 °C i.e. well below the glass transition [4] allowing a certain toughness.

PPSU can thus be envisaged for application such as aerospace and aeronautics (as skin of sandwich composites) [5], electrical component or medical devices [6] where its aromatic behaviour and high Tg allow various kinds of sterilization process. Polysulfones display a very low Heat Release capacity during combustion can also be suitable for applications where flame retardant properties are required [7]. This makes it one of the most technical thermoplastics on the market today.

PPSU are usually processed by injection moudling or extrusion but the need to manufacture parts with complex geometries makes it necessary to discuss on the possibility to investigate additive manufacturing (such as molten polymer filament layering 3-D printing) [8]. During the additive manufacturing process by Fused Filament Fabrication for example, high temperature can lead to polymer degradation, breaking down polymer chains, weakening the finished part and leaving residue on the inside of the melt channel [9]. This is the case even for high performances polymers where processing temperature in Fused Filament Fabrication or in Selective Laser Melting) can be narrow [10]. The existence of a crosslinking mechanism will limit the diffusion of chains across interface [11] which may prevent the consolidation of FFF manufactured samples and the possibility to obtain acceptable mechanical properties [12]. There is also an increasing societal pressure to re-use such polymers, at least in the case of "closed loop" recycling for polymers scraps. The degradation induced during service life or processing may also limit the possibility to reprocess those polymers.

It arises the need to understand the effect of thermal degradation on the mechanical properties and the thermal stability of those materials. The thermal stability of aromatic polymers was already addressed in previous papers dealing with apparent modelling of the degradation [13] but the fine understanding of macromolecular changes and their effect on mechanical properties remain an open question.

Finally, the aims of this paper are:

- to evaluate the thermal stability of PPSU in typical processing conditions in terms of temperature)
- to investigate the macromolecular changes involved by the thermal degradation,
- to propose some structure-properties relationships involved in the embrittlement of PPSU materials.
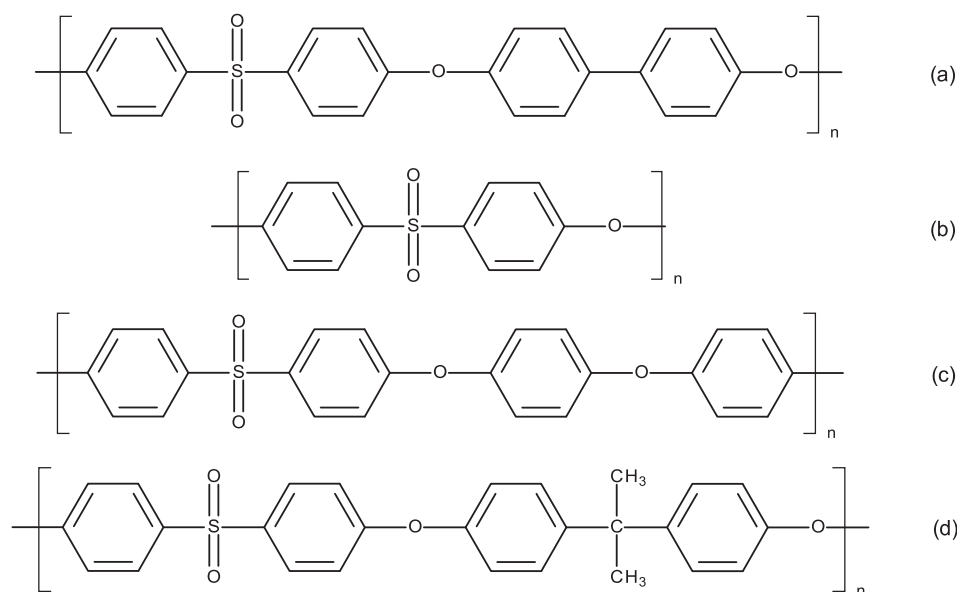
Fig. 1. Structure of investigated polymers: polyphenyl sulfone PPSU (a), polysulfone PES (b), Polyetherether sulfone (PEES) (c), bisphenol A polysulfone PESU (d).

For that purpose, we will address the degradation at 400 °C with some comparisons with samples degraded at lower temperatures. Even though additive manufacturing conditions is usually performed under atmospheric air, we will also investigate degradation under pure oxygen and under pure nitrogen, in order to investigate the purely "thermolytical" degradation processes (occurring in the bulk of polymer sample) and then the effect of oxygen (occurring in its surface). The knowledge of those two "extreme" behaviors is actually needed to describe the degradation in typical processing conditions under air.

2. Experimental

2.1. Materials

Several kinds of polysulfones (the structure of which being given in Fig. 1) were studied here, with a peculiar emphasis for PPSU.

Two kinds of PPSU samples (PPSU 1 and 2) were supplied as filament extruded by supplier for FFF purpose. Those latter were used as received. Some comparisons were performed with samples purified by refluxing in methanol during 24 h but only minor changes were observed so that PPSU's were used as received in the following.

For mechanical testing, PPSU filaments were pressed using a Gibitre laboratory press (2 min at 280 °C under 240 bars. Resulting films displayed a 50–60 μm thickness and then punched into 5B type dogbone specimens (according to ISO 527–2).

Some complementary tests were done with several grades of polysulfones (all as received) given in Table 1:

Table 1
Description of polysulfones materials used in this work for comparison purposes.

Name	supplier	ref	Informations
PES	Sigma Aldrich	191,094–50G	
PES	Sigma Aldrich	191,094–50G	
PSU	Sigma Aldrich	428,302–100G	M_n =16.0 kg mol^{-1}
PSU	Sigma Aldrich	182,443–5G	M_n = 22.0 kg mol^{-1}
PEES	Sigma Aldrich	440,965–250G	

2.2. Exposure conditions

Samples were either isothermally aged:

- in the cell of ThermoGravimetric Analysis device, either under nitrogen or oxygen atmosphere (see next paragraph),
- in ventilated ovens at 250 °C (AP60, System Climatic Service) and 280 °C (UF160plus, Memmert).

3. Characterization methods

3.1. ThermoGravimetric analysis (TGA)

Experiments were performed using a Q50 apparatus (TA Instruments) driven by QSeries Explorer software. Two kinds of experiments were performed on about 15 mg samples placed in a platinum pans:

- continuous heating from room temperature to 700 °C either under inert (pure N_2) or pure O_2 atmosphere at a 10 °C min^{-1} rate,
- isothermal ageing at 400 °C either under inert or pure O_2 atmosphere.

