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Polyethersulfones upcycling to luminescent materials by aminolysis

Johan Liotier^a, Leila Issoufou Alfari^b, Benoit Mahler^b, Thomas Niehaus^b, Christophe Dujardin^b, Simon Guelen^c, Vincent Schanen^c, Véronique Dufaud^{a,*}, Jean Raynaud^{a,*} and Vincent Monteil^{a,*}

Upcycling of polyethersulfone (PES), a high-performance polymer based on an aromatic-rich aryl-ether-based backbone, can advantageously yield both starting Bisphenol S (BPS) comonomer and valuable OLED derivatives, providing complete atom valorisation strategy for PES waste. Deprotonated selected amines proved particularly efficient at depolymerizing PES at moderate temperatures (~ 120 °C). The recycled monomer yields validate the back-to-monomer chemical recycling method for industrial compliance. The OLED derivatives afforded by the same simple process can easily be isolated and promote an innovative upcycling strategy using polymer-to-valuable chemicals, a very relevant approach to help tackle the ever-growing plastic waste remediation.

1. Introduction

Polymer waste, often commonly called plastic waste, is a major problem for nowadays world. The disposal of polymers, including thermoplastics, using obsolete landfilling or incineration methods creates many pollution issues. In this sense, recycling “plastics” is becoming a necessity to address ever-growing wastes and reduce the quantity released leaking into the environment. One way of recycling polymers is mechanical recycling. It consists in reprocessing the polymers by melting it, using for instance optimized extrusion processes.¹ This process is industry-compliant but usually yields downgraded materials.² Indeed, thermoplastics are reprocessed in the melt at high temperature and are thus prone to partial chain degradation (reduction in molar masses, functionalities and thus mechanical and chemical properties).^{3,4} To tackle this issue, the chemical transformation of this waste into useful intermediates or small molecules and even monomers where possible, *a.k.a* chemical recycling, has risen. Chemical cleavage of the polymer chain can be used in a circular strategy to come back to the monomer and eventually return to the virgin polymer without any loss of intrinsic properties.^{5,6} Another strategy is to cleave the polymer to obtain functional molecules or intermediates that are useful in a different industrial loop.⁷⁻⁹ If the properties of the new product are substantial, one can end up upcycling the polymer waste.¹⁰ It is the era of waste to chemicals rather than crude oil to chemicals.^{2,11,12} This strategy is also investigated for the valorisation of lignin to obtain functional aromatic rings from a renewable bio-based polymer waste and abundant resource.¹³⁻¹⁵ For industrial polymers, this strategy could be used to recycle/upcycle polymer wastes from the production chain or even post-consumer wastes at the end of their life cycle. This strategy is even more valuable and for the moment economically viable for high-value polymers, such as polyarylethers.^{16,17} In this vein, the aminolysis of polyethersulfone (PES) (Figure 1) has been investigated with ethylenediamine.¹⁸ This aminolysis provided a waste-to-functionalised oligomers and/or small molecules strategy, with amine and phenol products useful for the synthesis of other polycondensates, albeit with a hampered

control of functionality, or more likely for new platform industrial molecules.¹⁹ Herein, we develop an upcycling strategy that goes beyond back-to-monomer chemical recycling, additionally providing useful luminescent moieties from PES waste and selected amines as depolymerizing reagents.

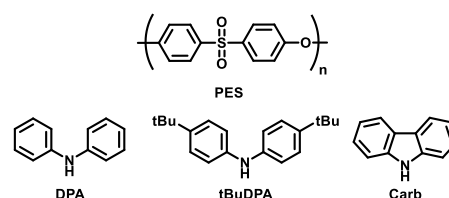


Figure 1: Structure of PES and selected amines.

