Synthesis and self-assembly of fluorene-vinylene alternating copolymers in “Hairy-Rod” architecture: side chain – mediated tuning of conformation, microstructure and photophysical properties

Demet Göen Colaka, Ioan Ciangaa,b, Luminita Ciangab and Yusuf Yagciä,c

Faculty of science and letters, Department of Chemistry, Istanbul Technical University, Istanbul, Turkey; b“Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania; cFaculty of Science, Center of Excellence for Advanced Materials Research (CEAMR) and Chemistry Department, King Abdulaziz University, Jeddah, Saudi Arabia

ABSTRACT
In the present work, we demonstrate that the side chain choice, as a tunable parameter, is an effective strategy to drive molecular ordering, packing motifs and overall microstructure of a conjugated polymer. By applying Wittig polycondensation novel 'rod-coil' structures, in 'hairy-rod' architecture, based on fluorenylene vinylene copolymers with well-defined oligomeric side chains were synthesized using 'T'-shaped or 'Cross'-shaped p-terphenyl macromonomers. The overall character of the copolymers was systematically varied by attaching of hydrophilic PEG 2000, hydrophobic polar oligo-ε-caprolactone or hydrophobic and non-polar oligostyrene side chains. Self-assembling of the copolymers by simple direct dissolution method was achieved in various solvents by modifying their selectivity in relation to the side chain or main chain. The morphology investigations demonstrated that unique nanofeatures obtained in each case (helical foldamers, vesicles, disks, or helical turns) depend on the nature, number, and position of the side chains which influence the photophysical properties. The 'hairy-rod' topology is also responsible for the self-assembly of the materials in molten state, as thermal analysis revealed, and the propensity of the new synthesized conjugated main chain for helical folding was evidenced, as well.

KEYWORDS
Conjugated polymers; poly(fluorene vinylene)s; 'Hairy-rods'; self-assembly

Introduction
Having started as a subject of scientific excitement, after almost four decades of research, it emerges that the development of conjugated polymers (CPs), as advanced soft materials, turned out to be a successful story. If the former listing of commercially available products using CPs was dominated by applications based on electrochemical properties (batteries, electrolytic capacitors, electrodes for plating baths, antistatic coatings),[1] today the goal of organic/polymer light-emitting device technology (OLED/PLED) was achieved and various products as information displays, touch screens, or general illumination OLED panels were brought to market.[2] Polymer electronics rise as a robust field at the intersection between chemistry, physics, and materials science,[3] the advances of which have been driven by the syntheses of π-conjugated macromolecules with increasingly complex structures.

Electronic device properties, function, and performance sensitively depend on both CPs chain conformation as well as intra- and inter-polymer chain interactions and, due to
their overriding importance, new methods to manipulate them are continuously being pursued.[4] It has been proven that, efficient and rapid migration of excitation and charges through CPs material could be reached by films having ordered structures from the nano to macroscale. [5] Generally, the molecular self-assembly (SA) in solution or in melt, is an elegant path to achieve reproducible materials structuring at the nanometer scale. To design and build macromolecules capable of forming a desired superstructure by SA, manipulating elemental monomer units through ‘bottom-up’ strategy, is a today important aspect in the CPs field.[6]

Excepting the fact that CPs are sensitive at almost all the external stimulus (electric, photo, electromagnetic, mechanic, electromechanic, etc.), their organizing capability through SA mediated by non-covalent interactions (n–π stacking, electrostatic, van der Waals, hydrophobic, hydrogen bonding) is notorious and could be usefully directed by their covalent linking with coil-like polymers. [7] A variety of rod–coil block copolymers (BCPs) containing non-conjugated [8] or n-conjugated [9] well-defined helical rods or oligomeric/polymeric π-conjugated rods were reported. Depending on the relative volume fraction of rigid and flexible segments and the chemical structure of these segments, rod–coil copolymers and their low molar mass homologs self-assemble into a variety of supramolecular structures through the combination of shape complimentarity and microphase separation of rod and coil segments as an organizing force.[11]

Both supramolecular shapes of the self-assembled formed entities of rod–coil copolymers as well as their stability can be manipulated by the variation of macromolecular architecture. In this context, conjugated rod–coil copolymers in ‘hairy-rod’ architecture, best described as ‘molecularly reinforced liquids; 12] become an exciting research field for the new materials having unexpected properties otherwise impossible to be obtained with the polymers with common topology.

‘Hairy-rod’ CPs (HR-CPs) as concept falls into ‘solvent skin’ concept that is related to the introduction of the flexible side chains onto the semi-rigid and rigid polymer chains in order to induce them solubility in common solvents with direct impact on their processing.[13] During the last two decades, the HR-CPs have benefited from the rise of new polymerization methods, notably of controlled radical polymerization, which allowed the obtainment of HR-CPs with well-defined oligomeric side chains attached on the main chain.[14]

Placed at the crossroads between linear conjugated rod–coil BCPs and molecular brushes (MB), HR-CPs share the benefits and peculiar features of the both copolymers related classes. For example, HR-CPs share with MB not only the shape persistence principle but also synthesis methodology,[15] i.e. ‘macromonomer technique; [6(a),14(a,b,d)] ‘grafting-from’ [14(c,f)] and ‘grafting-onto; [9,14(e)] In spite of being topologically related to MB, however, HR-CPs systems have some distinctive features like their inherent rod-like stiffness of the conjugated main chain that creates the orientational ordering effect as an important factor in the equilibrium behavior.[16]

In addition to volume fraction and degree of miscibility that are characterizing rod–coil BCPs, there are other molecular parameters influencing the morphology and physical properties of both MB and HR-CPs such as side chain grafting density and side chain length (molecular weight). Depending of the selected method for polymer synthesis, these parameters can be changed in a controlled manner, giving rise to a freedom in properties’ tunability for a specific envisioned application. More specifically, the inherent molecular tension induced by both side chain length and side chain grafting density may be used to tune the optical properties of HR-CPs [17(a)] and, device performances depend intrinsically upon these parameters.[17(b,c)] Side chain length can modulate the self-assembling and phase behavior of the polymers in solution [17(d)] as well as rod–rod interaction, allowing to control both thermal and morphological behaviors of the materials.[14(e)] A lower grafting density of poly(ethylene glycol) (PEG) side chains on a polythiophene main chain resulted in an improved electroactivity and electrostability.[17(e)] The influence of both parameters on cell viability [12,18(a)] as well as on cellular adhesion and proliferation,[17(e),18(b)] and on electro-biocompatibility of polymeric substrates was recently reported.[17(e),18(c)]

As in rod–coil BCPs, the presence of the conjugated rod in HR-CPs provides additional structural control factor and functionality including the π–π interaction and crystalline or liquid crystalline characteristics. In addition, in both linear and branched systems, the stiff asymmetry between the rod and coil blocks allows the phase separation to occur at a lower molecular weight than that of the coil–coil block copolymers. Furthermore, the self-assembled morphology of both types of rod–coil copolymers may lead to additional electronic processes such as excitation confinement and interfacial effects and the controlled nanosized structure could tune the electronic, optical, and optoelectronic properties of these materials.[10] Although HR-CPs have similar propensity for SA as their linear rod–coil BCPs analogs,[19] it seems that the morphology and the properties of HR-CPs are significantly better when used for electronic devices.[20] Moreover, ‘top-down’ nanostructured HR-CPs, (e.g. nanofibers by electrospinning), as a result of the topology, showed interesting features like high luminescence and water repellency [21(a)] or self-aligned and bundled fibers.[21(b)]
The seminal discovery of electroluminescent light emission from poly(p-phenylenevinylene) (PPVs) spawned an worldwide research effort in order to optimize their synthesis and investigating their physical properties. Various other electroluminescent CPs like poly(arylene vinylenes) (PAVs) with a good color-tunability have been synthesized through molecular engineering. Having similar structure to PPV, polyfluorene vinylenes (PFVs) represent an intriguing class of CPs that combines the structural characteristics of PPV with those of polyfluorenes and show high thermal stability and photoluminescence quantum yield. By comparing with pristine polyfluorenes, the vinylenic units in the polymer backbone induce a broadening absorption and a red-shifted photoluminescence emission.

Routes for PPVs/PAVs synthesis, like Gilch, Heck, Horner-Emmons, Suzuki-Heck cascade, and acyclic diene metathesis (ADMET) polymerization near to electrochemical or stepwise divergent approach have been applied for PFV homopolymer obtainment. It can be pointed out that the optical properties of this particular class of polymers are very sensitive to synthetic details and the thermal conversion process, which influence the chain length distribution, degree of interchain order, and isomeric properties. In order to obtain new materials with desirable properties for a particular application, copolymerization of different monomers offering a synergistic effect between characteristics of homopolymers could be a valid option. In the particular case of PFVs, copolymerization is the mean to tune electronic properties with eventually enhanced stability.

Thus, introduction of phenylene vinylenic units, as the hole-transporting moiety, in a PFV copolymer structure was performed and in some cases enhanced light-emitting efficiency compared to the parent homopolymer or other special properties like thermotropic behavior or light-emitting colors tunability were reported.

