

**OPTICAL SPECTROSCOPY AND
STRUCTURE OF
POLYSTYRENE FILMS AND
AU-POLYSTYRENE NANOCOMPOSITES**

Thesis submitted to
The University of Calcutta
for the degree of
Doctor of Philosophy (Science)

by

SUDESHNA CHATTOPADHYAY

March, 2007

Contents

1	Introduction	1
1.1	Supramolecular Assemblies	1
1.2	Intermolecular Forces and Their Manipulation	2
1.3	Polymers and Films: Cohesion and Surface Energy	6
1.4	Polymer Film: Nanoconfinement and Tunable Self-assembly	11
2	Experimental Techniques	17
2.1	Spin Coating	17
2.1.1	Principle and Theory	18
2.1.2	Instrumentation	21
2.2	Magnetron Sputtering	23
2.2.1	Principle and Theory	23
2.2.2	Instrumentation	25
2.3	Analysis Probes Used	26
2.4	Spectroscopy	27
2.4.1	Regions of the electromagnetic spectrum	27
2.4.2	Absorbance and Transmittance	28
2.4.3	Infrared Spectroscopy	29
2.4.4	Ultraviolet-visible Spectroscopy	35
2.5	X-ray Scattering	46
2.5.1	X-Ray Reflectivity (XRR)	48

2.5.2	Instrumentation	61
2.5.3	Sample-Cell	64
2.6	Scanning Probe Microscopy	65
2.6.1	Atomic Force Microscopy	66
2.6.2	Instrumentation	73
3	A Theoretical Background of Spectroscopic Analysis	76
3.1	Optical Absorption Spectra of Benzene and Polystyrene	76
3.1.1	Electronic Spectroscopy and Symmetry	76
3.1.2	Electronic states in benzene molecule	78
3.1.3	Molecular Optical Response	93
3.2	Optical properties of molecular aggregates	98
3.2.1	Optical response of ‘physical dimers’	99
3.2.2	Linear Optical Properties of Linear J-aggregates	104
4	Confinement Effects on Pristine Polystyrene Films	107
4.1	Motivation for studying Polystyrene Films	107
4.2	Outline of work	111
4.3	Delocalized Exciton in <i>PS</i> Film - Localized under nanoconfinement	113
4.3.1	Size-effect in Polystyrene Films	113
4.3.2	Exciton Localization	120
4.4	Inter- and Intra Molecular Rearrangement: Nanoconfined <i>PS</i>	129
4.4.1	Intermolecular repulsive potential	129
4.4.2	Benzene physical dimer in polystyrene:	137
4.5	Conclusion	147
5	Tunable Self-assembly on Nanoconfined Films	149
5.1	Self-assembled Growth of Monodisperse Au Nanoparticles on Nanoconfined <i>PS</i> Films	151

5.1.1	Outline of Work	151
5.1.2	Sample Preparation	152
5.1.3	Au Nanoparticles: Tuning of Self-assembly	152
5.1.4	The Growth Mechanism	160
5.1.5	Lower cut-off of <i>PS</i> thickness in <i>Au</i> nanoparticle formation	163
5.1.6	Conclusion	164
5.2	Tuning of Two-dimensional Self-assembly of Thiol-capped Au Nanoparticles through Nanoconfinement	166
5.2.1	Sample Preparation	167
5.2.2	Pattern Formation and Disappearance: Tunability in Network dimension through <i>PS</i> thickness	168
5.2.3	Tunability Through Concentration of Au-thiol Solution	172
5.2.4	Spectral characteristics of thickness dependent pattern	173
5.2.5	Conclusion	174
6	Conclusions and Outlook	175
6.1	Conclusions	175
6.2	Outlook	177