TGA cell was continuously purged by a 50 ml min^{-1} gas flow. Results were analysed using TA Analysis software.

3.2. Differential scanning calorimetry

DSC experiments were conducted using a Q10 apparatus (TA Instruments) driven by QSeries Explorer. About 5 mg samples sealed in hermetic pas were subjected to 10 °C min^{-1} heating ramp under 50 ml min^{-1} nitrogen flow. Results were interpreted using TA Analysis software.

3.3. Sol gel analysis

Samples (about 50 mg) were immersed in THF. The presence of a gel (unsoluble part) was visually observed.

3.4. Gel permeation chromatography

Samples were analysed using a GPC system comprising a Waters HPLC apparatus (Waters 717+apparatus) with a Styragel SE5 column with a tetrahydrofuran (THF) flow rate 1 ml min^{-1}. Detection was performed using a Waters 2414 Refractive Index ($T_{detector}$ = 40 °C). Apparatus was calibrated with unimolecular PS standards (supplied by Shodex).

3.5. Rheometry

Rheometric measurements were conducted using a DHR 20 rhetometer (TA Instruments). Samples were submitted to a 1% shear deformation at 400 °C under inert atmosphere supplied a 10 ml min^{-1} nitrogen flow. Plates diameter was 25 mm and gap was measured close to 1 mm.

3.6. Dynamical mechanical analysis

DMA tests were performed in tension mode using a Q800 apparatus (TA Instruments) controlled by QSeries Explorer. The samples were submitted to a 0.1% oscillatory strain at 10 Hz frequency and continuously heated at a 3 °C min^{-1} ramp. DMA cell was continuously purged with N_2 gas. Results were exploited with TA Universal Analysis software.

3.7. Tensile tests

Tensile tests were conducted using an Instron 4301 at a 10 mm min^{-1} elongation rate equipped with a 100 N load sensor. Apparatus was driven by Bluehill software. 5 virgin or aged specimens (punched from virgin pressed films and then aged) were tested with a 2 mm width and a 10 mm initial length.

4. Results

The aim of this section is to investigate first the thermal stability of PPSU's. For that purpose, non-isothermal ageing will be performed. In order to be closer to the "real" processing and use conditions, isothermal ageing will be performed at 400 °C and lower temperatures. Ageing will be monitored mainly by macromolecular changes induced by degradation in order to establish links with changes in mechanical properties.

4.1. Gravimetric study

High temperature stability was first checked by non-isothermal TGA under nitrogen (Fig. 1a) and oxygen (Fig. 1b). We stress on the fact that non-isothermal tests offer a simple way to estimate the thermal stability of polymers but do not allow to perform lifetime prediction. The resulting curves are classically interpreted by measuring:

- the onset temperature (basically the temperature at which mass loss auto-accelerates), or the temperature corresponding to an "arbitrarily" fixed mass loss level (here 5, 10, 20 and 30%). We have chosen here to measure those latter values, which seemed to us more reliable than the simple "onset temperature value".
- the char yield at 700 °C (possibly corresponding to a "pseudo-plateau" as verified by isothermally maintaining samples at 700 °C during 20 min). The value measured at 700 °C at the end of the ramp (η) is given in Table 2.

Values are given in Table 2 for PPS and compared to those of other members of the aromatic polysulfone family.

PPSU isothermal ageing was thus performed in typical processing conditions, i.e. at 400 °C under nitrogen or oxygen. In fact, due to the existence of the so-called Diffusion Limited Oxidation effect, the polymer degradation for processing conditions must be close to degradation under nitrogen atmosphere in the bulk of thick samples and close to the degradation under oxygen for superficial layers. For that purpose, samples were in situ degraded in TGA cell. Results are presented in Fig. 3.

Curves can be commented as follows:

- under inert atmosphere, PPSU degrades quite slowly even at 400 °C. PPSU 1 seems less stable than PPSU 2. The existence of mass loss means that some chain scissions occur, despite (as it will be seen later), crosslinking is also very important.
- in presence of oxygen, mass loss kinetics display an auto-accelerated character suggesting the existence of an oxidation mechanism responsible of supplementary mass loss. The degradation of aromatic C−H into H_2O, CO or CO_2 is a possible explanation but the investigation of those reactions goes out of the scope of the present work.

Samples were also continuously weighted for ageing at 280, 250, 220 and 200 °C under air. Here, PPSU 1 degrades slightly lower than PPSU 2,

- at 220 °C and below, mass stayed constant (at least up to 1000 h),
- at 250 and 280 °C, a certain mass loss is observed indicating the existence of some chain scission process. Figure SI-1 depicts the case of ageing at 280 °C.

4.2. Macromolecular changes

To better understand the macromolecular changes occurring during ageing, degraded samples (either in oven or in situ in TGA cell) were analysed by DSC to measure the residual glass transition value. Data are given in Fig. 4 in the case of PPSU 1 filaments before and after ageing. Thermograms display the expected shape of amorphous polymers. Initial glass transition value is around 220 °C for unaged polymers in agreement with previous papers [14]. For unaged PPSU, only the glass transition is visible at around 220 °C, this value being commented in the following section.

Table 2
Characteristics temperature for degradation and char yield (η) for polysulfones.