Copolymers of PFVs with biphenylene vinylenic, terphenylene vinylenic, anthracene, and naphthalene vinylenic as well as various heterocycles-containing PFVs were also obtained. PFVs copolymers with thiylene-vinylenic units, exhibiting multicolor luminescence or with non-linear optical (NLO) properties, potentially applicable in solar cells or PLEDs were also investigated.

It is worth to mention that PFVs copolymers with various functionalities were demonstrated to be useful materials for biomedical applications. Typically, cancer cells imaging or simultaneous cancer cells discrimination and differentiation under single-wavelength excitation were mediated by nanoparticles of PFVs. Such nanoparticles can also concomitantly act as fluorescent probe and drug tracer for in vivo applications or as highly efficient probes for two-photon cell imaging and two-photon photodynamic therapy. On the other hand, multi-spectral microparticles were prepared via bacteria-mediated assembly of CPs of PFVs type. These color-barcoded microparticles can enter into cells for imaging, and can also be used for multiplexed flow analysis by flow cytometry.

SA of non-invasive competent Escherichia coli and nanoparticles of a PFV copolymer resulted in a multifunctional bacterium-based novel system with multimodal anticancer activity. In another study, an ideal scaffold for cell culture, the two-photon fluorescence properties of which enable its monitoring in a non-invasive, real-time manner, was obtained from the combination between Bombylx mori silk fibers and a fluorene-vinylenic oligomer. Inspired by these considerations and following our previous research interest in synthesis and properties of PAs, we, herein, report a new polymeric structure with ‘hairy-rod’ topology, having as conjugated main chain a PFV copolymer structure.

The targeted goals of the present research are as follows: (i) materials structuring at the nanometer scale by SA in solution of the synthesized alternating copolymers in various solvents by modifying their selectivity in relation to the main or side chain via direct dissolution method; (ii) size and shape characterizations of the formed colloidal assemblies by integrated methods (H-NMR, dynamic light scattering – DLS and atomic force microscopy – AFM); (iii) obtaining thin films by drop-casting method on the supports with different surface energy; (iv) studying the photophysical properties of the synthesized materials in solution and film in order to establish how the peculiar structural characteristics as well as their processing are decisive factors in manipulating chain conformations and morphology that directly impact the properties.

Results and discussion

Molecular design and synthesis strategy

In the present study, we designed and synthesized the new CPs having ‘hairy-rod’ topology of the following structure through engineering both main and side chains by taking advantage of our experience in the related systems. The choice of the main chain type was made by taking into account that the presence of vinylenic bonds is beneficial as long as they reduce the torsional interactions.
importantly, on their conformations allowing the tunability of photonic and electronic properties.[33(d)]

Wittig polycondensation was used for the synthesis of the copolymers as outlined in Scheme 1. This type of polymerization is not stereospecific and gives rise also to the cis conformer of the vinylene linkage between adjacent rings increasing planarization and effective conjugation length and also reduce ionization potential and hole injection barriers.

Equally important, vinylene groups increase the rotational flexibility of polymer chain with decisive consequences not only on the polymer solubility, but more importantly, on their conformations allowing the tunability of photonic and electronic properties.[33(d)]

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Besides the trans one. However, due to its technical simplicity, it was successfully employed to yield copolymers with strictly alternating structure.[23] But, even if it could affect the coplanarity of the main chain, the presence of the cis vinylene linkage is a useful tool to modify physical properties. Indeed, it was demonstrated to be efficient in direct patterning of PPVs at the micrometer scale.[22(b)]

Inherently, such structures are not accessible by one-shot preparation but require more complex, hierarchical synthetic strategy with at least three independent steps (Scheme 1 and Scheme S1 in Supporting information).

Among the HR-CPS synthesis methods, the ‘macromonomer technique’ was chosen, due to its advantages related to well-defined grafting density and side-chain length, defect-free polymer structures and easy access to copolymer synthesis. Actually, this method enables the elaborate design, preparation and complete characterization of the side chains prior to the ultimate step-growth polymerization.[6(a),40]

Macromonomers can be obtained by polymerization from a monomer-based initiator via controlled polymerization methods, namely atom transfer radical polymerization (ATRP),[14(a,b)] nitroxide-mediated radical polymerization,[38] reversible addition fragmentation chain transfer,[41] ring-opening polymerization (ROP),[21,39,40(b)] or by terminal functional group transformation of a well-defined polymer chain to introduce monomer functionalities specific for CPs synthesis.[12,40(a),42] Both methods were used for the synthesis of 1,4-dibromo phenylene functionalized precursor macromonomers 1–4 (Supporting information (SI), Scheme S1). More specifically, compounds 1, 2, and 3 were obtained by the initiation method (ATRP of styrene or ROP of ε-caprolactone), while precursor macromonomer 4 was synthesized by polyethylene glycol (PEG) chain end functionalization. In the next step, p-terphenyl-based macromonomers with aldehyde functionalities (5–8 in Scheme 1), were synthesized to contain the oligomeric side chain as ortho/ortho-ortho substitutes at the middle phenylene ring by a Suzuki coupling of the precursor macromonomers 1–4 with 4-formylphenylboronic acid.[37(b)] p-Terphenyl structure was deliberately selected so as to impart light-emitting property as well as electrochemical and thermal stability. It is also a well-known mesogen and has been widely used to generate liquid crystals with high birefringence as it favors the self-organization of the calamitic units. Being attached as mesogenic side chains, an enhanced photoluminescence was observed due to the resonance energy transfer from the terphenyl pendants to the CP backbone.[43] p-Terphenyl derivatives are also known as helix mimetics (or pro-teomimetics) of two turns of the myosin light chain kinase α-helix and show functional analogy in binding with high affinity to calmodulin. As helical mimetics of Bad and Bak proteins it would inhibit Bcl-xL and may serve as anticancer therapeutics and potent terphenyl-based activators of the pro-apoptotic protein p53 have also been described.[44] Selection of the side chains is also an important issue for designing CPs. Some recent studies have focused on side chain engineering,[45] collectively observing that through their stimuli sensitivity (pH, temperature, light), nature (hydrophilic, hydrophobic, polar, non-polar, biocompatible, biodegradable), length, and grafting density, a plethora of properties can be manipulated. Oligostyrene, oligo-ε-caprolactone, and PEG 2000 side chains decorated T'-shaped or Cross'-shaped p-terphenyl macromonomers 5–8 were subsequently used in Wittig polymerization with 2,7-bis (bromomethyl)-9H-fluorene triphenylphosphonium salt leading to the formation of amphiphilic, amphipolar, or low mixing entropy alternating copolymers 9–12 (Scheme 1). The adopted synthesis strategy has allowed for exact control of branch points spacing as a result of the used polymerization method. Alongside, control of the number of branches per branch point was adjusted by appropriately choosing the functionality number of the initiators/reactive intermediate used for the corresponding precursor macromonomer synthesis (Scheme S1). Besides mono-branched macromonomers (Scheme 1), this work also involves the use of what Hadjichristidis et al. termed ‘double tailed’ macromonomers,[46] enabling to systematically change the nature, number, and the substitution pattern of the side chains on the PVFs conjugated backbones (Figure 1).

It is anticipated that the obtained materials by their SA capability given by the combination of the π-conjugated main chain with common, traditional flexible polymers counterpart to enable versatile modification of the properties in the response of the medium (solutions, surfaces). From the photo/electroluminescence materials properties point of view, also our approach is somehow a combination of the chemical change by branching with the well-known strategy of blending with a polymeric inert matrix, applied to CPs to avoid the detrimental effect of aggregation in solution and in film.[47]

Structural characterization and properties in bulk

1H-NMR spectroscopy was used to structurally characterize all the synthesized materials. The spectra of the copolymers 9–12 are presented in Figures 2 and 3 and those of the p-terphenyl T'-shaped or Cross'-shaped macromonomers 5–8 in Figures S1 and S2. A detailed discussion on 1H-NMR characterization, referring to both macromonomers and copolymers, is presented in Supporting information. In this section, only the general characteristcs, as well as the spectral peculiarities, are described. Regarding the macromonomers, the presence in all spectra of protons for
aldehyde functionality, at approximately 10 ppm, confirms their successful synthesis. On the other hand, it is worthy to point out that the macromonomers’ spectral features are intimately related to their molecular geometry (‘T’ shape or ‘Cross’ shape) and to the nature (polar, non-polar) and number of the substitutes. Thus, the non-symmetrical structure of ‘T’-shaped macromonomers 5 and 8 is responsible for the non-equivalence of all aromatic protons. Consequently, the aromatic region aspect of the spectra in Figure S1 is more complicated when compared with the similar one of ‘Cross’-shaped macromonomers 6 and 7 (Figure S2), having a symmetrical structure. Generally, the aromatic protons of the p-terphenyl moiety in all macromonomers appeared in the range 7.5–8.2 ppm. They are clearly discernible for the macromonomers 7 and 8 and only partially for the macromonomers 5 and 6, due to the overlapping with aromatic protons of oligostyrene side chains. This is more evident for ‘double tailed’ macromonomer 6 for which only the peak of aromatic protons in the vicinity of the aldehyde function (b type in Figure S2) is clearly attributable.