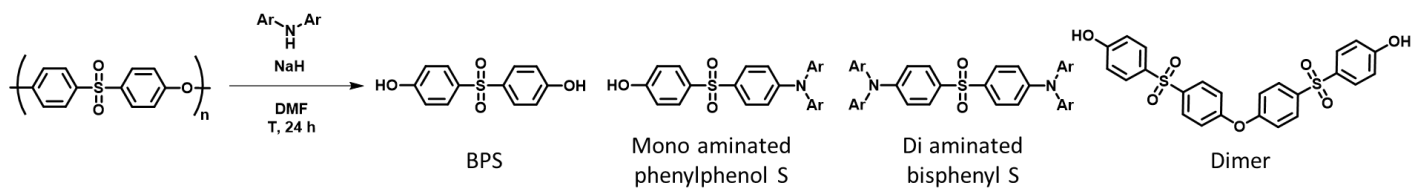
Indeed, the repeating unit of PES has an interest for the synthesis of luminescent materials presenting Thermally Activated Delayed Fluorescence (TADF).^{20,21} This kind of materials has already been reported and have valuable properties.²²⁻²⁴ These materials include aryl-amine motifs that could be harnessed through the use of parent anilines (or corresponding bases) for the aminolysis of the polymer. The three selected amines for the depolymerisation are diphenylamine (DPA), bis(4-(tert-butyl)phenyl)amine (tBuDPA) and carbazole (Carb). Their structures are presented in Figure 1. The targeted class of luminescent materials are very useful for the fabrication of OLEDs with high External Quantum Efficiency (EQE).²⁵⁻²⁷

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Electronic Supplementary Information (ESI) available: general procedure for aminolysis; absorption and emission spectra; DFT modelling; photoluminescence decay.

Table 1: Results of the aminolysis with different reaction conditions and amines; displayed yields are isolated yields.



Entry	Amine	Amine equivalent	Temperature (°C)	BPS yield (%)	Mono-aminated product (%)	Di-aminated product (%)	Dimer yield (%)	Conversion (%)
1	tBuDPA	2	100	0	/	/	/	/
2	tBuDPA	2	120	17	/	/	/	/
3	tBuDPA	3	120	52	25	0	17	94
4	DPA	3	120	34	13	21	31	100
5	Carb	3	120	50	12	21	17	100

Here, we report a new process of complete depolymerisation of PES using aryl amines to cleave the aryl ether bonds to obtain readily high-value fluorescent compounds that could be easily isolated as well as the return to the BPS comonomer, thus validating the back-to-monomer chemical recycling and additionally the upcycling to OLEDs strategy.

2. Material and methods

All reactants and solvents were purchased from Sigma Aldrich. The polyethersulfone (PES) Veradel® product with a $M_n \approx 45\,000$ Da was provided by SYENSQO. The absorption spectra were recorded with a UV-Vis spectrometer Evolution 220 from Thermo Scientific. The fluorescence spectra were recorded with an Edinburgh Instrument FS5 fluorimeter (equipped with an integration sphere for quantum efficiency measurements). LC-MS was performed at the CCSM (Mass Spectrometry Center at Villeurbanne) using a U3000 UPLC from Thermo Fisher Scientific and an Impact II mass spectrometer from Bruker.

3. Results and discussion

3.1. Aminolysis of PES

In order to depolymerise the PES chains by aminolysis, we decided to use the deprotonated forms, amides, to increase the intrinsic reactivity of the amines. Selected aromatic amines were reacted with NaH in DMF as previously described.²³ The use of DMF had another interest since PES is soluble in this solvent. As a result, PES could be added directly into the amide solution once preformed. After the reaction time, the reaction mixture was poured into iced water and acidified using 2 M HCl. Once acidified, some products crashed out and were filtrated. This solid mixture contained luminescent materials alongside oligomer products. The filtrate was then extracted by ethyl acetate to obtain pure monomer Bisphenol S (BPS).

Firstly, bis(4-(tert-butyl)phenyl)amine (tBuDPA) was used as amine for the optimisation of the depolymerisation process. The temperature and number of amine equivalents were optimised as presented in Table 1. The synthetic and purification protocols as well as the detailed characterizations of isolated products are displayed in the Supporting Information for each entry of Table 1. The ¹H NMR spectra of the filtered solids resulting from the optimisation are presented in Figure 2 alongside with the native PES and BPS spectra for comparison.