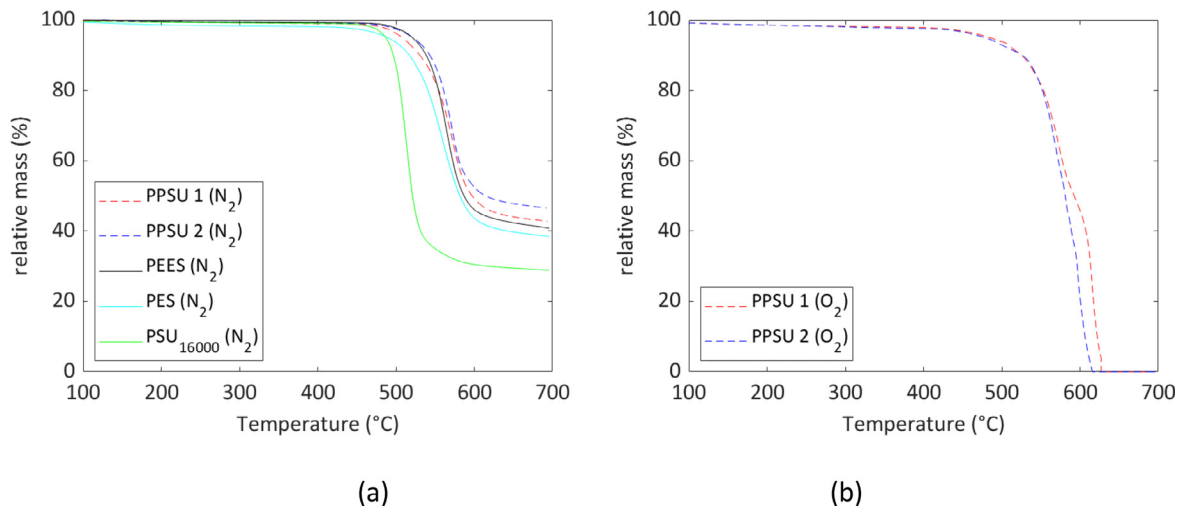| Atmosphere		PPSU 1	PPSU 2	PSU 1	PSU 2	PES 1	PES 2	PEES
N_2	$T_{5\%}$	508	521	487	495	489	513	521
	$T_{10\%}$	530	543	496	505	517	534	539
	$T_{20\%}$	555	561	505	513	541	552	554
	$T_{30\%}$	568	571	511	519	555	563	564
	η (%)	43	47	29	29	38	41	41
O_2	$T_{5\%}$	484	478	478	489	478	469	501
	$T_{10\%}$	525	526	494	505	500	496	527
	$T_{20\%}$	553	552	509	518	530	532	546
	$T_{30\%}$	567	564	518	525	545	546	555

Fig. 2. Non-isothermal TGA of polysulfones under nitrogen (a) or oxygen (b).

Glass transition values (T_g) were determined for several exposure conditions and plotted versus time in Fig. 5. Even though mass loss is observed (which is testimony of the occurrence of some chain scissions), T_g mainly increases. It means either that PPSU undergoes additional polycondensation (involving chlorophenyl and phenolate chain end groups for example) or crosslinking, as it will be discussed in the following. Specifically, we observed the following trends:

- for ageing performed at 400 °C under N_2 or under O_2, T_g increases in both cases but at a slower rate in presence of oxygen than under inert atmosphere. According to Fig. 2, mass loss is higher in presence of oxygen than under inert atmosphere. In other words, crosslinking occurs under nitrogen and possibly under oxygen (since a gel fraction was observed) but is delayed due to oxidation processes. Interestingly, the increase is higher for PPSU than for example PEKK aged in the same conditions [15]. It suggests that biphenyl groups contribute to crosslinking reaction.
- The same is observed at 250 °C and 280 °C under air: T_g continuously increases for PPSU fibers (2 mm diameter). The differences between thin films and fibers are relatively weak.

Usually, an increase in T_g means that macromolecular mobility decreases. In a case of a thermoplastic polymer, it suggests that molar mass increases either because crosslinking and/or because of post polycondensation (condensation reactions are reported to occur in solvent at temperatures ranging from 130 to 250 °C [1] and it is recognized here that we do not know if they also occur at higher temperatures or if chain ends might be degraded first). Gel Permeation Chromatography experiments were performed in order to monitor the changes in Average molar masses. According to Fig. 6, the maximum of the chromatogram is shifted towards higher elution times, which is in agreement with an increase in average molar mass. It can be seen that the broadness of the chromatogram (linked to the polydispersity index) also increases. Some values are given in Table SI-1 of SI.

Under the assumption of random chain scission and/or crosslinking [16], changes in average molar mass are given by:

$$\frac{1}{M_n} - \frac{1}{M_{n0}} = (s - cond) - x \tag{1}$$

$$\frac{1}{M_w} - \frac{1}{M_{w0}} = \frac{s - cond}{2} - 2x \tag{2}$$

in the case of a crosslinking mechanism leading to tetrafunctionnal nodes, or

$$\frac{1}{M_w} - \frac{1}{M_{w0}} = \frac{s - cond}{2} - x \tag{3}$$

in the case of a crosslinking mechanism leading to trifunctionnal nodes.

The exploitation of M_n and M_w changes showed that s – cond $\langle$ 0 and x $\rangle$ 0, which suggests that both mechanisms co-exist. In the absence of evidence of tri- or tetrafunctionnal nodes, we did not deepen the quantitative analysis using Eqs (1)–(3).

To better understand the nature of macromolecular changes and discuss on the existence either of polycondensation or crosslinking, rheometric measurements for PPSU in molten state were performed (Fig. 7). The following changes were observed: at early exposure time, the loss modulus G'' is higher than the storage (elastic) one G'. This latter progressively increases and becomes higher than G''. Such a behaviour is characteristic of the formation of a gel [17,18]. The same occurs for PEES and PES. Very interestingly, the gel times are higher for both PEES and PES than for PPSU polymers as it will be discussed later.
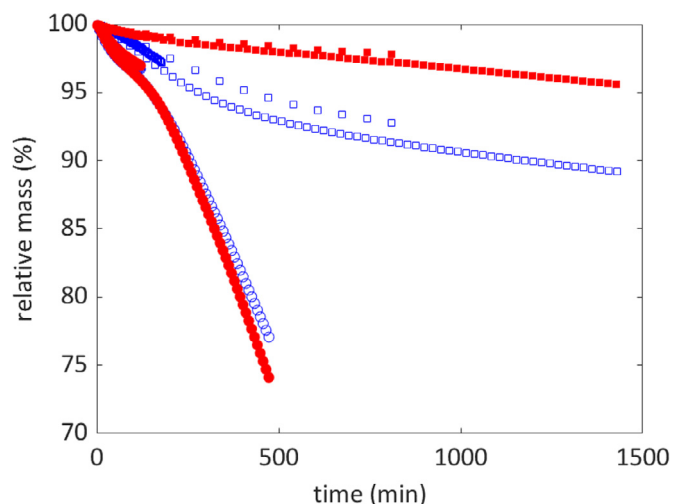