By analyzing the spectra in Figures S1 and S2, it can also be pointed out that the presence of the polar PEG 2000 and oligo-ε CL substitutes induces a down-field shifting.
that the presence in all spectra of clearly discernible peaks for \( p \)-terphenyl moiety as well as for the side chains permitted the calculations of the polymerization degree of said side chains. The obtained values fits those of the precursor macromonomers 1–4 presented in Scheme S1, confirming that the reaction conditions employed for the Suzuki reaction were appropriate.

**Figure 3.** \(^1\)H-NMR spectra of copolymers 10 and 11 in \( \text{CDCl}_3 \).
coupling does not affect the integrity of laterally attached side chains.

The copolymers’ expected structures are confirmed by 1H-NMR spectra presented in Figures 2 and 3. Thus, the fluorenyl ring presence is proved by the most down-field shifted peaks in the aromatic region. They correlate well with that of the aliphatic −CH₂− in fluorenyl ring, clearly discernible at 3.76 or 3.92 ppm in the copolymers 9, 12, and 10, respectively. The protons afferent to the vinylene linkages in both cis and trans configurations appeared in the range 6.0–7.3 ppm and are generally overlapped with other aromatic protons, especially in the copolymers 9 and 10, containing oligostyrene side chains. For this reason, the cis/trans ratio of above polymers was not possible to be calculated. Moreover, placing of PEG or oligostyrene substitute at the ortho position of the middle phenylene ring of p-terphenyl moiety renders the copolymers 12 and 9 regio-asymmetric. This gives rise to the presence in the both copolymers’ structure of four types of vinylene protons in both cis and trans configuration (Figure 2). Notably, the copolymers 10 and 11 show only two types of vinylene bonds. The calculation for cis/trans ratio was possible for the copolymer 11, using the peaks in the aromatic region (Figure 3), as detailed in the Supporting information. This calculation leads to a composition of 41% cis and 59% trans vinylene bonds, similar values as for the previously reported PPV, derived also from the macromonomer η7.[37(b)]

In the aliphatic region of the copolymers 11 and 12, the presence of the splitted peaks attributable to OCH₂ groups near to the ester linkage in both PEG 2000 and oligo-ε-CL side chains, placed at their connection points with the main chain, (protons x in Figures 2 and S4 and protons j in Figure 3), could be due to the influence of cis/trans isomerism sensitivity, as previously reported.[48] The use of these peaks for cis/trans ratio calculation of 11 conducted to the value of 44% cis and 56% trans, close to that obtained by previous method. Similarly, the cis/trans ratio of the vinylene linkages of the copolymer 12 was calculated as 47/53%.

Although cis/trans ratio values calculated for the copolymers 11 and 12 are high enough, they are far beyond of the upper limit (80%) that Wittig polymerization can allow.[22(b)] Taking into account that p-terphenyl is a stiff molecule with a non-planar geometry of the contained phenylene rings, we suggest that the steric hindrance imposed by the presence of the oligomeric side chains impacted the macromonomers’ conformation so that cis double bonds were incorporated at an enough high rate during polymerization to allow better intramolecular chain packing and to reduce the overall energy.

The macromonomers’ and their corresponding copolymers’ structure was also investigated by IR spectroscopy and a detailed discussion is enclosed in the Supporting information. Nevertheless, some important issues are worth to mention. Although neat PEG with molecular weight lower than 3000 preferentially crystallize into a monoclinic phase where the polymer chains adopt a 7/2 helical structure, it is known that PEG can also crystallize in a planar zigzag configuration under certain conditions such as mechanical strain, freeze-drying, and even blending.[49] A partial change in PEG chain conformation from helical to planar zigzag has also been observed in graft copolymers,[50] In the IR spectrum of PFV 12, (Figure S5), vibrations characteristic to crystallized PEG in a 7/2 helical structure are present, (1360, 1278, and 1059 cm⁻¹), besides to those of the trans zigzag conformation at 1241 and 963 cm⁻¹.[50] Moreover, the vibrations at 1325 and 993 cm⁻¹ attributed to PEG in amorphous state,[50] are missing in the spectrum of PFV 12, supporting the presence of the PEG 2000 side chains in the crystalline state.

In the IR spectrum of the copolymer 11, (Figure S5), the presence of the PCL crystallization-sensitive bands at 1726 cm⁻¹(νC=O ester), at 1294 cm⁻¹(ν C–O and ν C–C), and at 1189 cm⁻¹(ν OC–O) and the missing of the band located at 1161 cm⁻¹, (that characterize PCL in amorphous state),[50] confirms that the oligo-ε-CL side chains are in crystalline state, as well.

The apparent molecular weights of the synthesized macromonomers and derived copolymers were also evaluated by GPC measurements in three different solvents (THF, chloroform and DMF) depending on the specific solubility (see Table S1). The results of these measurements discussed in the Supporting information revealed different values for the same compound, very likely owing to copolymers’ peculiar architecture and their interaction with the chosen solvents. Due to the rod–coil composition, at the concentrations used for the measurements, the compounds are most probably in the associated supramolecular form. For all of these reasons and those detailed in the Supplementary information, these values must be considered with care. That’s why the molecular weight values obtained using 1H-NMR registrations for p-terphenyl macromonomers were used for copolymers’ recipe calculations. Due to the particular characteristics of the employed synthesis method and also the steric hindrance, it seems reasonable to assume that the obtained copolymers are oligomers.

Thermal behavior of the precursor macromonomers and the resulting alternating copolymers was assessed by DSC and TGA analyses. The obtained data are presented in Table 1 and in Figure 4, and in Figures S6–S8, respectively. The first run, in both TGA and DSC, was performed on the materials resulted by precipitation from the solutions (Figures S6 and S7 at 10 °C/min; Figures 4, S8(A) and (C)-a–c at 2 °C/min). The second heating and also the subsequent
runs were performed on the materials resulted after the controlled cooling of their molten state (Figures 4, S8(B) and (C)-d).

As can be seen from Figure S6, the degradation of the copolymers occurs in one step for the copolymers 9 and 11 and in two steps for the copolymers 10 and 12. The weight loss in the first degradation step of the copolymer 12 is likely to be due to the elimination of associated water in the PEG side chains. In the case of the copolymer 10, the weight loss in the first degradation step (230–290 °C) is not more than 5%, which could be due to some residual impurities.

For PFV homopolymers, generally, the 5% weight loss temperature \( T_{w5} \) varies between 300 [25] and 400 °C [34(b)]. A relatively lower thermal stability observed for the obtained alternating copolymers may be due to both their lower molecular weight and oligomeric side chains present in the PVFs structure.

Similar behavior was previously reported for the structurally related PPVs.[37(d)] Thermal stability, which is related to the conjugated main chain, decreases in the order of 12 > 9 > 11 > 10 correlates with the molecular weight of the copolymers determined by GPC in THF, (Table S1).

Another thermal characteristic of PFV based polymers is the glass transition temperature, \( T_g \). In the case of PFV homopolymers, it seems that the \( T_g \) values depend decisively on the method used for the synthesis rather than the alkyl type and length attached at the 9-position of the fluorene ring. It was reported that 9,9-di-n-octyl-substituted PFV homopolymer obtained by Gilch method showed a \( T_g \) of 173 °C,[25(a)] while the one synthesized by Suzuki-Heck cascade reaction presented a \( T_g \) of 56 °C,[24(c)] the same as the monodisperse 9,9-di-n-octyl-substituted fluorene-2,7-vinylene octamer synthesized by a divergent approach.[30] When the substitute at the 9-position of the fluorene ring was a branched one, e.g. di-ethyl-hexyl, the \( T_g \) of PFV synthesized by Gilch method decrease to 165 °C [34(b)] by comparing with its di-n-octyl substituted homologous.[25(a)] As it is evident from Table 1, the obtained alternating copolymers (as they were registered in the first heating run) show the thermal characteristics of the attached side chain. Thus, \( T_g \) for the oligostyrene and melting temperatures \( T_m \) for oligo-ε-CL and PEG side chains were noted, indicating microphase separation in the bulk state. Thermal transition related to \( T_g \) of the main chain was observed to some extent only in the case of the copolymer 9, in the first run (Figures S7 and 4(a)). For the other copolymers such transition was not detected. In the literature, the absence of \( T_g \) related to the random and regio-random copolymer structures was also pointed out.[51] In the case of the copolymers 11 and 12, the absence of \( T_g \) could be due to the presence of ester or ether polar groups in the crystallizable side chains. The higher electronegativity of such groups, compared to main chain electronegativity, promotes the appearance of some dipole moments and dipole–dipole interactions leading to an increase in \( T_g \). This phenomenon is additionally supported by the restricted motion of the main chain arising from the steric hindrance of the bulky side chains. Such restriction can give rise to \( T_g \) values that are over the initial degradation temperature.

Furthermore, it was also revealed that in the case of partially crystalline polymers, it is difficult to detect \( T_g \) by DSC. This is because the enhancement of the molecular motion in the amorphous region is restricted by the presence of the crystalline parts.[53] The absence of \( T_g \) of the copolymer 10 in its first run (Figure 4(b)) can be attributed not only to the number of the side chains on the branch point that impact the main chain motion but also to their conformation (extended or coiled).

