

1 *Abstract*

2 **Fluorescent EDOT-functionalized poly-e-**
3 **caprolactone: Synthesis, photophysical and self-**
4 **assembling properties in organic solvents and its**
5 **serendipitously noticed behaviour in protonated**
6 **media**

7 **Anca-Dana Bendrea, Luminita Cianga, Gabriela-Liliana Ailiesei and Ioan Cianga ***

8 "Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

9 **Keywords:** fluorescent nanoparticles; self-assembly; EDOT; oxidant-free polymerization

10 In the last few years several fluorescent poly-e- caprolactones [1-3] were designed, synthesized
11 and subsequently used as nanoparticles [1], nanofibers [2] or scaffolds [3] in various prospective
12 bioapplications. Meanwhile, our interest was directed toward electro - and photoactive moieties -
13 functionalized poly/or oligo-e- caprolactone, that worked as key building blocks (macromonomers)
14 for new grafted conjugated polymers or hybrid systems successfully used as biosensors [4,5] or
15 regenerative medicine [6]. In the same line, the present report is aimed to extend the investigations
16 and to highlight the properties in solution (photophysical, self-assembling) of 3, 4-
17 ethylenedioxythiophene-functionalized poly-e- caprolactone (EDOT-PCL) synthesized by ring-
18 opening polymerization (ROP). The results of the studies in two organic solvents (chloroform and
19 acetonitrile), having different selectivity in relation with the constitutive parts of EDOT-PCL,
20 revealed its propensity for self-assembling, proved by Dynamic Light Scattering (DLS)
21 measurements, while fluorescent emission maxima in the range 310-430 nm, depending on the
22 solvent were evidenced, as well. Moreover, its capability for spontaneous oxidant-free
23 oligomerization, presumably due to and under the action of acidic character of CDCl₃,
24 serendipitously noticed during ¹³C-NMR registration, was subsequently validated by experiments
25 performed in chloroform in the presence of hydrochloric acid. This is an interesting and
26 applications-oriented useful observation which supports that recently demonstration of oxidant-
27 free polymerization of common EDOT in the only presence of some organic acids [7] could also be
28 extended to EDOT-containing more complex structure.

29 **References**

- 30 1. Huang, S., Liu, S., Wang, K., Yang, C., Luo, Y., Zhang, Y., Cao, B., Kang, Y., Wang, M., *Nanoscale*, **2015**, *7*,
31 889-895.
32 2. H. J. Diao, K. Wang, H. Y. Long, M. Wang, S. Y. Chew, *Adv. Healthcare Mater.*, **2016**, *5*, 529-533.
33 3. S. Huang, K. Wang, S. Wang, Y. Wang, M. Wang, *Adv. Mater. Interfaces*, **2016**, 1600259.
34 4. B. G. Molina, A. D. Bendrea, L. Cianga, E. Armelin, Luis J. del Valle, I. Cianga, C. Alemán, *Polym. Chem.*,
35 **2017**, *8*, 6112-6122.
36 5. B. G. Molina, L. Cianga, A. D. Bendrea, I. Cianga, C. Alemán, E. Armelin, *Polym. Chem.*, **2019**, *10*, 5010-
37 5022.
38 6. B. G. Molina, A. D. Bendrea, S. Lanzalaco, L. Franco, L. Cianga, L. J. del Valle, J. Puiggali, P. Turon, E.
39 Armelin, I. Cianga, C. Aleman, *J. Mater Chem B*, **2020**, doi.org/10.1039/D0TB01259A
40 7. E. Tomšík, I. Ivanko, J. Svoboda, I. Šeděnková, A. Zhigunov, J. Hromádková, J. Pánek, M. Lukešová, N.
41 Velychkivska, L. Janisová, *Macromol. Chem. Phys.* **2020**, 2000219.



© 2020 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons by Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).