Fig. 3. Gravimetric study at 400 °C under inert (■, □) or pure O_2 atmosphere (○, ●). Open symbols correspond to PPSU 1 and closed ones to PPSU 2.
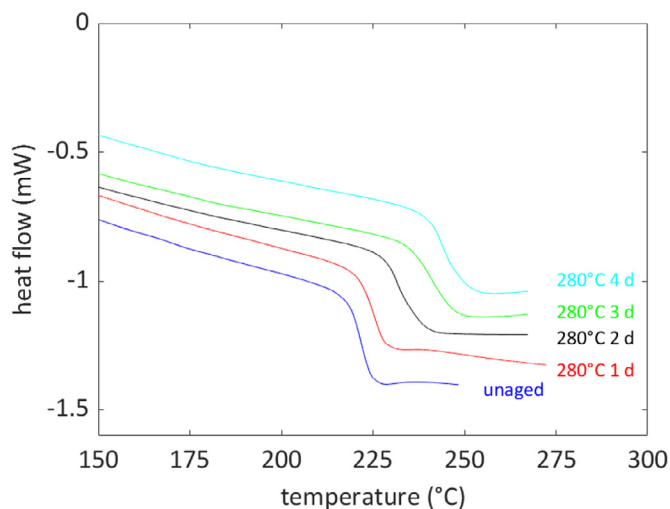
Fig. 4. DSC thermograms of PPSU 1 aged at 280 °C under air.

(a)

(b)

(c)

Fig. 5. T_g changes of PPSU 1 and 2 after several ageing conditions: 400 °C (a), 280 (b) and 250 °C (c). NB: opens symbols correspond to thin samples aged under air (at 250 and 280 °C) or samples aged under pure O_2 (400 °C) meanwhile closed symbols correspond to thick samples (filament) aged under air (250 and 280 °C) or thick samples aged under pure N_2 (400 °C).

Consistently with TGA experiments under nitrogen (Fig. 3), PPSU 1 degrades faster than PPSU 2. The existence of crosslinking was also confirmed by sol gel analysis: aged samples (either in oven in situ in TGA cell) were immersed in tetrahydrofuran. An insoluble fraction characteristic of a polymeric network was observed. The analysis of residual soluble fraction (Fig. 6) also displays an interesting feature: chromatograms are progressively shifted towards high elution times meaning that molar mass progressively increases.

4.3. Changes in mechanical properties

To understand the consequences of ageing on mechanical properties in a first simplified approach, we performed ageing tests on thin films aged at 250 and 280 °C after several time intervals. In such ageing conditions, films could be aged without undergoing geometrical changes unacceptable in terms of mechanical testing meanwhile "macromolecular changes" (estimated for example from Fig. 5) are consistent with those of filaments investigated in this work.

Stress strain curves are overlapped in Fig. 8. They call for the following comments:
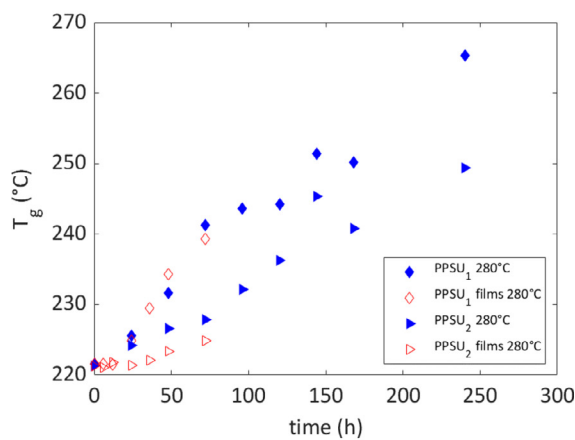
- for unaged samples, a certain plastic deformation is observed with an average ultimate strain higher than 100%,
- after ageing, ultimate elongation is progressively decreased. A certain plastic deformation remains, however possible,
- elastic modulus and yield stress does not display significant changes, within the experimental incertitudes.

DMA analyses were conducted in the aim of establishing macromolecular changes and mechanical properties. PPSU displays two main transitions characteristic of its amorphous behaviour:
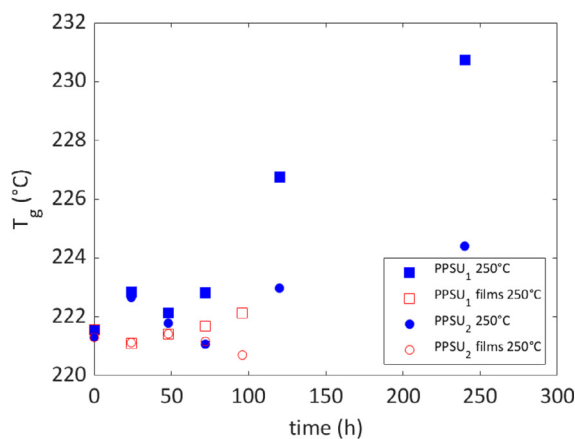
- a sub-glassy transition (γ relaxation) located at around -100 °C (Fig. 10) and associated to a local mobility (Fig. 10). This one is common with other polysulfones such as PES (explaining why those glassy polymers actually display a plastic behaviour) but less intense meaning that the responsible groups are in lower concentration in PPSU than in PES and in PEES which is in line with the interpretation of Aitken et al. [19] according to which this relaxation would be due to either diphenyl sulfones or sulfones groups.
- the α-relaxation associated to T_g
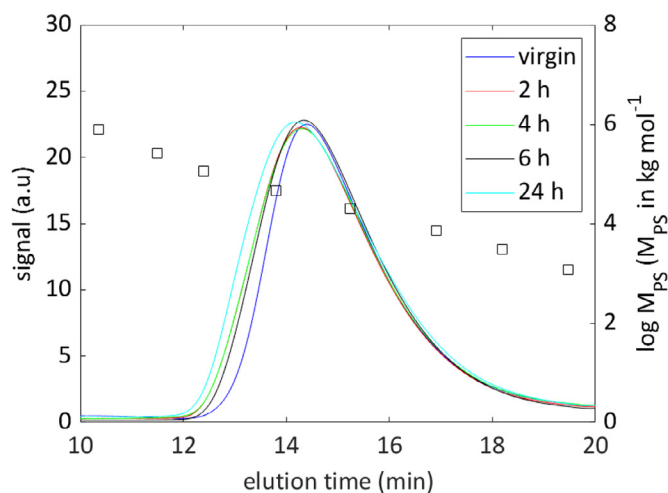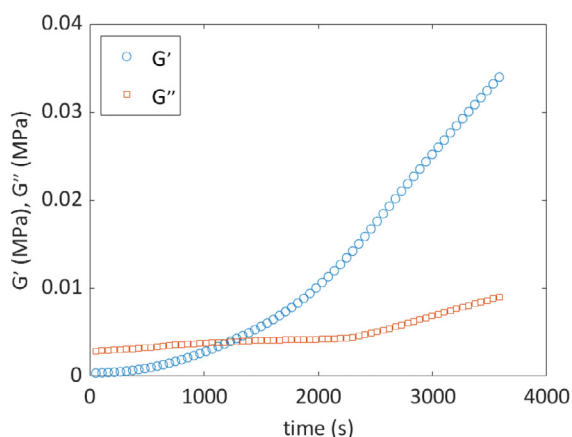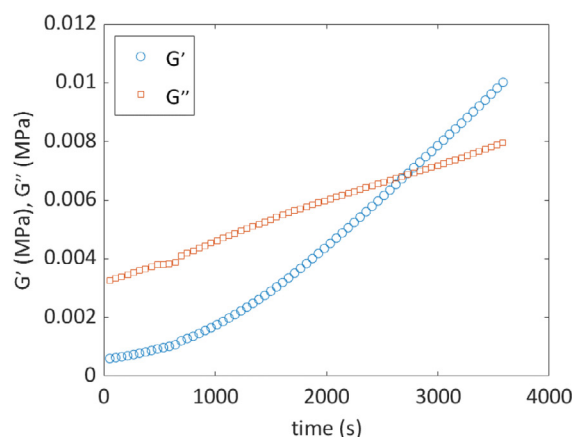- above T_g, there is almost no rubbery plateau, as expected for a polymer with short chains [20].

