H.F.R.I.
Hellenic Foundation for Research & Innovation

Description of the funded research project

1st Call for H.F.R.I. Research Projects to Support Faculty Members & Researchers and Procure High-Value Research Equipment

Title of the research project: "NANOTECHNOLOGY APPLICATIONS OF POLYMER BRUSHES FORMED ONTO SURFACES FROM LINEAR TRIBLOCK TERPOLYMER PRECURSORS."


Apostolos Avgeropoulos

Principal Investigator: APOSTOLOS AVGEROPOULOS, PROFESSOR

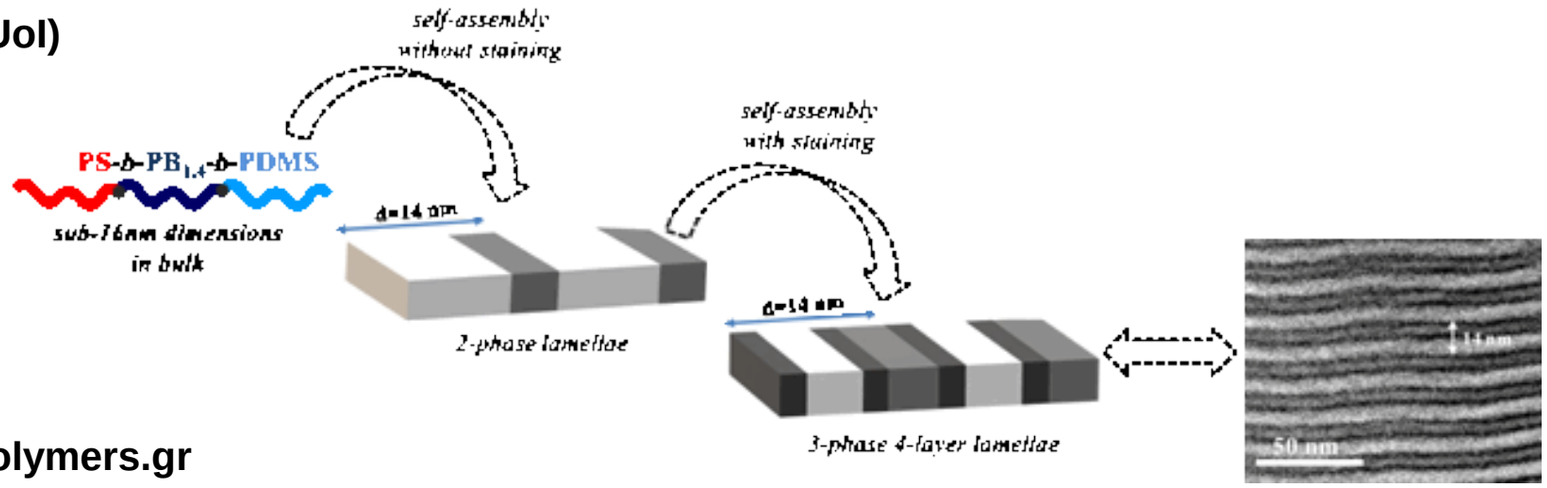
Reader-friendly title: NANOPOLYBRUSH

Scientific Area: PHYSICAL SCIENCES

Institution and Country: HELLENIC FOUNDATION for RESEARCH and INNOVATION (H.F.R.I.) ,GREECE

Host Institution: UNIVERSITY OF IOANNINA (UoI)

Collaborating Institution(s):
1. MIT / USA
2. RICE UNIVERSITY / USA
3. NATIONAL TSING HUA UNIVERSITY / TAIWAN



Project webpage (if applicable): nanopolybrush.project.uoi.gr, polymers.gr

Budget: 200,000.00 €

Duration: 30 months

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Research Project Synopsis

The aim of this research is to synthesize new A-b-B-b-C and B-b-A-b-C type linear triblock terpolymers of low molecular weight for applications in nanotechnology. In these sequences A will be the poly(butadiene) (PB) block, B would be the polystyrene (PS) and C the poly(dimethylsiloxane) block (PDMS).
In the proposed samples the PB block will display either a high microstructure of -1,4 (~ 92%) and will be denoted as $PB_{1,4}$ or a high microstructure of -1,2 (~ 100%) and will be denoted as $PB_{1,2}$. Therefore, four different triblock terpolymers are proposed, which are: $PB_{1,4}$-*b*-PS-*b*-PDMS, $PB_{1,2}$-*b*-PS-*b*-PDMS, PS-*b*-$PB_{1,4}$-*b*-PDMS and PS-*b*-$PB_{1,2}$-*b*-PDMS respectively.
Since the requirements in today's nanotechnology applications are urging for low dimensions (sub-10nm), low molecular weights are proposed in the current research proposal. The choice of these systems lies in the already studied PS-*b*-PDMS copolymers having a strong microphase separation since it is possible to control the order and thickness of their thin films on various surfaces due to the high Flory- Huggins (χ) interaction parameter value.
The addition of the PB block is aimed in order to avoid the use of PS-OH or PDMS-OH homopolymers as polymer brushes as already reported in the literature.
It should be noted that for the four sample sequences proposed, their composition and characterization in bulk and/or thin films has not been reported in the literature yet.
Even the microphase separation of the three blocks is an important contribution to the study of the structure/properties relationship since the molecular characteristics will be particularly low and the order-disorder transition state is likely to be approached if they are studied prior to annealing (thermal or vapor solvent) and after annealing.
Also, the study of triblock terpolymers in nanolithographic techniques for nanotechnology applications has not been reported in the literature.