Starting from the fact that the copolymers contain two mesogene moieties in their structure, (p-terphenyl and fluorenyl), and also knowing that HR-CPs are prone to SA likewise in molten state, a detailed DSC investigation was also performed. Different heating–cooling rates were employed and several experiments were run on the thermally treated samples after different periods of time. However, no transition temperatures were evidenced during these investigations. Instead, an unexpected phenomenon was registered in the first cooling run of all copolymers. No distinct signal appeared even at the cooling rate of 2 °C/min (Figure 4). Although no explanation was provided, such phenomenon was reported for other PFV copolymers,[34(b)] This programmed DSC study presented in Figure 4, revealed a very slow relaxation phenomenon for all the type of side chains, especially for oligo-ε-CL and PEG in the copolymers 11 and 12, that recover their crystalline state after 48 or

| Table 1. Thermal properties of dialdehyde macromonomers and PFVs. |
|------------------|------------------|------------------|------------------|------------------|
| 5                | 104              | 275              | 371              | 0.42             |
| 9                | (55;5;105)       | 300              | 373              | 16.88            |
| 6                | 98               | 220              | 357              | 0.85             |
| 10               | 106 (50;105)     | 230              | 353              | 1.44             |
| 7                | 54               | 318              | 360              | 3.02             |
| 11               | 55 (51;54)       | 260              | 303              | 15.09            |
| 8                | 52               | 300              | 371              | 0                |
| 12               | 51              | 200              | 350              | 25.24            |

* Determined from DSC analysis – first run at 10 °C/min in Figure S7.
* Initial degradation temperatures.
* Temperature for which the weight loss is 10%.
* Char yield at 600 °C.
* From TGA measurements presented in Figure S6.
* From Figure 4(a) at a heating rate of 2 °C/min after 24 h rest.
* From Figure 4(b) at a heating rate of 20 °C/min after 24 h rest.
* From Figure 4(c) in the cycle heating-cooling-heating.
* From Figure 4(d) in the cycle heating-cooling-heating.
24 h, respectively (Figure 4(c) and (d)). The explanation for this intriguing phenomenon can be explained in terms of inter-chain interactions that could take place in the molten state. Such interactions are based on either or both of the following suppositions: (i) the π–π stacking between conjugated main chains is so high that prevents the side chain crystallization or, (ii) based on the length, number and affinities with the conjugated main chains, the side chains become ‘arrested’ between the rigid main chains, fact that delays and hinder their crystallization. It seems, as well, that the high strength of the π–π stacking between conjugated main chains induced a very high rigidity to the copolymer 9 so that in its second heating, at 10 °C/min, the

$T_g$ of the main chain does not appear at all and it is recovered only after 24 h rest (Figure 4(a)). For the copolymer 10 it was distinguishable after the all running cycles and 48 h rest at room temperature (Figure 4(b)).

In order to present a visual image of the phenomena registered by DSC measurements and to give an outline for the properties in the melt of the copolymers 11 and 12, in a relatively macroscopic scale, polarized optical microscopy (POM) was used (Figure S8). It can be seen that in the first heating run performed with 2 °C/min, at 42 °C, the copolymer 12 starts melting (Figure S8(A)-a) and at 49 °C (Figure S8(A)-b), under pressing, the birefringence of the thin texture is obvious. With increasing temperature,
some area becomes darker (Figure S8(A)-c 53 °C) and also bright, aligned rods are clearly visible (Figure S8(A)-d, 78 °C). During the cooling cycle, the aligned rods become closer (Figure S8(B)-a) and bigger in size (Figure S8(B)-b and c), the yellow-greenish birefringent zone, (most probably formed by self-assembled π-conjugated rods), is being spread into a red ‘matrix’ of PEG in amorphous state (Figure S8(B)-d). No spherulites of the crystallized PEG in ‘classical’ shape, that move away the rigid rods from one another, as previously reported, were visible. [12] A similar phenomenon when PEG segments did not reconcrystallize during cooling was observed for an amphiphilic linear copolymer.[54] The lower values of $T_m$ for PEG side chains that phase-separate after 24 h rest at room temperature in desiccator (Table 1) could be attributed to the confined crystallization that frequently results in restriction of crystal thickness.[49] In the case of the copolymer 11, at 35 °C in the first heating run, a birefringent thin texture composed of bright rods can be observed (Figure S8(C)-a) that develop into a completely melted oligo-$\varepsilon$-CL matrix at 53 °C (Figure S8(C)-b), in which the bright aligned rods can be seen covering the investigated area at 70 °C (Figure S8(C)-c). The only image that keeps its shape under cooling at 2 °C/min is the one presented in Figure S8(C)-d in which the rods slightly increased in size, are spread in an amorphous oligo-$\varepsilon$-CL matrix. This is very likely to be due to the well-recognized PCL lower crystallization rate.[55(a)] It was recently asserted that PCL segments, having a low degree of polymerization (e.g. 20 monomer units), in a coil–rod–coil topology, seems not sufficient to induce crystallization of PCL.[55(b)] In our particular case, the copolymer 11 recovered its phase separated state with the side chain in crystallized state after 48 h (Figure 4(c)), even if each oligo-$\varepsilon$-CL ‘tails’ has less than 20 repeating units most probably due to its ‘hairy-rod’ architecture.

**Self assembling in solution and morphology of thin films**

Before discussing the experimental results concerning the solvent-induced SA of the synthesized materials, it is essential to point out the characteristic aspects related to this phenomenon for conjugated rod–coil copolymers,[56(a)] in the light of which these results were interpreted. The SA of conjugated rod–coil copolymers is fundamentally different from those of conventional coil–coil block-copolymers because it is complicated by anisotropic interactions and liquid crystalline behavior of the rods. Also this phenomenon is strongly associated with the balance between at least four thermodynamic parameters: (i) the Flory–Huggins strength of segregation, ($\chi$N) (N-molecular rod length), which parameterizes the interaction between chemically dissimilar blocks; (ii) the Maier–Sauep interaction strength ($\mu$N) relating the rod–rod alignment tendency; (iii) the coil volume fraction and (iv) geometrical asymmetry ($\nu$) of the system defined as the ratio of the coil radius of gyration and the rod length. [56] The interplay among all of the mentioned interactions drives to the equilbrium structures that are distinct from coil–coil copolymers and cannot be easily predicted.

The above results revealed that the obtained materials have ‘coil-rich’ rod–coil co-oligomer structures. In our investigation, water and chloroform were used as solvents for the copolymer 12 and the other three copolymers, respectively. If water is a coil-selective solvent for PEG side chains in 12 and chloroform is a rod-selective solvent for the copolymer 11, in the case of the copolymers 9 and 10 chloroform was chosen due to its known high solubility related to oligostyrene side chains.[57] However, when the whole structure of the copolymers 9 and 10 is considered, it can be assumed as a neutral solvent. These assumptions are based on the values of the Hildebrand solubility parameters of both used solvents and of the constitutional building blocks of the synthesized copolymers that are presented in Table S2.

Generally, the enthalpy of mixing between a polymer and a solvent depends on their solubility parameters difference and therefore, good mixing is observed when they have similar solubility parameter values.[58] For the conjugated main chain, the value of polyfluorene (PF) solubility parameter was considered.[59] The polymer–solvent interaction parameter ($\chi$) values for the side chains in the copolymers were also taken into account, choosing for investigations the good solvents.[60] It was hypothesized that, in good solvents, the side chains will adopt the most extended conformation, which should prevent the conjugated chain aggregation even in the conditions of spatial constraints imposed by the supramolecular entities formed via SA.[61]

The method used for SA is the so-called ‘direct dissolution method’ that was reported as an appropriate approach for both amphihilic [12] and non-amphiphilic [62] rod–coil copolymers. To prove solvent-induced SA of the reported materials, DLS measurements of the solutions and AFM analysis for the films obtained from these solutions were conducted. DLS proves the formation and allows the size evaluation of the self-assembled structures in solvated state, while AFM tapping mode height and phase images were used to highlight visually the shape and size of copolymers SA morphology in dry state. Supports having different surface energies, (hydrophilic mica and hydrophobic, non-polar highly ordered pyrolytic graphite-HOPG), were used in order to assess the behavior of self-assembled entities formed in solution at their contact with a compatible or a non-compatible surface (study for the copolymers 10 and 12). A concentration-dependent investigation of the
with the additional features of the 1H-nMr spectra. It is not the case for the proton signal of the aldehyde chain end group (placed after 9 ppm in all the spectra), for which an up-field shifting is observed for water and DMSO solutions in the aromatic region are clearly visible in D₂O registration, indicating the increasing solvents dielectric constant). However, this is not the case for the proton signal of the aldehyde chain end group (placed after 9 ppm in all the spectra), for which an up-field shifting is observed for water and DMSO by comparison with chloroform. Even if it is difficult to distinguish between intrinsic solvent effects and those that occur as a result of change in the solute conformation due to the specific solvent effects, from the observed shifting of these signals, it can be assumed that the aldehyde chain ends are implied in other non-bonding interactions than those with the solvent.[65]

Another experiment that contributes to prove the foldamers formation was the fluorescence measurement of 12 by gradually modifying the water dispersion concentration. It was observed that the fluorescence intensity follows a linear dependence on the concentration (Figure S10), in a similar manner to that previously described for polythiophene derivatives as performed by UV–vis measurements.[64] This behavior is consistent with a non-supramolecular assembled form of the polymer. On the other hand, a decrease in fluorescence intensity with increasing particle size was often remarked for other CPs nanoparticles formed in water.[66] In our case, such dependence was not observed (Table S3 and Figures S20 and S10), meaning that different kinds of entities are formed in water dispersion of 12. The UV–vis and fluorescence measurements of the copolymer 12 at concentration of 0.04 mg/mL in solvents with different polarities are presented in Figure S11. As it can be seen from this figure, the increase in λ_max for both absorption and fluorescence (more evident for fluorescence measurements at both excitation wavelengths) does not follow the order of solvent polarities. It is clear that the solvent effect on the luminescence property of 12 cannot solely be accounted by the solvent polarity. A similar behavior was reported for other CPs with propensity for folding in solution.[67]

The water dispersion of the copolymer 12 at polymer concentration of 0.04 mg/mL was deposited by drop casting on both mica and HOPG surfaces and their films were obtained by freeze-drying technique in order to keep as much as possible the real-space imaging of the formed entities in their solvated state. The AFM images in tapping mode and phase mode on mica are presented in Figure 5(A)-a and b (Figures S14 and S15 for full size images), and in tapping mode on HOPG in Figure 5(B).