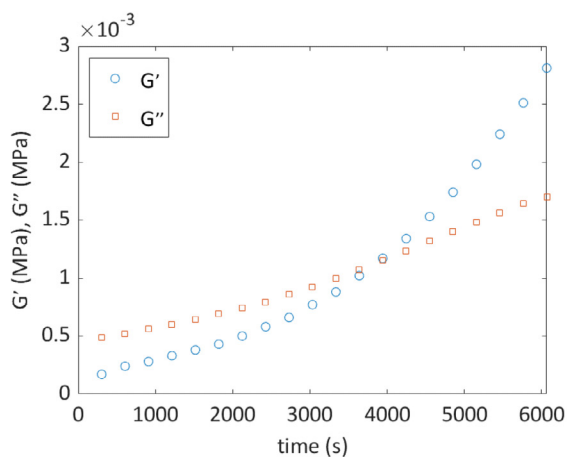**Fig. 6.** GPC Chromatograms of PPSU 1 aged at 280 °C under air (□ symbols correspond to PS calibration).

During ageing, the main changes in the α relaxation domain are consistent with a predominant crosslinking behaviour: T_g increases meanwhile a rubbery plateau appears due to the increase of molar mass (Fig. 11).
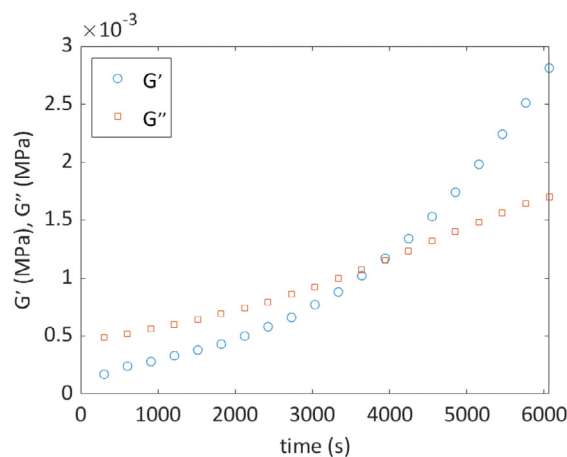
5. Discussion

The aim of this section is to explain the observed changes and make a link between all the observations obtained in this multiscale study. For that purpose, we will:

- discuss on the macromolecular changes,
- comment the glass transition changes in link with molar mass changes,
- discuss on the effect of macromolecular mobility on embrittlement.

5.1. On the mechanisms of degradation

To better discuss on the possible degradation mechanisms, we started from the reported values of bond energies available for example in the case of bisphenol A polysulfone [21,22] which were confirmed by a machine learning based quantum approaches for repetitive units close to PPSU [23] and other polysulfones (see Supplementary data). It seems clear that, for PPSU, the Ar-SO$_2$ bond still is the weakest bond in PPSU (Fig. 12).

At high temperatures, a chain scission mechanism is expected to occur in particular for the Aromatic ring – sulfur bond which seems the weakest link of polymer backbone (as assumed by Rambogin et al. [24]):
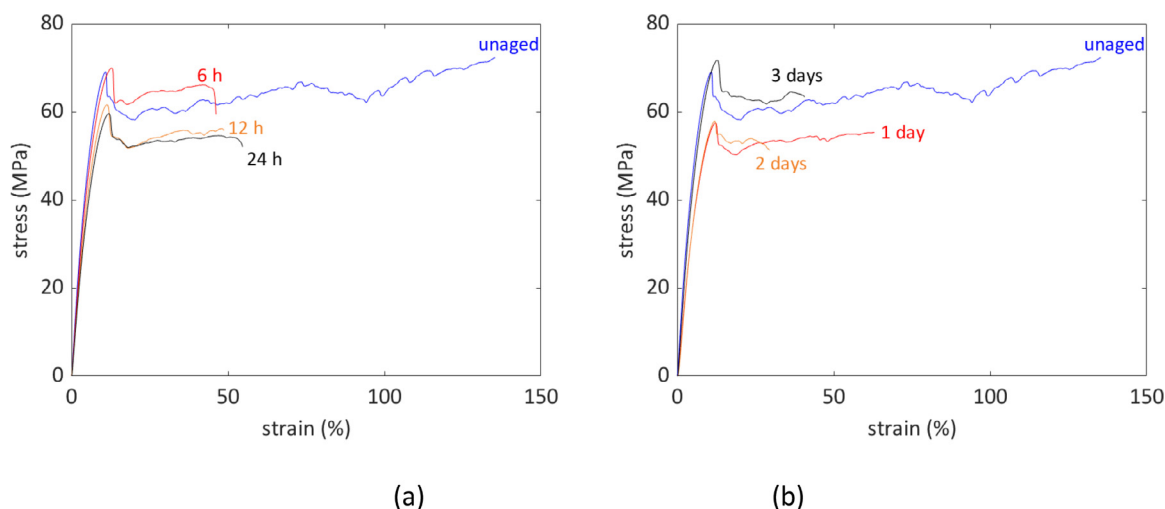

