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Synthesis, Self-Assembling and Photophysical Properties Exploration of Water Self-Dispersible, Grafted Poly(p-Phenylene Vinylene)s with Nonionic, Hydrophylic and Biocompatible Side Chain

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INTRODUCTION & AIM

- **Photonic nanomedicine promotes the progress of early detection and diagnosis of diseases, new modalities of light-guided and light-activated therapies, providing opportunities to advance healthcare technology with unprecedented precision and safety;**
- **Originally designed for the use in electronic and optoelectronic devices, conjugated polymers (CPs) have emerged as one of the most appropriate agents for biophotonics;**
- **Taking the advantages of light harvesting, of light emitting and of photosensitizing capabilities, poly(p-phenylene vinylene)s (PPVs) found applications for various type of bioapplications;**
- **The present communication introduces new amphiphilic, grafted *g*-PPVs, able to self-assembling in aqueous media, forming micellar fluorescent nanoparticles with enhanced stability;**

Table 1. GPC data of **PPV** grafted polymers

Sample	$M_{n,GPC}$ (IPD)[a]	$M_{n,GPC}$ (IPD)[b]
PPV-PEG	3825 (1.13)	44580 (1.13)
PPV-PMeOx	276* (1.02)	8834 (1.07)
PPV-PEtOx	705* (1.07)	10950 (1.1)

a-GPC measured in THF; b-GPC-measured in DMF;
IPD-index of polydispersity; * - unrealistic values

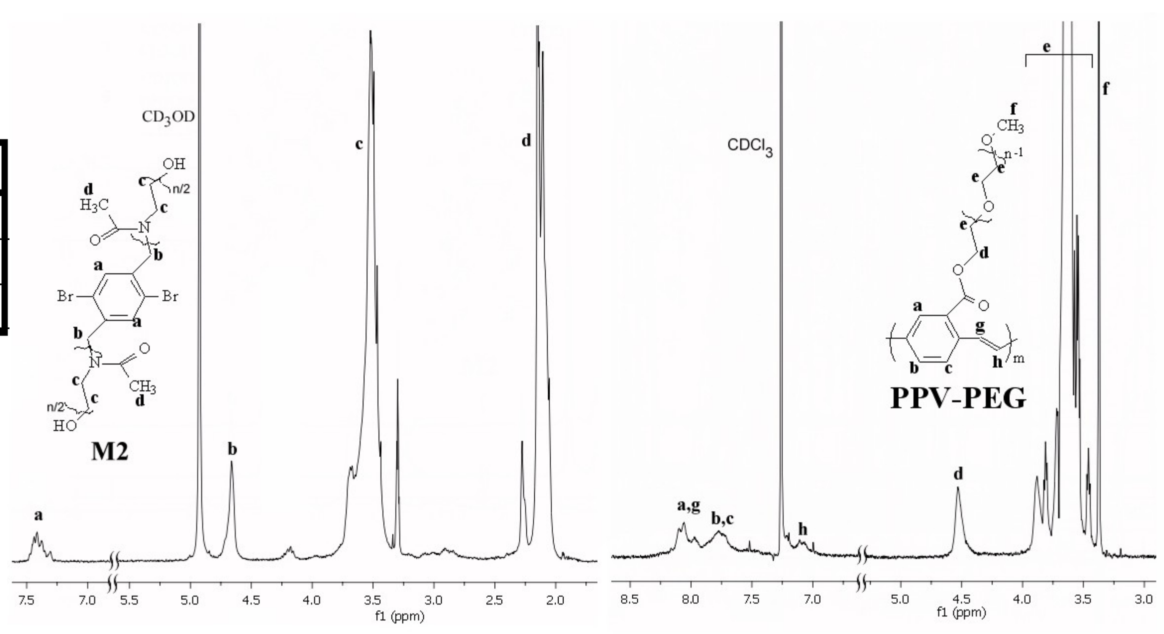


Figure 1. [1]H-NMR spectrum of macromonomer **M2** in CD_3OD and of **PPV-PEG** in $CDCl_3$