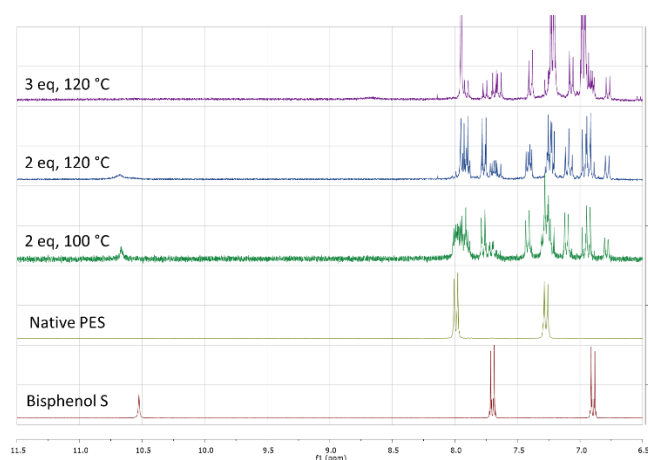


Figure 2: ¹H NMR of the depolymerisation process obtained with tBuDPA at 100 °C and 120 °C with 2 and 3 equivalents of amine alongside with the ¹H NMR of the native PES and commercial BPS.

Firstly, all presented reactions have resulted in the degradation or depolymerization of the native PES. Indeed, the signals corresponding to the starting polymer do not appear anymore in the filtered products rather suggesting the formation of diverse products (see also ESI, with NMR spectroscopy and liquid chromatography corresponding analyses). With two equivalents of amine at 100 and 120 °C, a complex signal appears at 7.85 and 8.05 ppm corresponding to PES oligomers. These signals diminish from 100 °C to 120 °C and this decrease corresponds to the diminution of the number of signals obtained by Liquid Chromatography (LC) (See ESI, Figures S2 and S6). With three equivalents at 120 °C, excess of amine is present in large

Table 2: Optical characteristics of **DiDPA**, **DPA-OH**, **tBuDPA-OH**, **DiCarb** and **Carb-OH**. (Absorption: 2.10^{-5} M in DCM; Emission: dilution to obtain an optical density of 0.1 in DCM, Excitation at the λ_{\max} absorption)

Product	λ_{\max} absorption (nm)	ϵ ($L \cdot mol^{-1} \cdot cm^{-1}$)	Optical Band Gap (eV)	λ_{\max} emission (nm)	QY (%)	FWHM _{em} (nm)	Brightness B ($L \cdot mol^{-1} \cdot cm^{-1}$)
DiDPA	350	31 800	3.21	435	85	77	26 900
DPA-OH	330	20 700	3.23	440	83	79	17 300
tBuDPA-OH	335	21 100	3.14	470	61	91	12 800
DiCarb	340	27 800	3.36	420	70	75	19 500
Carb-OH	337	12 400	3.42	420	49	76	6 100

quantity but the signal corresponding to the oligomer product appears as better-resolved doublets likely belonging to a single product (see also ESI, part 1). The extracted **BPS** obtained from these reactions could thus be quantified since it matched our reference **BPS** monomer. At 100 °C, no **BPS** was obtained (Table 1, entry 1). However, at 120 °C, a 17 % yield of **BPS** (calculated in comparison to the repeating unit) with 2 equivalents of amine and a 52 % yield with 3 equivalents. More equivalents of amines were then needed to push the reaction to completion. This increase leads to the apparition of the aminated/nitrogen-containing compounds but also increases the formation of **BPS**. This surprising effect could be attributed to the strong basic behaviour of the amide tempering its nucleophilicity or more likely by the fact that these amines/amides are also excellent departing/leaving groups. If the non-aromatic intermediates (Meisenheimer complexes) are stable enough, some -OH groups could be formed during the HCl quenching of the reaction. This effect could explain why the product distribution does not follow a statistical behaviour. This also suggest that the added arylamine moiety influences the addition of the second functionality. After purification of the solid product, we could evidence that with these last conditions, the longest oligomer product obtained is a **BPS**-dimer, therefore validating a nearly complete conversion of the native **PES** to small molecules.