(a)

(b)

(c)

(d)

Fig. 7. Changes of storage and loss modulus of PPSU 1 (a), PPSU 2 (b), PES (c), PEES (d) at 400 °C under inert atmosphere.

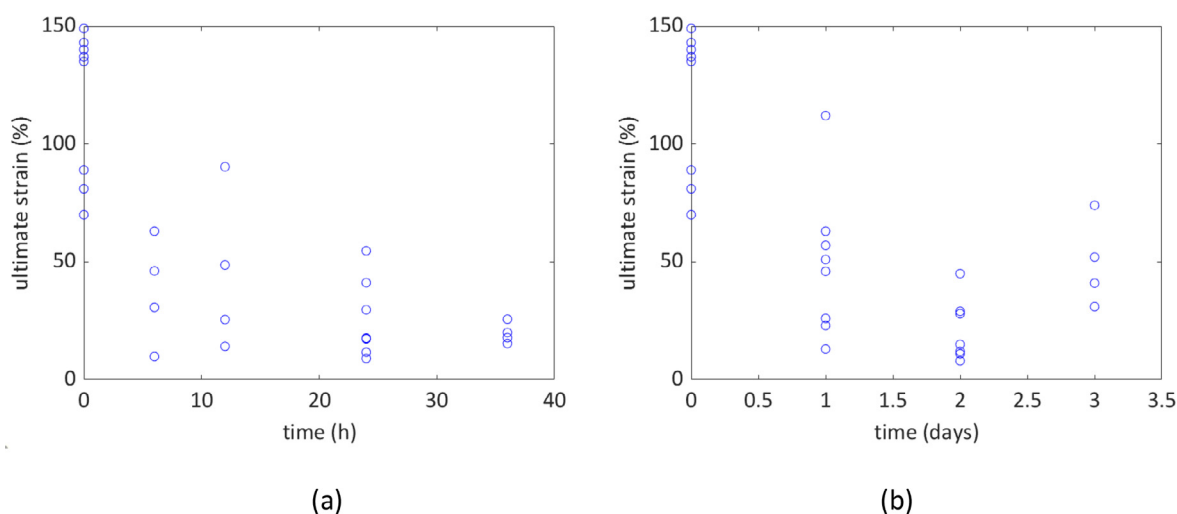**Fig. 8.** Stress strain curves for PPSU 1 aged at 280 (a) and 250 °C (b) under air.

Fig. 9. Changes of ultimate strain for PPSU 1 aged at 280 (a) and 250 °C (b) under air.

Table 3
Calculation of Glass transition for several polysulfones and comparison with literature data (0, 1 and 2 correspond to the occurrence of groups in considered polymers).

Group	Y_{gi} (K kg mol^{-1})	PSU	PPSU	PES	PEES
-Ar-SO$_2$-Ar-	111	1	0	1	1
-Ar-C(CH$_3$)$_2$-Ar-	87	1	0	0	0
-O-Ar-O-	47.5	0	1	0	1
-Ar-	35	0	1	0	0
>SO$_2$	32.5	0	1	0	0
-O-	4	2	0	1	0
-Ar-Ar-	85	0	1	0	0
Calculated T$_g$ (°C)		199	226	222	215
Theoretical T$_g$ (°C)		190 [27]	217–220 [28]	223–230 [29,30]	205–220 [31,32]

Despite this primary reaction leading to chain scission, crosslinking seems the most prominent reaction. A possible explanation is the following: either chain end radical reacts by coupling or addition with an aromatic ring to give a tetrafunctional or a trifunctional node. According to some authors, the trifunctional crosslinking is favored, at least in the case of high temperature irradiation induced crosslinking [25]. Another possibility is that radical isomerizes and give "middle chain" alkyl radicals reacting to give a tetrafunctional node. This complexity explains why we did not try to discuss our data using Eqs. (1)-3.

According to Scheme 1 and 2, the concentration in chain scission s would be equal to the concentration in crosslink, leading to an increase of both M_n and M_w until the formation of an unsoluble gel. Using now Eq. (1)-3, it seems at least clear that the appearance of a gel means that x is higher than s/4 or maybe s/2 depending on the crosslinking mechanism.

The exact nature of mechanisms for ageing under air (including the contribution of oxygen) remains a grey area. On one side, TGA measurements at 400 °C clearly evidence that oxygen accelerates degradation. On the other side, the difference between very thin
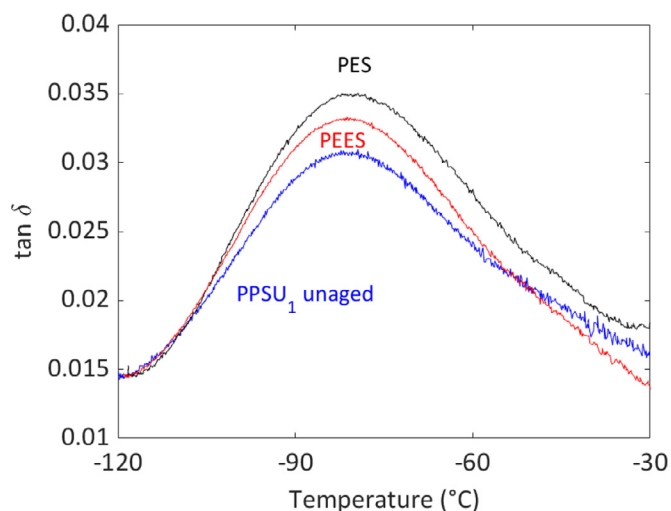
Fig. 10. Dynamical mechanical analysis of polysulfones in the low temperatures domain.

films and "thick" filaments are minor (Fig. 5). Moreover, it can be noted that under pure oxygen, PPSU 2 degrades faster than PPSU 1 meanwhile under inert atmosphere and under air, PPSU 1 degrades faster. In other words, oxygen would play a minor role for the investigated ageing conditions.

