

## Synthesis of novel fullerene-functionalized polysulfones for optical limiting applications <sup>☆</sup>

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### ABSTRACT

High-performance materials in the optical field, with special reference to optical limiting applications, can be obtained by combining nonlinear optical (NLO) active molecules with high optical quality hosts. An interesting method is the synthesis of fullerene–polymer systems. In this paper novel fullerene–polysulfone samples were obtained by direct fullereneation between a commercial sample of polysulfone and fullerene, using electrophilic aromatic substitution reactions in the presence of  $\text{AlCl}_3$  as catalyst. The synthesis was successful; the molecular structures of the samples, confirmed by  $^1\text{H}$  NMR, IR, and UV analyses, indicate that fullerene is covalently bonded to the polysulfone chains.  $\text{C}_{60}$  is random distributed along the macromolecules, in amounts varying from 0.5 to 3.2 mol%. The  $\text{C}_{60}$ –polysulfone materials show a very high thermal stability, a glass transition temperature depending on the  $\text{C}_{60}$  content, and interesting optical limiting properties.

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### 1. Introduction

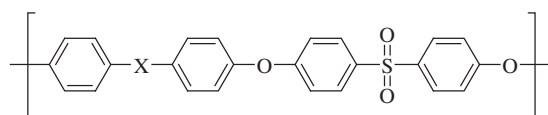
Since its discovery at the end of the 20th century,  $\text{C}_{60}$  fullerene showed unexpected and interesting properties, such as superconductivity, ferromagnetism, anti-HIV bioactivity, and optical nonlinearity (NLO). In particular, its optical limiting (OL) properties were thoroughly researched: among different classes of materials, fullerenes are some of the most promising high-performance molecules at 532 nm. Optical limiting occurs when the optical transmission of a material decreases with increasing laser fluence, a property fit for the protection of sensors and the human eye. For fullerene and its derivatives, it is fully established that the primary NLO mechanism is the reverse saturable absorption (RSA). Under photoexcitation, RSA involves absorption from excited states with cross-sections larger than ground-state, therefore leading to nonlinear absorption [1].

However,  $\text{C}_{60}$  is hardly processable into a solid material due to its very low solubility in most organic solvents. Different strategies have been pursued based on physical procedures or chemical syntheses, using unmodified or functionalized fullerenes [2–5]. The optical limiting properties of these new, nano-structured, advanced materials have been thoroughly analyzed [6–8]: differences

were found depending on the material state, be it solution or solid film [9,10]. Anyway, it appears that a convenient way to exploit the peculiar characteristics of fullerenes is to combine them with the good processability of polymers by preparing  $\text{C}_{60}$ -containing polymers.

In the case of polymeric host materials, one of the most common problems for NLO applications is the aggregation of  $\text{C}_{60}$  leading to an adverse effect on the RSA efficiency. The covalent attachment of fullerenes to polymeric chains helps to solve this problem: several synthetic strategies have been developed, based, for example, on the use of prefunctionalized polymers or  $\text{C}_{60}$  derivatives. The direct fullereneation between  $\text{C}_{60}$  and polymers is probably the most efficient and economic way to incorporate  $\text{C}_{60}$  cages into the polymer chains. Many fullerene-functionalized polymers, like polycarbonates and polystyrenes, were prepared in this way [11–14]. Innovative  $\text{C}_{60}$ -containing polymers are easily processable and display novel superior properties:  $\text{C}_{60}$ –polycarbonate, for example, has higher solubility in common organic solvents than  $\text{C}_{60}$  and polycarbonate (PC) separately.

Among polymeric matrices, the poly(arylene ether sulfone)s, characterized by the following chemical structure:



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are an interesting class of materials. In particular, when  $-X-$  is  $-C(CH_3)_2-$ , a strong engineering thermoplastic is obtained. This is the most popular polymer in the class of the poly-(arylene ether sulfone)s and is often referred to as polysulfone (PSU).

Therefore, by considering the PSU, the presence of the diphenylene sulfone group in the backbone chain adds important and peculiar features to the polymer. Due to its electron-acceptor properties, the structure is highly resonant and imparts high strength to the chemical bonds. Moreover, the diphenylene sulfone group is responsible for a notable resistance to heat or ionizing radiations, thanks to its ability to dissipate energy without chain scission or cross-linking. As a consequence, PSU possesses good thermal stability and oxidation resistance. On the other hand, ether and isopropylidene linkages impart chain flexibility, making the material easily processable at practical temperatures. PSU can also safely come into contact with food and potable water. It is therefore an engineering material that can be exploited in high performance applications.

PSU is also characterized by good optical properties, like clarity and transparency, which make it suitable, for example, for solar film and ophthalmic lenses preparations [15,16]. In cross-linked copolymers PSU was also studied with reference to optical waveguide devices [17]. Moreover, PSU possess a high glass transition temperature required for second-order nonlinear optical polymers [18,19].