The influence of other amines with varied steric hindrance and electronic properties on the depolymerisation extent and selectivity was then investigated under the optimized conditions (120 °C and 3 equivalents of amine) and the results are included in Table 1.

Once again, full depolymerisation of **PES** was achieved with a 34 % and 50 % yield in **BPS** monomer for respectively diphenylamine (**DPA**) and carbazole (**Carb**).

This filtered product from the complete depolymerisation could be purified by silica gel column chromatography and three products were isolated: Di-aminated bisphenyl S, Mono aminated phenylphenol S and **BPS**-dimer. These products were obtained in different ratio depending of the selected amine. Interestingly, the di-aminated product is not obtained with the **tBuDPA**. Only the mono-aminated product (**tBuDPA-OH**) is obtained with a 25 % yield. This could be explained by the steric hindrance of the *tert*-butyl unit and the low angle between the phenyl units of bisphenyl S (Figures S24 to S26).

In the case of the depolymerisation with the **DPA** and **Carb**, it is interesting to note that the yields of the mono and di-aminated products are very close. The mono-aminated product is obtained in a 13 % and 12 % yield respectively and the di-aminated product is obtained in a 21 % in both cases.

For each experiment, **BPS** and **BPS**-Dimer are obtained in large quantities. Interestingly, the yield of these products obtained with **tBuDPA** and **Carb** are very close (around 50 % of **BPS** was obtained for each amines and 17 % of the **BPS**-dimer). In the case of the reaction with **DPA**, both products are obtained in a similar yield (around 30 %). These products hold a great industrial potential because they can be used as starting materials to readily obtain recycled **PES**, since they represent one of the two complementary comonomers of the AA/BB type polycondensation reaction to produce **PES**.

3.2. Characterisation of the luminescent materials

Five luminescent products could be obtained from the aminolysis of **PES** and are referred to as **DiDPA**, **DPA-OH**, **tBuDPA-OH**, **DiCarb** and **Carb-OH** (Figure 3). The absorption of the materials was recorded in DCM (2.10^{-5} M) and their luminescent properties were analysed with an excitation beam set at the maximum of absorption of the analysed solution (solution diluted to obtain an optical density of 0.1). The optical characteristics are presented in Table 2 and the absorption and emission spectra are presented in Figure 4a, Figure 4b and SI section 2.

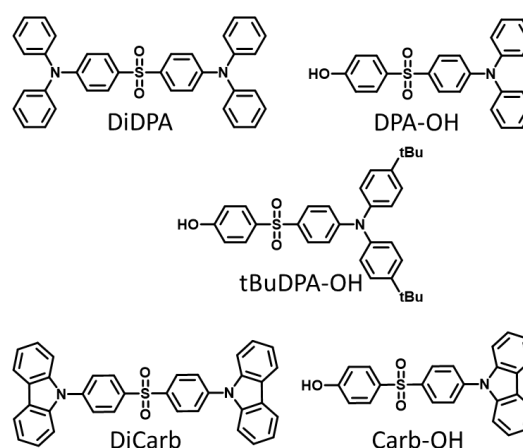


Figure 3: Structures of the five luminescent materials obtained by aminolysis of **PES**.

The comparison between the molecule **DiDPA** and **DiCarb** with their mono-aminated homologues **DPA-OH** and **Carb-OH** shows that the presence of two donating unit implies a higher molar extinction coefficient ϵ than their mono-aminated counterparts going from 31 800 $L \cdot mol^{-1} \cdot cm^{-1}$ to 20 700 $L \cdot mol^{-1} \cdot cm^{-1}$ for the **DPA** products and