It can be observed that clusters of the particles with a similar and ordered shape were formed, having a ‘core-shell’-like type constitution, more visible in the phase contrast mode (Figure 5(A)-b) and with size around 160–200 nm (Table 2). The observed regular shape could be

| Copolymer | Particle size in solution (nm) (% of population in sol.) | Particle size (nm), type and shape in dry state by AFM |
|-----------|----------------------------------------------------------|-------------------------------------------------------|
| 9⁺        | 19 (22); 91(78)                                          | 150 ÷ 170 (core-shell disk-like aggregates)³         |
| 10⁺       | 7.36(92); 28.4(8)                                        | 87 ÷ 125 (helical turns); 82 ÷ 215 (spherical core-shell and vesicles) |
| 11⁺       | 38.7                                                     | 108 ÷ 111 (vesicles)⁴                                |
| 12³       | 37(14); 145(86)                                          | 162 ÷ 221; (collapsed foldamers as a ‘core-shell’-like particles) |
|           |                                                          | 70 ÷ 100; ‘core-shell’ spherical nanoparticles         |

Table 2. Particle sizes by DLS measurements in solution and AFM analysis of the films.

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size and morphology was performed for the copolymer 12, for which 1H-NMR measurements in three different solvents were also registered (Figure S9). The PEG-side chain decorated copolymer 12, being water self-dispersible due to its amphiphilic nature, is supposed to be able to form fluorescent micellar ‘core-shell’ type nanoobjects in a similar manner to that reported for other PEG-containing ‘hairy-rod’ conjugated copolymers.[12,40(a)]

Indeed, the DLS measurement of the water dispersion of 12 at the concentration of 0.04 mg/mL revealed the presence of the self-organized entities with a two-population presence, the one with the highest size being at a higher percentage (Table 2, Figure S12).

On the other hand, it is well established that NMR technique is useful to prove the existence of such colloidal ‘core-shell’ type particles because in the spectrum registered in water the characteristic signals for the hydrophobic part are diminished or even disappeared. [63] It was not the case for the copolymer 12, when the 1H-NMR spectrum was registered in D₂O (Figure S9(C)). As water is a poor solvent for the conjugated main chain, other phenomenon should play a role in its water dispersion. Similar behavior was reported for a water dispersible non-ionic polythiophene by Meijer et al. who demonstrated its intramolecular helical folding.[64] If foldamers were formed in water in the case of copolymer 12 as well, this assumption also has to be confirmed by other evidences. As the signals for the aromatic region are clearly visible in D₂O registration, (Figure S9(C)), the above assumption may be sustained by other evidences. as the signals for the aromatic region are clearly visible in D₂O registration, indicating the increasing solvents dielectric constant). However, this is not the case for the proton signal of the aldehyde chain end group (placed after 9 ppm in all the spectra), for which an up-field shifting is observed for water and DMSO by comparison with chloroform. Even if it is difficult to distinguish between intrinsic solvent effects and those that occur as a result of change in the solute conformation due to the specific solvent effects, from the observed shifting of these signals, it can be assumed that the aldehyde chain ends are implied in other non-bonding interactions than those with the solvent.[65] Another experiment that contributes to prove the foldamers formation was the fluorescence measurement of 12 by gradually modifying the water dispersion concentration. It was observed that the fluorescence intensity follows a linear dependence on the concentration (Figure S10), in a similar manner to that previously described for polythiophene derivatives as performed by UV–vis measurements.[64] This behavior is consistent with a non-supramolecular assembled form of the polymer. On the other hand, a decrease in fluorescence intensity with increasing particle size was often remarked for other CPs nanoparticles formed in water.[66] In our case, such dependence was not observed (Table S3 and Figures S20 and S10), meaning that different kinds of entities are formed in water dispersion of 12. The UV–vis and fluorescence measurements of the copolymer 12 at concentration of 0.04 mg/mL in solvents with different polarities are presented in Figure S11. As it can be seen from this figure, the increase in λ_max for both absorption and fluorescence (more evident for fluorescence measurements at both excitation wavelengths) does not follow the order of solvent polarities. It is clear that the solvent effect on the luminescence property of 12 cannot solely be accounted by the solvent polarity. A similar behavior was reported for other CPs with propensity for folding in solution.[67] The water dispersion of the copolymer 12 at polymer concentration of 0.04 mg/mL was deposited by drop casting on both mica and HOPG surfaces and their films were obtained by freeze-drying technique in order to keep as much as possible the real-space imaging of the formed entities in their solvated state. The AFM images in tapping mode and phase mode on mica are presented in Figure 5(A)-a and b (Figures S14 and S15 for full size images), and in tapping mode on HOPG in Figure 5(B).

It can be observed that clusters of the particles with a similar and ordered shape were formed, having a ‘core-shell’-like type constitution, more visible in the phase contrast mode (Figure 5(A)-b) and with size around 160–200 nm (Table 2). The observed regular shape could be
attributed to the collapsed foldamers in helical form, more probable in ‘face-on’ mode, due to the PEG side chains affinity for hydrophilic mica surface. A hypothetical behavior of the copolymer 12 in water as well as in film on mica is presented in Figure 6.

The drawings in Figure 6 suggest that the oligomeric chains of 12 are helically folded. As copolymer 12 is amphiphilic in nature, the driving force for such folding behavior could be the solvophobicity of the non-polar aromatic backbone in polar environment, resulting in an intramolecular segregation, analogous to nanophase separation usually encountered in amphiphilic block-copolymers.[68]

$^1$H-NMR, UV–vis and fluorescence spectroscopy, and AFM microscopic results corroborate the assumption that the folding was induced most probably by intramolecular π–π stacking between non-adjacent moieties in the backbone and their solvophobic interactions and that, the helical geometry was encoded in the backbone topology as well as in its constitutive parts.

The helicogenicity of p-terphenyl,[43] and the discotic, polycyclic aromatic fluorenyl [69] is well known. The role of the side chains was to disfavor the random main chain collapsing into disordered structures, as well as conferring the proper dispersibility to the molecule. Moreover, the presence of the ester group as the connector of PEG could contribute to the folded structure stability [70] and the high amount of the vinylene linkage in cis configuration could give to the chain a more rotational freedom thus favoring the helical folding in a similar manner as observed for m-phenylene ethynylene (mPE) foldamers.[71]

In our case, the chain-end interactions presented in Figure 6(A) should also be considered. The aldehyde chain-ends could interact each other mediated by water solvent via hydrogen bonding, while the hydrophobic triphenyl-containing vinylene chain-ends may interact by π–π stacking favored by the hydrophilic medium. In this way, longer foldamers could be formed. Such interactions could justify, on the one side, the presence of two populations of objects in dispersion as determined by DLS measurements, (those with the higher size in a high percent, Table 2), and, on the other side, the presence of the shallow peak at approximately 600 nm in fluorescence spectrum (Figure S11(B)). It can be reasoned that the polar aldehyde groups will be directed preferentially toward PEG shell, while the hydrophobic chain ends will be directed toward hydrophobic inside of the formed helical tubes.

Figure 5. AFM images and cross-sectional analysis of ‘core-shell’ type nanoparticles of copolymer 12 obtained from its dispersion at $c = 0.04$ mg/mL: (A) – a: height image, b: phase image on mica; (B) – height image on HOPG.
with values around 70–100 nm (Figure 5(B)). These values are also smaller than those obtained by DLS. The shape modification could be triggered by the HOPG hydrophobic surface, while the decrease in size of the new-formed spherical ‘core-shell’ nanoparticles could be due to the shrinking by evaporation of ‘structured water’ from the PEG shell.[12] In order to see how the shape and size of supramolecular entities could be modulated, for the copolymer 12, investigations by varying the concentration of dispersions and their films on mica support were also performed (Figures S13 and S20, Table S3 in the Supporting information). The study revealed that concentration could be a decisive factor influencing the density of the nanoparticles on the support surface as well as their ‘shell-shell’ interaction during the solvent evaporation. At the highest investigated concentration, a transition of ‘core-shell’ nanoparticles to a lamellar, ‘terrace’-like morphology is taking place. It is also significant that, irrespective of dispersion concentration, the shape of the particles detected in aFM is the same, differing only in size (Figures 5(a) and S20(a)–(c)).

