FUNCTIONAL HAIRY CORE-SHELL NANOFIBERS *VIA* BLOCK COPOLYMER SELF-ASSEMBLY

SUNITA SANWARIA

DEPARTMENT OF TEXTILE TECHNOLOGY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

AUGUST 2015

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by

SUNITA SANWARIA

Department of Textile Technology

Submitted
in fulfilment of the requirements of the degree of
Doctor of philosophy

to the

Indian Institute of Technology Delhi

AUGUST 2015

Certificate

This is to certify that the thesis titled '***Functional Hairy Core-Shell Nanofibers via Block Copolymer Self-Assembly'*** being submitted by **Ms. Sunita Sanwaria** to the Indian Institute of Technology Delhi, for the award of ***Doctor of Philosophy*** degree, is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and fulfilled the requirements for the submission of thesis which has attained the standard required for a PhD. Degree of this Institute**.** The work carried out to complete this thesis has not been submitted for the award of degree or diploma in any institute in part or full.

(Dr. Bhanu Nandan)
Assistant Professor
Department of Textile Technology
Indian Institute of Technology Delhi
Date:
Place:

(Dr. Rajiv Srivastava)
Assistant Professor
Department of Textile Technology
Indian Institute of Technology Delhi
Date:
Place:

ACKNOWLEDGEMENTS

Firstly I wish to express my gratitude to my supervisors Dr. Bhanu Nandan and Dr. Rajiv Srivastava, Department of Textile Technology, IIT Delhi, for supporting the idea and giving me opportunity to undertake this work. Their motivation skills, constant guidance, timely suggestions always helped me during the tenure of this research work. I shall be grateful to them for their invaluable suggestions and untiring help, which they have shown right from the beginning till the successful completion of this endeavor.

I am thankful to the Head, Department of Textile Technology for providing infrastructure facility and cooperation for smooth completion of this research work. I would also like to express thanks to my SRC members: Prof. Manjeet Jassel, Prof. Mangla Joshi, and Dr. Sameer Sapra for their valuable inputs and suggestions during the course of this work.

I am thankful to Prof. Manfred Stamm and Dr. Andriy Horechyy, Leibniz Institute for Polymer Research, Dresden, Germany for providing access to microscopy facilities. I am also thankful to Prof. Hsin-Lung Chen, Department of Chemical Engineering, National Tsing-Hua University, Taiwan for helping in the SAXS measurements.

I am thankful to Department of Chemistry, IIT Delhi for providing UV-Visible Spectroscopy facility. I am also thankful to AIRF Centre (Jawaharlal Nehru University, Delhi) and SAIF (All India Institute of Medical Sciences, Delhi) for providing TEM facility.

I am thankful to Mr. V.K Kala, Mr. Amarjeet, Mr. A.K. Sehgal and other members of the textile department for their support.

I would also like to acknowledge my college, Deshbandhu College, for allowing me to undertake the Ph.D. work and grant leave for higher studies. I am thankful to my fellow colleagues Mythili and Harika for encouraging me all the time. I extend my gratitude to my colleagues Mr. Jit Pal and Mr. Sajan Singh for their willingness to help in any situation. I am also thankful to Pratick, Archana, Esha, Thangapandian and all other members of our research group for their constant support and encouragement.

I owe thanks to my parents for their support, help and understanding during the entire period of this research work. And special thanks to my sister Ms. Swadesh Sanwaria for her immense support during the entire tenure.

Lastly, I express my sincere thanks to all those who have helped me directly or indirectly during the course of my research work.