The comparison of T_g increase in PEKK (see [15]) and PPSU (Fig. 5), in char yield for PPSU vs other polysulfones (Fig. 2a) and in kinetics of gelation of PPSU vs PES and PEES (Fig. 7) suggests that, in a certain extent, the presence of biphenyl group favors the crosslinking despite its "rigidifying role" on chain dynamics (as it will be developed in the next paragraph). DMA result show that the γ relaxation is almost unchanged with ageing. According to [19], this relaxation is due to sulfones or bibenzyl sulfone groups suggesting that these latter are not degraded during ageing meanwhile biphenyl groups would be the principal site of crosslinking. This remains to be firmly established in future works.

5.2. On the glass transition values

The glass transition values for unaged polymers can easily described in terms of structure properties relationships such as those proposed by Van Krevelen [26]:

$$T_g = 1000 \frac{\sum Y_{gi}}{M_{UCR}} \quad (4)$$

Where M_{UCR} is the molar mass of the whole repetitive unit (i.e. the monomer) and Y_{gi} the contribution of elementary groups (sulfones, aryl…) to T_g.

The contribution of common constitutive groups is well-known for elementary groups (e.g. sulfones, ethers, aromatic ring) but grey zones remain on their values when they are combined together in the case of aromatic polymers. For example, the direct use of the set of values given in [26] did not allow to predict the glass transition observed for PPSU (this work) and PSU for example [27]. We thus employed the following approach:

① PES and PESU are the two most documented members of the family of aromatic polysulfones. The contribution for Ar-

SO_2-Ar, Ar-C(CH$_3$)$_2$-Ar and $>O$ are given in Van Krevelen's monograph [26] and allow a nice agreement between experimental and theoretical values

② In the case of polyether ether sulfone, the only possibility to reconcile experimental and theoretical values is to increase the contribution for O-Ar-O (from 37.4 to 47.5 K kg mol^{-1})

③ In the case of PPSU, using the contribution of Ar and SO$_2$ groups given in Van Krevelen's monograph, and 47.5 K kg mol^{-1} for O-Ar-O, the only possible agreement can be obtained by increasing significantly the Y_{gi} contribution for biphenyl group (from 70 to 85 K kg mol^{-1}), highlighting the positive effect of this group on rigidity.

Calculations are summarized in Table 3.

During ageing however, average molar mass values are modified because of chain scission and/or crosslinking. Molar mass and T_g are correlated by the Fox Flory formula based on the assumption that free volume comes from chain ends [33]:

$$T_g = T_g - \frac{k_{FF}}{M_n} \quad (5)$$

k_{FF} is a priori unknown for PPSU but it can be shown that it is directly proportional to $T_{g\infty}$ [34]:

$$k_{FF} \sim a \cdot T_{g\infty} \quad (6)$$

Making for example comparisons between PC for which: $(T_{g\infty})_{PC} = 434$ K and $(k_{FF})_{PC} = 187$ K kg mol^{-1}, and PPSU, for which $(T_{g\infty})_{PPSU} \sim 510$ K, it gives $(k_{FF})_{PPSU} \sim 220$ K kg mol^{-1}. According to Fig. 13, experimental data fit well with the "Fox Flory " linear regression based on those calculations.

It is noteworthy that there are only few data corresponding to T_g above 225 K which can be justified as follows: according to Eq. (3), the appearance of a gel corresponds to a crosslink concentration $x_{gel} \sim 1/M_{w0} \sim 0.033$ mol kg^{-1}. Using now Eqs (1) and (5):

$$T_g - T_{g0} = k_{FF} \cdot (x + cond - s) \quad (7)$$

So that, if crosslinking predominates: $T_g - T_{g0} \sim k_{FF}.x$ so that $(T_g)_{gel} \sim T_{g0} + 6$ K, in agreement with the here above observation.

5.3. On the embrittlement mechanisms

During ageing the following trends are observed:

① there is almost no change of yield stress. This result is quite surprising in a first approach since it is well known that [35]:

$$\sigma_y = C(T_g - T) \quad (8)$$

Where σ_Y is the yield stress, T_g the glass transition temperature and T the temperature at which samples are mechanically tested.

In other words, changes in T_g should result in change in σ_Y. This is for example well verified in the case of physical ageing of polyamides by water diffusion where the presence of water induces both a decrease in T_g and in σ_Y [36]. Here, despite a clear crosslinking, σ_Y remains almost constant within the timescale of embrittlement. Let us fist note that according to initial values of σ_Y and T_g, the Kambour parameters (C in Eq. (8)) should be around 0.3 MPa K^{-1}. According to Fig. 5, T_g increases by less than 5 °C
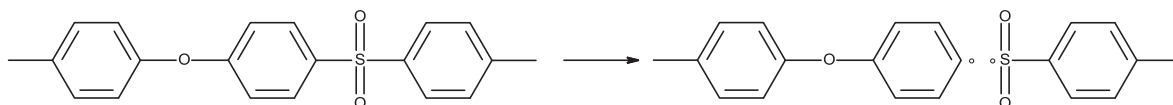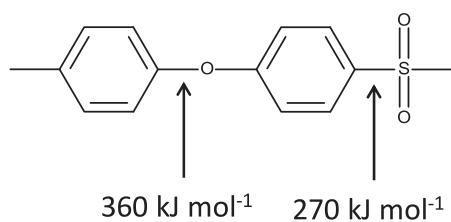