Few NLO active polysulfones, obtained by adding chromophores to the PSU structure, have been reported so far. In 1998, McCarron et al. [20] prepared side-chain NLO active polysulfones through the reaction between chromophores and lithiated PSU. In 2004, PSU qualified as a good host material for electro-optic polymer devices in telecommunication applications [21]. In 2005 Lu et al. described the successful synthesis and characterization of two novel polysulfones containing second-order nonlinear optical chromophores, with high resonant and non-resonant second-order coefficients [22]. Moreover, in 1994, Berrada et al. [23] described the preparation of new conductible polymers, including polysulfones carrying  $C_{60}$  as pendant group. The synthesis was performed by bounding the  $C_{60}$  to the monomer before the polymerization step.

Given the results showed in the literature, it seemed very interesting to try and combine the excellent features of the polysulfone host with the NLO properties of fullerenes, in order to obtain high-performance materials in the optical field. The present paper reports the synthesis of new fullerene-polymers, obtained by direct reaction of  $C_{60}$  and PSU, commercially named Udel. These new samples were extensively characterized: chemical, thermal and optical analyses evidence high quality materials with optical limiting features.

## 2. Experimental part

### 2.1. Materials

High-purity (98%)  $C_{60}$  (Aldrich Chemicals Co. Inc.) was used as received and kept in a dark place before use. Anhydrous  $AlCl_3$  (99.9%) (Sigma-Aldrich Co. Inc.) was used without purification. The solvent, 1,1,2,2-tetrachloroethane, was purchased from Fluka Chemical Corporation and distilled from calcium chloride prior to use. Hexane, dichloromethane (DCM), methanol, tetrahydrofuran (THF), 1,1,2,2-tetrachloroethane (TCE), from Carlo Erba, were reagent grade and no further purification was made. TCE was dried by distillation with  $CaCl_2$  before use.

Polysulfone (PSU) was purchased from Aldrich Chemicals Co. Inc. and was purified before use by dissolution in dichloromethane and precipitation in methanol.

### 2.2. Synthesis

The preparation of  $C_{60}$ -PSU 5 (Table 1) is described here, as an example of the general reaction procedure.

A baked 50 mL three neck round-bottom flask, equipped with a magnetic stirrer, was charged with 0.938 g (2.12 mmol) of PSU, 0.0782 g (0.108 mmol) of  $C_{60}$  and 20 mL of TCE under nitrogen atmosphere. After the complete dissolution of the reagents (over 1 h), the resulting homogeneous mixture was transferred with a syringe to another baked 100 mL three neck round-bottom flask, equipped with a magnetic stirrer and a condenser, containing 0.144 g (1.08 mmol) of  $AlCl_3$  under nitrogen at room temperature. The mixture was then heated to 140 °C for 24 h and, by that time, the initial purple color had switched to dark brown. The mixture was then cooled to room temperature and quenched by drop-by-drop addition of 20 mL of  $H_2O$ /THF mixture (50/50, V/V). The quenched mixture was transferred to a separation funnel and washed with  $H_2O$  (3 × 30 mL). The organic layer was collected and dried over  $Na_2SO_4$ . After filtration, the solvent was evaporated under reduced pressure, leaving brown oil on the flask. The oil was dissolved in 20 mL of dichloromethane and precipitated in 1 L of hexane: the fullerene was solubilized.

The purification procedure was repeated several times in order to thoroughly eliminate the unreacted  $C_{60}$  from the fullereneated-PSU chain solution. A partial loss of the derivatized polymer occurs during the dissolution procedure in hexane.

The resulting powder was filtered off and vacuum-dried at room temperature overnight. 0.856 g of slightly brown polymer was obtained (91% of yield), whose  $C_{60}$  content was estimated to be 2.58 mol% (4.02 wt%) using UV calibration curve. The final product, precipitated and filtrated, appears as a pale yellow powder.

**Table 1**  
Molecular characteristics of the samples.

Sample	$C_{60}$ /PSU feed ratio (wt%)	$C_{60}$ /PSU feed ratio (mol%)	Fullereneated PSU			
			$M_w$ ( $10^{-3}$ ) <sup>a</sup>	$M_w/M_n$ <sup>a</sup>	$C_{60}$ /PSU final ratio <sup>b</sup> (wt%)	$C_{60}$ /PSU final ratio <sup>b</sup> (mol%)
PSU	–	–	62.0	3.8	–	–
Mechanical-mixture	1.85	1.14	62.0	3.9	1.11	0.69
$C_{60}$ -PSU 1-24 h	3.58	2.20	56.0	4.4	1.32	0.82
$C_{60}$ -PSU 1-48 h	3.58	2.20	56.8	4.4	1.57	0.99
$C_{60}$ -PSU 1-72 h	3.58	2.20	54.4	4.8	1.53	0.87
$C_{60}$ -PSU 2	1.71	1.05	59.1	4.6	0.77	0.48
$C_{60}$ -PSU 3	3.58	2.20	49.2	2.4	2.45	1.54
$C_{60}$ -PSU 4	4.72	3.58	51.4	4.7	3.12	1.98
$C_{60}$ -PSU 5	8.34	5.12	40.5	4.8	4.02	2.58
$C_{60}$ -PSU 6	8.47	5.20	47.6	4.9	4.97	3.21

<sup>a</sup> Measured by GPC in chloroform.

<sup>b</sup> Measured by UV-Visible spectrophotometer.

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