from 27 800 L.mol⁻¹.cm⁻¹ to 12 400 L.mol⁻¹.cm⁻¹ for the **Carb** products. In addition, we observe a small hypsochromic shift between the absorption maximum of the di-aminated and mono-aminated products going from 350 nm to 330 nm for the **DPA** products and from 340 nm to 337 nm for the **Carb**. The fact that the absorption of the compounds bearing **Carb** is lower than the ones bearing the **DPA** could be explained by DFT (Figures S24 and S25). In fact, the HOMO-LUMO overlap is lower in the case of the **Carb** compared to **DPA**. This could facilitate the π - π^* transition in the case of **DPA** explaining the lower absorption intensity of the **Carb** family.²⁸ In the case of the **tBuDPA-OH**, the absorption maximum is located at 335 nm, which corresponds to a 5 nm bathochromic shift of the absorption band compared to **DPA-OH**. This is due to the addition of the *tert*-butyl units making the DPA unit slightly more donating. The ϵ of **tBuDPA-OH** is 21 100 L.mol⁻¹.cm⁻¹, which is very close to the one of **DPA-OH** since the conjugated part is not modified.

For the emission, **DiCarb** and **Carb-OH** both have a maximum of emission at 420 nm with a similar full width at half maximum (FWHM_{em}) of 75 and 76 nm. The quantum yields (QY) of the two molecules differ and are equal to 75 % for **DiCarb** and 49 % for **Carb-OH**. As a result, the brightness of **DiCarb** (19 500 L.mol⁻¹.cm⁻¹) is higher than the one of **Carb-OH** (6 100 L.mol⁻¹.cm⁻¹). **DiDPA** and **DPA-OH** have a maximum of emission at 435 and 440 nm respectively with FWHM_{em} of 77 and 79 nm. The QY and brightness of the DPA family are 85 % and 26 900 L.mol⁻¹.cm⁻¹ and 83 % and 17 300 L.mol⁻¹.cm⁻¹ respectively. In the case of **tBuDPA-OH**, the maximum of emission is at 470 nm with a FWHM_{em} of 91 nm. Its QY is 61 % and its brightness is 12 800 L.mol⁻¹.cm⁻¹. We can see an interesting shift of the emission band with the increase of the donating strength of the amine. We observe that we go from 420 nm for the **Carb**, the least donating unit, to 470 nm for the **tBuDPA**, the most donating unit. The FWHM_{em} of the compounds **DiDPA**, **DPA-OH**, **DiCarb** and **Carb-OH** are around 75 nm but the FWHM_{em} of **tBuDPA-OH** is 91 nm. This is visible to the naked eye as the emitted light of this compound is whiter. The xy coordinates could be calculated from the emission spectra and are presented in Figure 4c. Only **tBuDPA-OH** seems to stand out from the group by being closer to the white neutral colour.