The copolymer 11, containing oligo-ε-CL side chain symmetrically attached on the both side of the conjugated main chain, has an amphipolar character and was studied for its self-assembling in chloroform solution at the same concentration as the copolymer 12 in water. It is known that PCL has a partial to high solubility in chloroform at room temperature[73] and shows one of the lowest value of the $\chi$ parameter at temperatures ranging from 100 to 120 °C.[60] DLS study of this copolymer revealed the presence of the supramolecular entities with an uniform size of approximately 39 nm (Table 2), formed most probably due to the significantly different solubility parameters of the main chain and side chains, leading to a geometrical asymmetry of the system, enhanced by the amphipolar nature of the whole structure. The aFM analysis of the film obtained on mica substrate under solvent saturated atmosphere revealed that this procedure allowed the crystallization of oligo-ε-CL side chains and formation of characteristic ‘fractal’-like morphology in the region of supersaturated solution (Figure S21(a)). In Figures 7(a)-a and S16 (full size) near to these micrometer structures (left side, upper corner), spherical entities organized together in a ‘worm’-like shape were detected (clearly visible in phase contrast mode-Figure 7(A)-b), the cross-sectional profile analysis of which demonstrated the self-assembling of chains as vesicles (Figure 7(B)). In the dry state, on the investigated surface, they showed a high degree of uniformity with the size between 108 and 118 nm. As long as chloroform is a rod-selective solvent for the copolymer 11, (Table S2), having a short–length rod fraction, this copolymer tends to form bilayer vesicles to accommodate the tendency of the larger coils to occupy

![Figure 6](image-url). Hypothetical behavior of copolymer 12 in water and in film on mica.

Such helical tubes most likely will be oriented in a vertical position in relation to the mica surface (Figure 6(B)) as the most favorable one for the highest contact of PEG shell with the hydrophilic surface. After the water evaporation, these tubes will collapse into the particles having the regular shape as those observed in AFM tapping mode image (Figure 5(A)-a and b).

In order to verify if the supposed helical tubes are really formed in water dispersion of copolymer 12, specific optical rotation ($\lbrack \alpha \rbrack_{25}^{589}$) measurement at a concentration of 0.13 mg/mL was performed, as well (experimental part in the Supporting information). Expectedly, the copolymer 12 alone in water displays no detectable chiral medium since the polymer should exist as a helical racemate (Figure 6(A)).[72] However, when hydrophobic, polar D-camphor was added as a chiral guest, the specific rotation of the solution showed a value of $\lbrack \alpha \rbrack_{25}^{589} = +40^\circ$, significantly increased when compared with that of the sample solution contained only D-camphor ($\lbrack \alpha \rbrack_{25}^{589} = +25^\circ$, experimental part in the Supporting information). This experiment confidently confirms that the chains of amphiphilic copolymer 12 in water collapse intra-molecularly into helical conformation to minimize solvent-backbone contacts while maintaining favorable solvent-side chain interactions for solvation.

The morphology of film obtained from water dispersion of the copolymer 12 on non-polar and hydrophobic HOPG substrate shows spherical particles, significantly smaller,
The study of the copolymers \( \text{9} \) and \( \text{10} \) in chloroform revealed interesting phenomena referring to the conformation of ‘hairy-rod’ type polymeric architecture in a good solvent for both main and side chains. Several theoretical studies on the conformation of densely grafted comb-type polymers in good solvents stated that the main backbone become elongated due to the high steric hindrance of the side chains, the whole conformation resembling with a ‘bottle brush.’\[76\] There are also reported experimental results confirming the above theoretical assumption and the fact that molecules having such architecture, with a conjugated main chain, exist in a non-aggregated form in solution.\[17(a),40(b),76,77\] The AFM of the films revealed an extended to almost cylindrical shape of the

![Figure 7. AFM of copolymer 11 on mica, (A) – a: height image, b: phase image and (B) cross-sectional traces of the vesicle schematically presented.](image)
circular shape with a diameter ranging from 100 to 120 nm and 4–6 nm in height can be observed. These particles may appear as disks when the cross-sectional analysis is considered (Figure 8(B)-a). A hypothetical way for the formation of ‘core-shell’ disk-like particles is presented in Figure 8(C).

The interconnected cellular structure-forming element in Figure 8(A)-a, was measured (Figure 8(B)-b) to be approximately 10 nm in height and 200 nm as width, which, in spite of the similar appearance of the films, is higher in size than those of a polythiophene ‘hairy-rod’ with PS side chains.[77(a)] The authors tentatively assigned the observed film morphology to the kind of a bi-continuous phase structure. One of the methods to attain such microphase-separated morphology in block copolymers is the solvent annealing at room temperature when the thin film morphology results from an interplay between dewetting and micro-phase separation.[81] The method employed for the film formation of 9 in

![Figure 8](image-url)

Figure 8. (A) – AFM a: height and b: phase images; (B) cross-sectional analysis of film structures; (C) schematic model of the morphology development of the copolymer 9 from bulk to solution and film state.

conformation of individual brush. On the other hand, the block-copolymer self-assembling may take place in a non-selective solvent when other specific interactions exist,[78] which is also the case for a rod–coil block-copolymer.[79] The data presented in Table 2, referring to the copolymer 9 in chloroform solution, support the supposition that it exists in solution in assembled form, the particles with the highest size being in the highest percentage. In the AFM height image, (Figure S21(b)), the film surface of the copolymer 9 shows an interconnected cellular structure likely to be formed from fused isolated lamellae during solvent evaporation. This phenomenon was frequently observed for PS-based poly(macromonomers) because of the low affinity of PS to mica.[77] The incomplete coverage results from the dewetting of the substrate during evaporation of the solvent, thus preventing thinning of the solution layer below a certain equilibrium thickness.[80] In the AFM height and phase images presented in Figures 8(A) and S17 (full size), particles with
non-selective chloroform can be considered as a kind of solvent vapor annealing i.e. solvent was allowed to evaporate very slowly. The observed SA microstructures in film of 9 (Figure S21(b)) could be the result of such material processing, but needs independent detailed investigation for a proper assignment.

A plausible reason for the ‘core-shell’ disk-like aggregates presence in the film structure seen in Figure 8(A) is related to the general behavior of PPV polymers in good solvents. Unlike the other kind of CPs, more specifically polythiophenes, it was reported that good solvents induce a planarization of conjugated chain in PPV.[82] As chloroform is a good solvent for conjugated main chain in the copolymer 9, its planarization can take place in solution and formed conformation exhibits stronger hydrophobic inter-chain interactions, leading to significant intermolecular aggregation.[83] Such planarization-induced aggregation (Figure 8(C)) could favor rod−rod interaction, both in solution and in film state, specifically driven by π−π interaction. This interaction could be enhanced by the ratio between the main and side chain lengths during the planarization resulting in the formation of the ‘core-shell’ disk-like aggregates observed in Figure 8. Experimentally, a totally different behavior was encountered for the copolymer 10 in chloroform solution as well as in the film formed therefrom. According to the DLS results presented in Table 2, the highest percentage of the populations existing in the solution of the copolymer 10 has a size value lower than 10 nm, suggesting a possible molecularly dissolved state in chloroform as good solvent for both rod and coil building blocks. This significant difference between the copolymers 9 and 10 in solution can be mainly ascribed to their structural and architectural difference, namely the number and position of the incorporated PS side chains relative to the main chain. While the double number of the side chains on the repeating unit could be responsible for the enhanced solubility of 10 at the same weight concentration as that for 9, the ‘centipede-like’ architecture of 10 could be responsible for the particles with lower size in the high percentage in solution (Table 2). Assuming that the observed values can be attributed to a totally solved chain in chloroform, i.e. to main chains in a more planarized form,[82] this should directly impact the fluorescence behavior. However, this situation is less probable for the copolymer 10, for which the fluorescence measurements indicated Förster resonance energy transfer (FRET) phenomenon (vide infra). FRET is known to be efficient in CPs, but is also conformation dependent. More specifically, for MEH-PPV polymer, it was found that the extended conformation restricts FRET and reduces its efficiency.[84] A relatively faster FRET is characteristic for the collapsed sections of the chains or for shorter oligomers in globular shape. In these conformations, the transfer of the

energy occurs by moving excitations between two nearby but not directly connected sections of the chain – so-called ‘through-space’ energy transfer – that is much faster and efficient than ‘along-chain’ energy hopping. This means that it is very unlikely that, in chloroform solution, the main chain of the copolymer 10 to be in extended form. On the other side, due to their high solubility in the used solvent, oligostyrene side chains are in extended conformation. Consequently, their repulsion and steric hindrance is so high as the main chain cannot be in a collapsed form but more likely in a folded one.

The presence of several types or supramolecular organized entities can be detected from the AFM images of the films obtained from this solution on both mica and HOPG supports (Figures 9, 10, S18, S19, and S21(c)). It means that some of them are formed during the solvent evaporation of the copolymer 10, driven by the following two possible interactions, namely: (i) between solution and surface and (ii) intra/interchain interactions in solution.