Therefore, the proposed research is considered original and innovative.

Project originality

The proposed original research activity refers for the first time to the synthesis of specific linear triblock terpolymers wherein the poly(butadiene) block will undergo chemical modification to produce reactive -OH groups through which the PB will be grafted onto various substrates.
In particular, the modified PB block exhibits low molecular weight in order to increase the binding capacity onto the surface, and to avoid miscibility during the self-assembly of the residual diblock copolymer, which is expected to microphasially separate.
It is noteworthy, in the proposed original research that the block to be grafted onto the substrate surface is associated with the selective wetting and chemical affinity of the other two blocks of the triblock terpolymer. The whole approach proposed in the research proposal has not been previously reported in the literature and is considered to be innovative for nanolithography techniques and for their use in nanotechnology polymer applications in general.
Triblock terpolymers of the A-b-B-b-C type have not been studied as thin films for nanotechnology applications where A, B and C are three blocks of different chemical composition.
It is proposed, to study terpolymers where two of the three blocks will be PDMS and PS of the A-b-PS-b-PDMS and PS-b-A-b-PDMS types respectively, where A will be a block able to microphase separate with both PS and PDMS (increased value of the interaction parameter χ between the different block pairs).
For thin films of PS-b-PDMS diblock copolymers, various techniques/methods have been reported in the literature to show improved order and/or orientation, significantly reducing the interfacial diffusion effect between the surface and the specific polymeric material.

Expected results & Research Project Impact

In the literature there are no research results referring to thin films based on more complex systems bearing three versus two blocks which improve the order and/or the orientation of the final thin films by greatly reducing the interfacial diffusion effect between surface and polymeric material.
Innovation in the proposed research lies in the use of a block A that is "sacrificed" to improve the order and orientation of the final film. It is proposed to use as block A the poly(butadiene) with high microstructure of -1,4 or poly(butadiene) with high microstructure of -1,2.
The synthesis of triblock terpolymers bearing functional groups in at least one of the blocks so that the modified segment will play the polymer brush role will be successful.
In the proposed systems of $PB_{1,4}$-b-PS-b-PDMS, $PB_{1,2}$-b-PS-b-PDMS, PS-b-$PB_{1,4}$-b- PDMS and PS-b-$PB_{1,2}$-b-PDMS types respectively, a physical adsorption study on the surface will be performed for the smallest block ($PB_{1,4}$ or $PB_{1,2}$) and the results will be compared with those obtained by chemical modification of the type -1,2 vinyl bonds to -OH functional groups. Differences and/or similarities will be recorded.
It should be mentioned again that such a comparison is novel and innovative since it has not been reported in the literature and is probably attributed to the lack of the ability to synthesize controlled polydienes with specific microstructure (either ~ 92% -1,4 and ~ 8% -1,2 or entirely 100 % - 1,2).
Thin film studies of complex systems bearing three and not just two segments has not been reported in the literature.
The major outcome will be the improvement of the self-assembly and/or orientation of the final thin films leading to an adjustable decrease of any defects and the possibility to reach sub-10 nm structures will be efficient.

The importance of this funding

- **The proposed research will lead to high innovation and novel end products by combining chemical selectivity, functionality, in the sub-10 nanometer scale which will be used as new “polymer brushes”.**
- **The research activity is considered innovative and pioneering, since it fully responds to three basic parameters:**
  - ✓ **It is research of high standards and requirements.**
  - ✓ **It leads to the design, construction and production of final products with immediate application and cost-effectiveness.**
  - ✓ **It will lead to high society impact.**
- **Except from the experienced researchers (2 faculty members and 1 teaching and technical staff) 2 more researchers (1 Post-doctoral Associate and 1 PhD student) will be employed concluding to the avoidance of brain drain overseas.**
- **Through the collaborations with three very important Universities from abroad the members of the research team will be able to cope with other scientific environments of very high standards and requirements.**

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