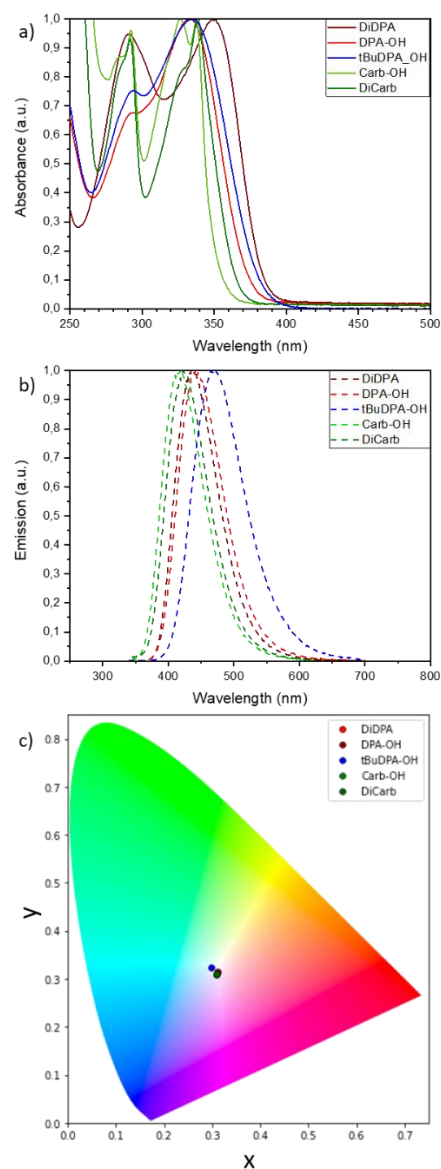


Figure 4: a) Absorption spectra of **DiDPA**, **DPA-OH**, **tBuDPA-OH**, **Carb-OH** and **DiCarb** (2.10^{-5} M in DCM); b) Emission spectra of **DiDPA**, **DPA-OH**, **tBuDPA-OH**, **Carb-OH** and **DiCarb** (dilution to obtain an optical density of 0.1 in DCM, Excitation at the λ_{\max} absorption); c) xy colour coordinates obtained for the emission of each molecules placed on the 1931 chromaticity diagram (calculated with Python)²⁹

The photoluminescence (PL) decay was measured for **DiDPA** as it has the most intense luminescence. The results are presented in ESI (Figure S27). As already described in the literature,²³ the PL decay follows a bi-exponential behaviour as follows:

$$\text{Eq1:} \quad A = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + B$$

The first exponential component corresponds to a normal fluorescence behaviour with a decay time τ_1 of 5.1 ns. The second exponential corresponds to thermally activated delayed fluorescence with a decay time of 79.2 ns. These properties corresponds to literature,²³ which confirms that our methods of upcycling can yield the same product with similar properties as a classical synthesis.

Conclusions

We provide a new strategy to recycle/upcycle **PES** in a single operation. We developed an aminolysis process achieving complete conversion of **PES** to useful separable small molecules. On the one hand, this reaction allows to recover ~50 % of **BPS** monomer and some dimer which could be used as starting materials for the repolymerisation of **PES** – with Cl- or F-based comonomers – by providing the OH-containing necessary comonomer of the polycondensate. On the other hand, by carefully selecting the amine structural features, we obtained five luminescent materials, which could be fully characterised. To push the formation of these materials, one could think to work on the quenching methodology to avoid the formation of the –OH substituted compounds. However, harnessing **PES** depolymerization, we could for instance derive the straightforward synthesis of **DiDPA** compound yielding an 85 % quantum yield with a FWHM_{em} of 77 nm and similar PL properties from an industrial waste material. We will continue on developing the waste-to-chemicals strategy to valorise other high-value polymer waste.

Author Contributions

Conceptualization: JL, VD, JR, VM

Methodology: JL, VD, VM, JR

Resources: SG, VS

OLED characterization: JL, LIA, BM, TN, CD

Project administration, Supervision: SG, VM, VD, JR, VM

Writing – original draft, review & editing: JL, VD, VM and JR with participation of all authors

Conflicts of interest

There are no conflict of interest to declare.

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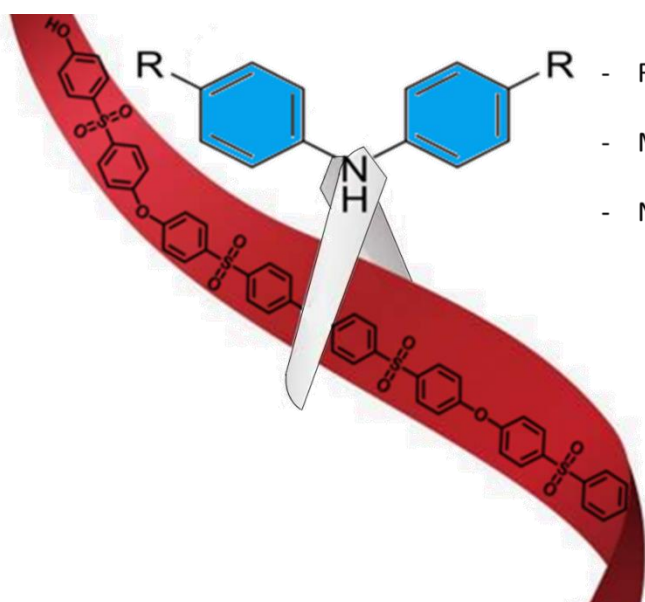
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- Full conversion of PES to small molecules
- Monomer and dimer obtained for repolymerisation
- New luminescent materials obtained from polymer waste