Sunita Sanwaria

Abstract

Recently, a lot of interest has been shown for the synthesis of functional shaped polymer nano-objects due to their potential application in tissue engineering, drug delivery, catalyst carrier, fillers for polymer matrices etc. One of the convenient approach to prepare such polymer nano-objects is *via* block copolymer self-assembly. In this case, the self-assembled domains of block copolymer could be isolated as individual nano-objects by selectively swelling the matrix phase of the block copolymer structure. In the present work, we demonstrate this concept using a cylinder forming polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer. The PS cylindrical domains were isolated as individual nanofibers by swelling the P4VP matrix in methanol which is a non-solvent for PS chains. The isolated nanofibers (cylinders) had a core-shell structure with PS as the rigid core and P4VP blocks constituting the hairy shell. The nanofiber diameter could be easily tailored by either varying the molecular weight of the block copolymer and/or by mixing PS homopolymer with the PS-b-P4VP block copolymer. Furthermore, the nanofibers could also be transformed to core-shell nanospheres either by aging or heating the nanofiber dispersion.

The core-shell nanofiber/nanosphere were further used as templates to direct the assembly of functionalities such as inorganic nanoparticles. In this case, the P4VP shell could easily be used as host because of the excellent reactivity of pyridine group towards inorganic surfaces. This was demonstrated by loading gold (Au) and cadmium sulphide (CdS) nanoparticles on P4VP shell of the nanofiber. Moreover, by directly performing the sol-gel chemistry on the P4VP shell and later on removing the organic phase, pure silica and titania nanotubes and hollow nanospheres were also fabricated. The inert PS core of the nanofibers were also used as host for the nanoparticles by suitably functionalizing the nanoparticles with oligomeric PS shell. The silver (Ag) nanoparticles incorporated this way in the PS core were found to pack in an interesting helical symmetry. It was further demonstrated that both core and shell of the nanofibers could be loaded with two different targeted functionalities which enables the combination of their properties in a single structure. This was aptly shown by fabricating Ag/Au and Ag/CdS multifunctional polymer nanofibers where the Ag nanoparticles were in the core and Au or CdS nanoparticles decorated the shell of the nanofibers.

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List of Symbols and Abbreviations

PS-b-PMMA	polystyrene-block-poly(methyl methacrylate)
N	degree of polymerization
X	Flory-Huggins interaction parameter
f	volume fraction
PS-b-PI	polystyrene-block-polyisoprene
CPB	cylindrical polymer brushes
BCP	block copolymer
ATRP	atom transfer radiated polymerization
ROP	ring opening polymerization
NMP	nitroxide mediated polymerization
MWD	molecular weight distribution
PBIEM	poly(2-(2-bromoisobutyryloxy)ethyl methacrylate
PS	polystyrene
PAA	polyacrylic acid
P*t*BA	poly(t-butyric acid)
PCL	polycaprolactam
PDMAEMA	poly(N, N-dimethylaminoethyl methacrylate)
PS-b-PCEMA	polystyrene-block-poly(2-cinnamoyloxyethyl methacrylate)
PBMA	poly(butyl methacrylate)
PS-b-P4VP	polystyrene-block-poly(4-vinylpyridine)
PS-b-P2VP	polystyrene-block-poly(2-vinylpyridine)
PTEPM-*b*-PS	poly 3-(triethoxysilyl)propyl methacrylate block-polystyrene
PtBA-b-PGMA	poly(tert-butyl acrylate)-block-poly(glycidyl methacrylate)

EDA	ethylenediamine
PA	propargylamine
PI-b-PEO	polyisoprene-block-poly(ethylene oxide)
PDP	3-n-pentadecylphenol
POEGMA	poly(oligo (ethylene glycol) methacrylate)
TALH	titanium (IV) bis(ammonium lactate) dihydroxide
PHEMA	poly(2-hydroxyethyl methacrylate)
PMAEMA	poly(2 methylamino)ethylmethacrylate
ln^{+3}	lanthanum ion
SEM	scanning electron microscope
TEM	Transmission electron microscope
EFTEM	Energy filtered Transmission electron microscope
DLS	Dynamic light Scattering
SAXS	Small angle x-ray scattering
AFM	Atomic force microscopy
TEOS	tetraethylorthosilicate
TTIP	titanium isopropoxide
CdS	cadmium sulphide
PS- b -PAMA	poly(allyl methacrylate)
PSS	polystyrene sulfonic acid
$NaBH_4$	Sodium borohydride
Au	gold
Ag	silver
SPR	surface plasmon resonance
hPS	homopolystyrene