The Figure 9(A) (see Figure S18 for full size) presents the AFM image of 10 on a mica surface of 2 × 2 μm, in which helical turns entities are dominating. The presence of this morphology correlates well with the DLS results, as well as with those of fluorescence (vide infra). If the cross-sectional analysis in Figure 9(B) is considered, it can be claimed that these entities are comparable with those usually observed for nanoring type. For a more accurate assignment, a surface of 1 × 1 μm was examined in tapping mode, which revealed an ‘edge-on’ arrangement of helical turns with a uniform size and with regular left-handed screw sense (Figures 9(C) and S19 for full size). Moreover, clusters of such helical turns can be seen also in this image forming helical nanotube-like aggregates.

The ‘edge-on’ arrangement of the observed helical turns may be favored by the large incompatibility between hydrophilic mica and hydrophobic molecules as a whole but especially by that of the oligostyrene side chains that come intimately in contact with the support surface. In this way, the contact area between the copolymer chain and support surface is minimized. The observed clusters of the helical turns are oriented almost in a normal direction in relation to the surface. However, these structures seem to be firmly fixed on the mica surface. Such behavior may arise from the favorable interaction between the positively charged mica (due to the presence of alkali ions on the freshly cleaved surface) and the electron-rich Br atoms that are connected at each oligostyrene side chain ends. The related supramolecular organization is presented in Figure 9(D). The observed nanostructures in thin film of 10 on mica can be explained based on the above discussion referring to the copolymer 12, namely that the synthesized conjugated main chain has the propensity for helical folding. Also it is very interesting that this phenomenon
During the film formation, while the chloroform is evaporated, the equilibrium is shifted toward aldehyde-support and aldehyde–aldehyde interaction, a scenario that fits both the firmly sticking of turns on the surface and their association in the observed nanotube-like aggregates.

The film surface morphology is changed when hydrophobic, non-polar HOPG was used as support. As can be seen in Figure 10, the 'core-shell' nanoparticles and vesicles of nanometer size were formed during the solvent evaporation from the solution of the copolymer 10. By comparing these two different supramolecular organizations, it can be concluded that, in the case of the copolymer 10, the supports surface energy characteristic is an important driving force triggering the morphological changes during the film formation.

All of these results revealed that by changing the type and the number of the side chains attached to the PFV main chain, appropriately choosing the selectivity of the solvent in relation to the side chains. In the case of the copolymer 10, the helical turn formation is also solvophobically driven as in the case of 12. Most probably, the sterical factors as well as the high immiscibility and stiffness asymmetry between the conjugated main chain and flexible side chains are also playing a decisive role. The stability of the formed helical turns could be assured by the π–π stacking interaction occurring between a non-adjacent p-terphenyl moiety and a fluorenyl one as demonstrated by the FRET phenomenon (vide infra). It is also important to notice that, due to the differences between water and chloroform properties, previously discussed aldehyde chain-end inter-chain interactions, schematically represented in Figure 6(A), now are not possible, being also well known the strong interaction of aldehyde functional group with chloroform.[85]

During the film formation, while the chloroform is evaporated, the equilibrium is shifted toward aldehyde-support and aldehyde–aldehyde interaction, a scenario that fits both the firmly sticking of turns on the surface and their association in the observed nanotube-like aggregates.

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All of these results revealed that by changing the type and the number of the side chains attached to the PFV main chain, appropriately choosing the selectivity of the
solvents in relation to the both side chains and main chain as well as the surface energy characteristics on which these solutions were dropped, the shape and size of the self-assembled nanostructures in solution and in film can be modulated.

**SA-induced modulation of photophysical properties**

To follow the influence of the chain conformations onto the photophysical properties, the synthesized copolymers were investigated by UV–vis and fluorescence measurements. These analyses were performed both in solution and film using the same solvents as for the self-assembling study (chloroform for the copolymers 9–11 and water for the copolymer 12, at concentration of 0.04 mg/mL) (Figures 11, S22(A) and S23 and Table 3). Photophysical properties in film were followed using quartz as support for all the synthesized copolymers. In order to understand the influence of the surface characteristics on the fluorescence emission, for the copolymer 12, mica was used as well, (Figure 12). On the other hand, to investigate how the solvent changing can modulate the photophysical properties, the absorbance and fluorescence measurements were performed also in DMSO for all synthesized copolymers (Table 3).

The UV–vis spectra of copolymers are presented in Figure S22 and can be roughly divided in two regions: one region approximately in the range of 240–300 nm and another one in the range of 310–400 nm, corresponding to the carbonyl groups and p-terphenyl moieties, and fluorenyl moieties, together the new conjugated segments, respectively. From the Figure S22(A), it can be also pointed out that both the nature and number of the side chains attached at the middle phenylene ring of the p-terphenyl moieties influence \( \lambda_{\text{max}} \) (abs). Thus, when the copolymer 9 is compared with the copolymer 10, a bathochromic shift of approximately 20 nm can be observed as the number of the oligostyrene side chains decrease. Moreover, a similar bathochromic shift with the same amount was observed when the side chains change their nature from non-polar (copolymer 10) to a polar one (copolymer 11) (Table 3). Obviously, such shifting does not depend only on the nature of the substitutes but also on the middle phenylene torsional angle and the regioisomerism at the vinylene linkages. Accordingly, it results that the average conjugation length of the main chain is probably higher in the vesicles of the copolymer 11 than in helical turns of the copolymer 10. These claims were further supported by fluorescence properties of both copolymers (Table 3, Figure 11). More specifically, the values of the \( \lambda_{\text{max}} \) for the copolymer 11 are 4 nm bathochromically shifted compared to those of copolymer 10. The estimation of the optical band gaps of the copolymers in solution was made using the registered absorption spectra by applying Einstein’s energy formula \( E_g = \frac{hc}{\lambda_{\text{max}}} \) [86] and the data are presented in Table 3. Close or identical values were found for the copolymers.
The fluorescence measurements of the copolymers were performed in solutions by the excitation at two different wavelengths (Figure 11). Generally, fluorescence traces cover broad range of approximately 250 nm with emission maxima placed between violet-blue and blue regions. By comparing with PFV homopolymer,[24(c),25−30] which usually shows a maximum emission at around 460 nm with a vibronic replica at 491–497 nm, the reported copolymers emission maxima are 30–55 nm blue-shifted. When more related n-hexyl substituted-PFV copolymer is considered, the blue shift is only 20–25 nm.

![Figure 11](image)

**Figure 11.** (A) Fluorescence spectra of copolymers in solutions excited with wavelengths in 200 nm range; (B) fluorescence spectra of copolymers in solutions excited with wavelengths in 300 nm range.

### Table 3. Photophysical properties of copolymers in solution and in film state.

| Polymer | Solvent | In solution | In film |
|---------|---------|-------------|---------|
|         |         | \(\lambda_{\text{abs}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | \(\Phi_{\text{FL}}\) (%) | \(E_g\) (eV) | \(\lambda_{\text{abs}}\) (nm) | \(\lambda_{\text{em}}\) (nm) |
| 9       | CHCl₃   | 242;260;280;380 | (370;424;456)⁴ | 10.26 | 2.75 | 241;310 | 299;395 |
|         | DMSO    | 260;280;380;420 | (394;422;445)⁴ | nd | nd | nd | nd |
| 10      | CHCl₃   | 241;259;359 | (389;422;448)⁴ | 27 | 2.78 | 242;315 | 300;400 |
|         | DMSO    | 260;270;359;380;415 | (290;328;536;396;410;427;452)⁴ | nd | nd | nd | nd |
| 11      | CHCl₃   | 241;280;310;379 | (357;392;426;444)⁴ | 35.5 | 2.88 | 242;315 | 297;395 |
|         | DMSO    | 260;285;370;385;415 | (426;444)⁴ | nd | nd | nd | nd |
| 12      | CHCl₃   | 240;268;365 | (327;355;372;396)⁴ | nd | 2.75 | nd | nd |
|         | DMSO    | 262;291;379;430 | (330;413;445;467)⁴ | nd | nd | nd | nd |
| H₂O     | 292;374 | (405;432;455;600)⁴ | 0.44 | | 241;310 | 315;426⁷ |

⁴Fluorescence spectra obtained using \(\lambda_{\text{em}} = (\lambda_{\text{abs}}/\text{max})\) in the region of 200 nm.
⁵Fluorescence spectra obtained using \(\lambda_{\text{em}} = (\lambda_{\text{abs}}/\text{max})\) in the region of 300 nm.
⁶Absolute fluorescence quantum yield of solutions.
⁷Optical band gap estimated from the onset wavelength of optical absorption in solutions, \(E_g = 1240/\lambda_{\text{onset}}\).
⁸Fluorescence spectra of films obtained using \(\lambda_{\text{em}} = (\lambda_{\text{abs}}/\text{max})\) on quartz support.
⁹Fluorescence spectrum on mica support; bold numbers – wavelength band maximum; bold italic numbers – wavelength band maximum with the highest intensity; non-bold numbers – shoulders.