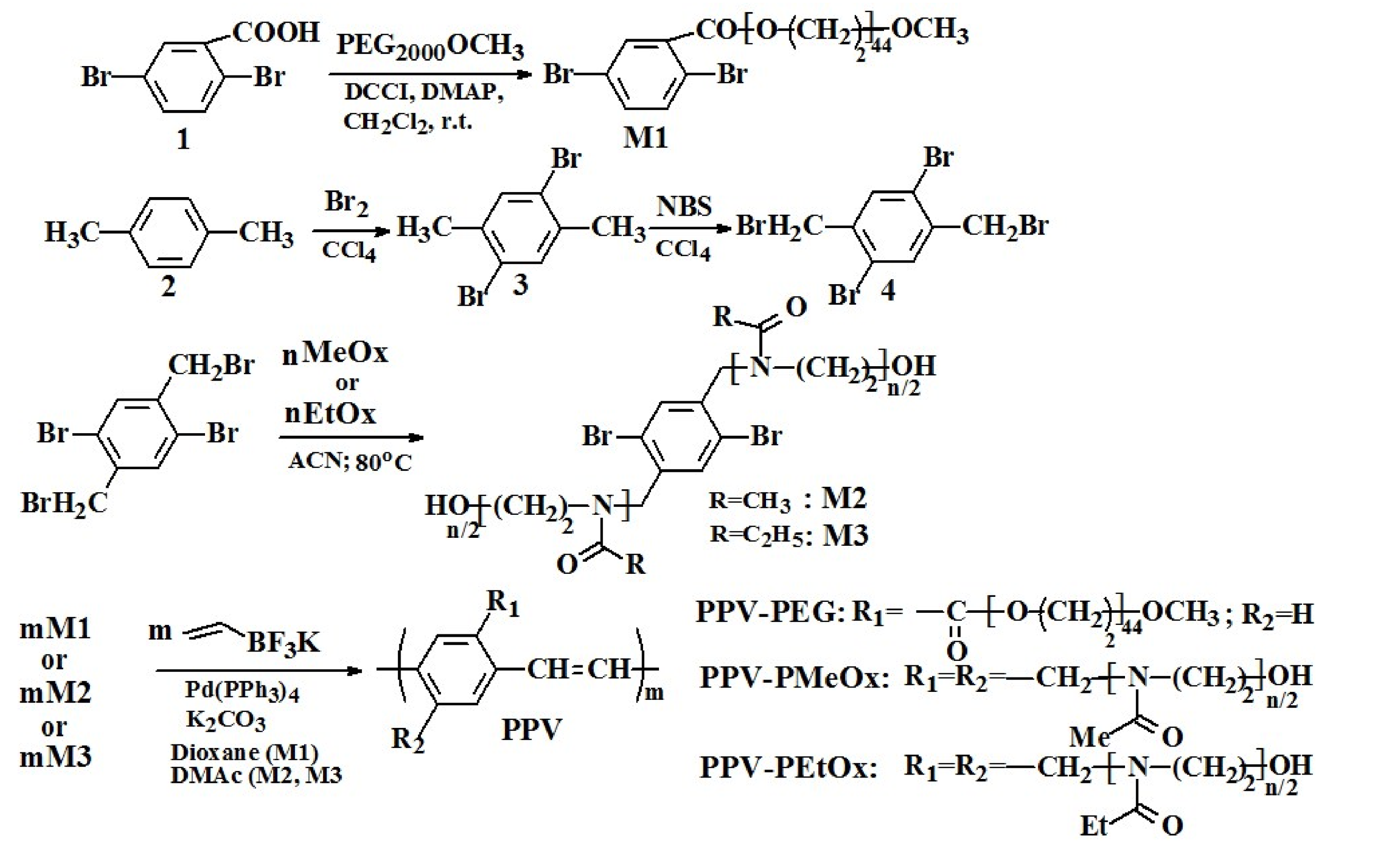
- The lower molecular weight of PPV-PMeOx and PPV-PEtOx, as resulted from GPC measurements (Table 1), could be due to the lower reactivity of bromine function induced by POXA.

RESULTS & DISCUSSION

- Three new dibrominated macromonomers were synthesized by end-group functionalization of PEG2000 monomethylether, poly(2-methyl-2-oxazoline) (PMeOx) or poly(2-ethyl-2-oxazoline) (PEtOx), all of them known as hydrophilic and biocompatible polymers.

Macromonomer **M1** was obtained by "chain end-functionalization" approach, while **M2** and **M3** by "initiation" method, applying controlled cationic ring-opening polymerization (CROP);

- The appropriate combination of the "macromonomer technique" with Suzuki-Heck cascade polycondensation was used for grafted polymers **PPV-PEO, PPV-PMeOx** and **PPV-PEtOx** synthesis .



Scheme 1. The route for synthesis of macromonomers (**M1**, **M2** and **M3**) and of their derived ***g*-PPVs**

DLS and AFM visualization prove that all the synthesized polymers get self-assembled in water