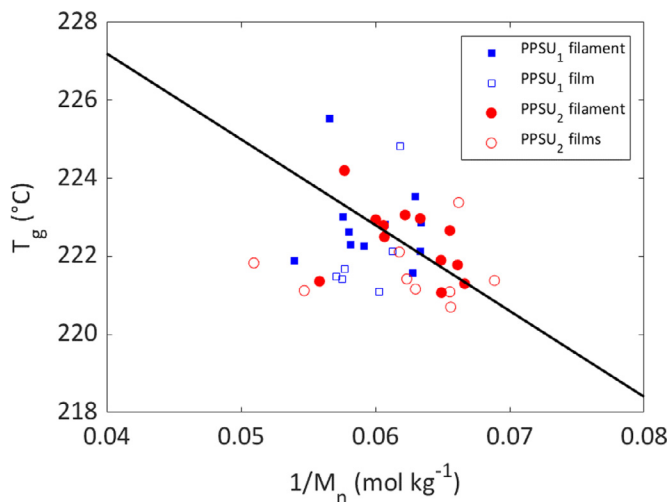**Scheme 1.** Possible primary chain scission event.
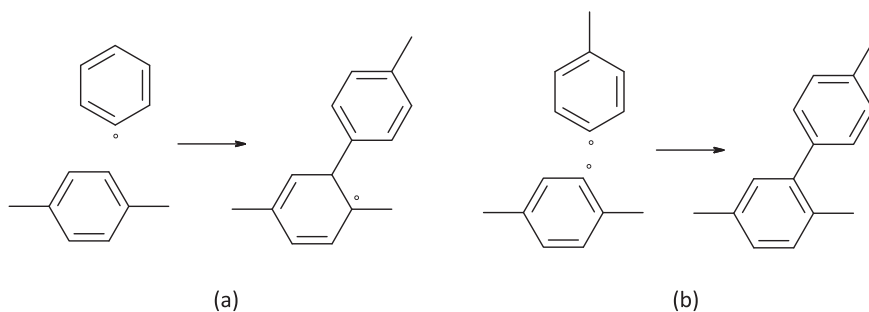
Scheme 2. Possible crosslinking mechanism by addition (a) or coupling (b).

(a)

(b)
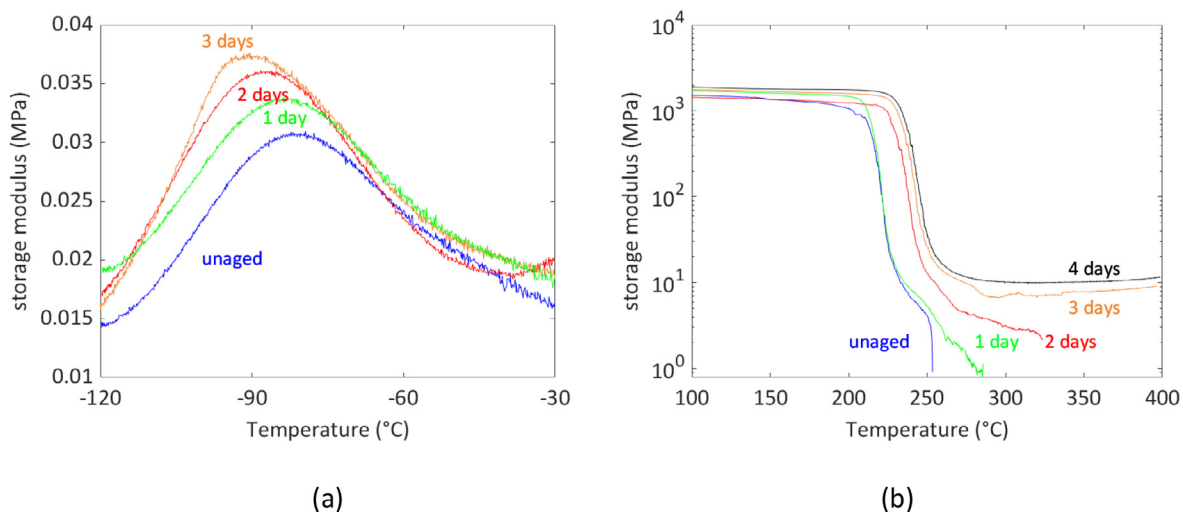
Fig. 11. Dynamical mechanical analysis of polysulfones (virgin and aged at 280 °C) in the low (a) and high (b) temperatures domain.

Fig. 12. Estimation of some Bond Dissociation Energies in PPSU.

Fig. 13. Fox Flory plot of virgin and degraded PPSU's (straightline corresponds to theoretical Fox Flory plot: $T_g = 236 – 220/M_n$).

during the first 24 h ageing at 280 °C (i.e. the time to embrittlement, according to Fig. 9) meaning that σ_y should increase only by 1.5 MPa. In the same time, there is no argument justifying that C remains constant. Having in mind that C value depends on molecular parameters such as the free volume associated to short motions allowing plasticity), it might strongly change during chemical ageing.

② The slight decrease in elastic modulus is also worth to be discussed. From a theoretical point of view, elastic modulus of amorphous glassy polymers depends on the density of cohesive energy and the occurrence of sub glassy relaxations. Here, it seems that sub glass relaxations are hardly changed by ageing suggesting that the small elastic modulus decrease would come from the disappearance of very cohesive groups and possibly their conversion into less cohesive ones.

③ The other main visible effects of ageing are the decrease in ultimate strain. It seems consistent with the fact that the appearance of crosslink nodes seems to decrease the capability of polymer to reach high stretching ratio (identically for example to elastomers). PPSU seems to stay partly ductile (in the conditions of mechanical tests) which is consistent with the fact that the relaxation associated to sub glassy transition does not vanish during ageing (Fig. 11a).

6. Conclusion

This paper deals with the thermal degradation of PPSU in rubbery conditions. The degradation was shown to induce a major crosslinking, in particular in processing conditions (as observed in particular by rheometric measurements). The overall crosslink-

ing occurring during thermal degradation and the various processing steps limits the possibility of multiple recycling steps of those polymers (even if it the degradation at lower temperatures should also be investigated to fully conclude). It seems that the presence of bibenzyl groups favors this crosslinking, as illustrated by some comparisons of crosslinking kinetics in molten state with other aromatics polymers. From a mechanical point of view, PPSU loses a great part of its plasticity but never gets totally brittle. The exact nature of mechanisms (observed at molecular scale) remains open together with a more detailed understanding of structure–stability relationships involved in the stability of polysulfones, in particular with the influence of synthesis methods and end chain nature on chemical stability [37].

Declaration of Competing Interest

We hereby confirm that we have no conflict of interest with the paper

Acknowledgements

Supplementary materials

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