The fluorescence measurements of the copolymers were performed in solutions by the excitation at two different wavelengths (Figure 11). Generally, fluorescence traces cover broad range of approximately 250 nm with emission maxima placed between violet-blue and blue regions. By comparing with PFV homopolymer,[24(c),25−30] which usually shows a maximum emission at around 460 nm with a vibronic replica at 491–497 nm, the reported copolymers emission maxima are 30–55 nm blue-shifted. When more related n-hexyl substituted-PFV copolymer is considered, the blue shift is only 20–25 nm.

solution in CHCl₃ and DMSO. The increase in copolymer optical \(E_g\) by comparing with PFV homopolymer (2.6 eV) [24(c),26(b)] is most probably due to the incorporation of the p-terphenyl comonomer. The comparable values of \(E_g\) of the copolymers 9, 10 and 12 could be determined by the formation in the main chain of the lowest energy segments having similar extension.[24(c)] The distinct increase in \(E_g\) for the copolymer 11 could be a consequence of its vesicular self-assembled shape reflected in the conjugated chain conformation, being the only one copolymer in this report studied in main chain-selective solvent.
This behavior can be ascribed to the oligomeric nature of the attached side chains as well as to the peculiar chain conformations imposed by the geometry of the entities formed by SA. It is worthy to notice that, when excited copolymer 10 at 362 nm and copolymer 11 at both 259 and 368 nm, they fluoresce at around 444 nm (deep blue emission). This is significant for application viewpoints, as long as materials with emission in this region are very important for light-emitting devices.[87] A special behavior was also observed for the copolymer 10 having oligostyrene side chains attached at the 2 and 5 position of the middle phenylene ring in p-terphenyl. As can be seen from the Figure 11 and data in Table 3, regardless of the wavelength of excitation, the values of $\lambda_{\text{max}}$ (em) are similar. This behavior can be explained by a FRET phenomenon taking place when the excitation is performed at 259 nm. It can be supposed that the g-terphenyl-containing moieties usually absorbing in this region, non-radiatively transfer its energy to the fluorenyl moieties and other conjugated segments of the copolymer absorbing at the emitted wavelength (Figure S24). It can be seen that the emission spectrum of macromonomer 6, which ranged between 290 and 500 nm, exhibited good overlap with UV–vis absorption spectrum of the copolymer 10. In the previous section of the article it was demonstrated that assemblies formed in solution by the copolymer 10 are ‘helical turns’ shaped. This geometry, favored by the high percent of the vinylene linkages in cis configuration, most probably mediates the more efficient ‘through space’ energy transfer between non-adjacent chromophores. As is also shown in Figure S24, the spectral separation of the copolymer 10 emission and the absorption of the macromonomer 6 are significant. Hence, this separation may have led to a pronounced reduction of self-absorption losses, which are very important for materials with NLO applications.[34(b)]

The absolute fluorescence quantum yields of the copolymers in solutions were also determined and presented in Table 3. It seems that also these values are influenced by the conformation of the copolymer main chain in the formed supramolecular structures.

UV–vis and fluorescence spectra of the copolymer films obtained from the investigated solutions are presented in Figure 12. It can be observed that in film state the copolymers absorb only in the high frequency region and the emission is centered at around 400 nm, approximately 50 nm blue-shifted when comparing with that of the solutions. For the copolymer 12, when the support for film was changed from quartz to mica, a significant difference was observed in the fluorescence spectrum, namely a red shift for mica with a $\lambda_{\text{max}}$ (em) at around 440 nm (deep blue). This modification is strictly related to the differences in film morphology driven by the surface characteristics of the chosen support.

It is very important to point out that the ‘hairy-rod’ architecture of the reported copolymers shows the advantage of allowing the modulation of the inter-chain interactions as well of the main chain conformation by simply changing the quality of the solvent in relation to the side chains.

The photophysical properties of copolymers were investigated also in DMSO (Table 3). For the copolymers 9, 10, and 11 the solvent shifting from good solvent chloroform to a relatively poor DMSO leads to more coiled and consequently shorter oligostyrene or oligo-ε-CL side chains and to theoretically a main chain with more twisted and shorter conjugated segments.[22(d)] These configurational changes are expected to induce a blue shift of both absorption and fluorescence. In contrast, the experimental results presented in Table 3 for the measurements of the above-mentioned copolymers in DMSO indicates a red shift of the values, especially for $\lambda_{\text{max}}$ (em), with the highest magnitude for copolymer 9. This unexpected behavior can be explained by SA-mediated formation of the nanostructures in solution.

In the case of copolymer 12, by changing the solvent from water to DMSO to chloroform corresponds to improve its quality in relation to the main chain, while for the PEG side chains means a decrease, especially for chloroform. In the case of DMSO, the experimentally obtained results confirm the theoretically expected red-shifted values (Table 3 and Figure S11), especially motivated by a more planarized main chain. The blue-shifted values obtained in chloroform can be reasoned by only the morphology of supramolecular self-assembled structures supposed to be formed in this solvent. In this case, the main chain conformations in these newly formed assemblies depend on their peculiar geometrical constraints, so the copolymer 12’s behavior is totally different from that of a true solution. When fluorescence data in Table 3, (bold italic numbers) are followed for the two investigated solvents, it can be pointed out that in the case of chloroform, as better solvent for the conjugated main chain, apparently the number of the attached side chains is the most influential factor. In the case of DMSO, both the number and type of the side chains are equally important for the observed fluorescence manipulation. In contrary to the expectations, the red-shift of the fluorescence of the copolymers in poorer DMSO clearly evidences that their photophysical properties are morphologically driven.
It appears that the self-assembling phenomenon is taking place also in the molten state. In order to rationally encoding molecular interactions that can control the assembly structure in solution, well-defined side chains, different as nature, number, and position in relation to the conjugated main chain were used to systematically change the overall character of the copolymers. Thus, beside the amphiphilic, water self-dispersible copolymer 12, and the amphipolar copolymer 11, low mixing entropy copolymers 9 and 10 were obtained, as well. The self-assembling in solution was followed by employing direct dissolution method, choosing as dispersion media those solvents for which the copolymers, as a whole, show the highest dispersibility and in which the side chains can exist in the most extended conformation. In fact, the solvents acted as selective for the side chains in the case of the copolymer 12, and main chain – selective for 11, while for the copolymers 9 and 10 the chosen solvent was neutral.

What it is really surprising and also remarkable for these materials is the shape uniqueness of the self-assembled entities formed in each case. The morphological investigations showed the propensity of the synthesized conjugated main chain for helical folding regardless of the number and type of the side chains, only by manipulating the quality of the solvent. So, monobranched PEG-substituted copolymer 12 in water formed non-aggregated intra-chain helical foldameric structure while double branched oligostyrene-substituted copolymer 10 in chloroform formed helical turns. Their formation and also their stability are the result of a combination of structural factors (backbone topology and geometrical peculiarity of its constitutive parts) with ‘through space’

**Figure 12.** UV–vis (A) and fluorescence (B) spectra of copolymers in films on quartz (q) or mica (m) surfaces.

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**Conclusions**

In this study, we report new conjugated alternating copolymers of PFV type, obtained by a hierarchical synthetic strategy and containing ‘T’-shaped or ‘Cross’-shaped p-terphenyl macromonomers in their structure. These macromonomers, decorated with well-defined side chains (PEG, oligostyrene or oligo-ε-CL) possess dialdehyde functionality that enabled the synthesis of new ‘rod-coil’ type copolymers in ‘hairy-rod’ topology by employing Wittig polycondensation. The structural characterization showed that the obtained materials are oligomeric in nature and present a higher amount of the vinylene linkages in cis configuration arising from the steric hindrance imposed by the presence of the oligomeric side chains. Thus, the whole structure adopts itself to the most energetically favorable conformation.

The expected microphase separation induced by the stiff asymmetry between the rod and coil blocks was experimentally confirmed in bulk by DSC measurements. In conjunction with POM, these measurements revealed the absence of a main chain T_g in some cases and a relaxation phenomenon of the side chains during the cooling cycles. In the case of the copolymers containing crystallizable side chains (PEG or oligo-ε-CL), the main chain T_g absence was attributed to the possible presence of dipole moments and dipole–dipole interactions that increase the T_g value over the initial degradation temperature. In addition, the restricted motion of the main chain due to the steric hindrance of the bulky side chains should also be considered. As revealed by the POM micrographs, in the molten state, the investigated materials may be considered as ‘molecular composites,’ in which the conjugated rods reinforce a matrix formed by the melted side chains.
non-bonding interactions (intramolecular $\pi-\pi$ stacking between non-adjacent moieties in the backbone and/or hydrogen bonding) and solvophobic interactions, as well. Experimental findings demonstrate the impact of the morphology in solution and in film on the conjugated main chain conformation essentially reflecting to the photophysical properties. These statements are best represented by the morphology-dependent FRET for the copolymer 10 and also by the existence of vesicles for 11 and helical turns for 10 having similar fluorescence characteristics.

Due to their distinct properties such as water dispersibility and biocompatibility, these materials could find applications in biomedical field as well as in opto- and bio-electronics.

Supporting information

Experimental part; the $^1$H-NMR and IR characterization; GPC measurements; concentration dependency; Schemes, figures and tables (PDF).

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Disclosure statement

No potential conflict of interest was reported by the authors.

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