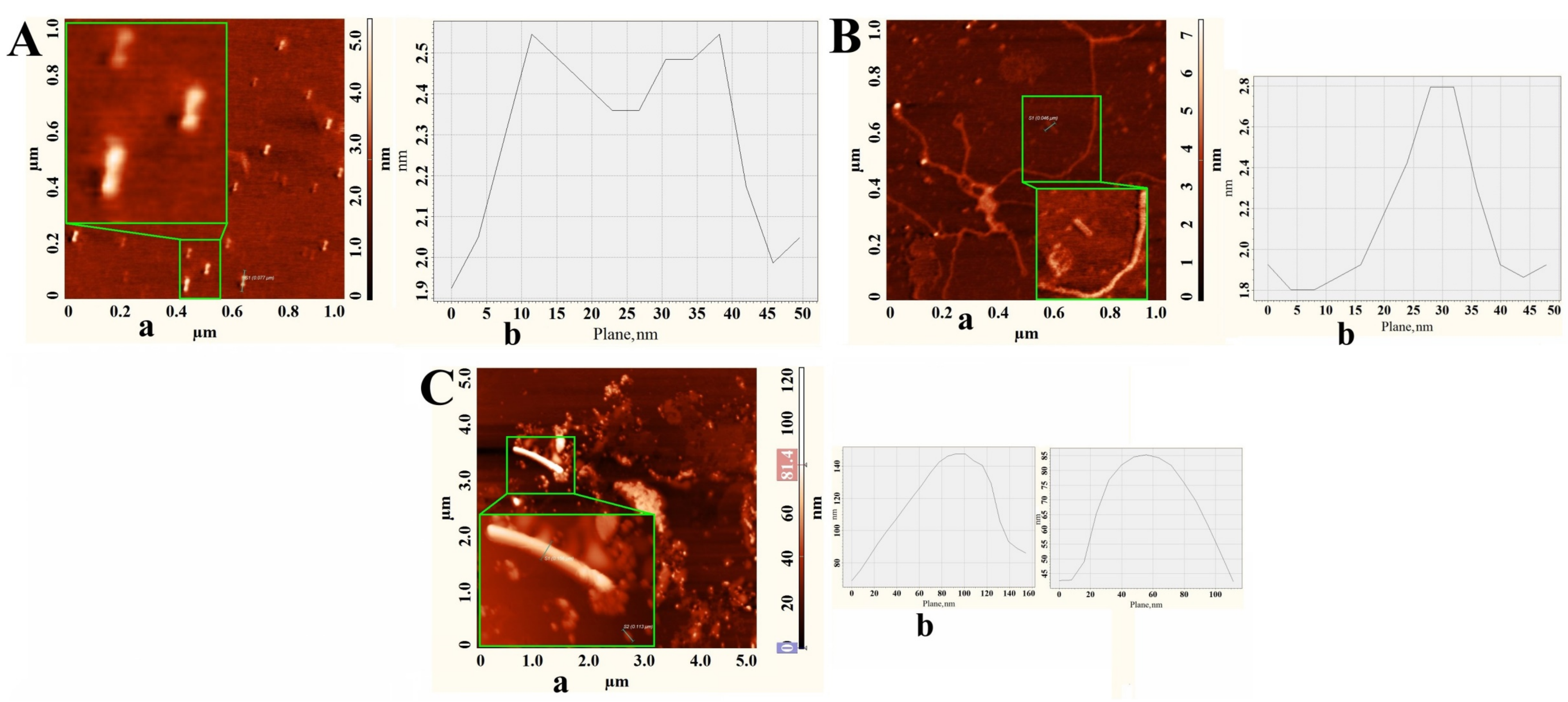


Figure 2. AFM micrographs of (**A**)-**PPV-PEG**; (**B**)-**PPV-PMeOx**;(**C**)-**PPV-PEtOx**; (**a**)-height contrast and (**b**) –cross-sectional traces

Table 2. Dependence of particle size on polymers' concentration in water and some optical data

Sample	Concentration (mg/mL)	Size (nm)	$\lambda_{abs}/\lambda_{em}$(nm)[a]
PPV-PEG	0.001	-*	nd
	0.01	6.1;806	418/524
	0.1	-*	nd
PPV-PMeOx	0.001	Data600;4830	nd
	0.01	-*	nd
	0.1	28	331/403
	1	373;5290	nd
PPV-PEtOx	0.001	72.5;4960	nd
	0.01	16.5; 4430	nd
	0.1	1.58;134	267/403;420
	1	383;4030	nd

*Obtained values exceeded the apparatus maximum limit; nd-not determined;
[a] the values of the peak maxima, obtained in water, by UV-vis and fluorescence spectroscopy

CONCLUSION

- **The applied molecular design successfully conducted to new polymers the properties of which experimentally prove the validity of adopted strategy.**
- **The dependence of the photophysical properties on the size of the micelles as well as on the presence of some biomolecules (like proteins) will be studied in the future.**
- **The assessment of biocompatibility, of photostability and photosensitizing capability, as well as of the propensity for biodegradability under the action of enzymes as myeloperoxidase, esterase or lipase will allow to find the potential for bioapplications of synthesized PPVs.**

Figure 3. UV-vis (left side) and fluorescence (right side) spectra of **g-PPVs**, in water at 0.01 mg/mL