

**REPUBLIC OF TURKEY  
YILDIZ TECHNICAL UNIVERSITY  
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**FABRICATION AND CHARACTERIZATION OF NANOSTRUCTURES  
BY SELF-ASSEMBLY**



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A thesis submitted by İlknur Hatice ERYILMAZ in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** is approved by the committee on 23.11.2016 in Department of Chemical Engineering, Chemical Engineering Program.

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In this thesis work, the impact of different ternary solution composition on the final morphology of Poly (methyl methacrylate) nanostructures has been investigated. Poly (methyl methacrylate) has a wide usage in different engineering sectors. Among other applications, it is used in tissue engineering applications thanks to its transparent, biocompatible and good wear resistance properties. Obtained nanostructures have been examined in respect to their morphological parameters such as fibre/dot width and intern pattern distance.

I would first like to thank my thesis co-advisor Dr. Alessandro Fraleoni Morgera of the Department of Engineering and Architecture at University of Trieste. Dr. Alessandro Fraleoni Morgera supported a lot my study and related research, I thank for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis within my exchange student program for 11 months. I could not have imagined having a better advisor and mentor for my study. Assoc. Prof. Ali Ekrem Muftuoglu was always open whenever I ran into a trouble spot or had a question about my research. I would thank also Assoc. Prof. Jale GÜLEN, who made a great effort on my graduation way.

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İlknur Hatice ERYILMAZ

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## LIST OF SYMBOLS

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$\alpha, \beta, \gamma$	Angles between crystal structures
T	Absolute temperature
cm	Centimetre
nm	Nanometre
$\mu\text{m}$	Micrometre

## LIST OF ABBREVIATIONS

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AS	Auxiliary Solvent
CHCl <sub>3</sub>	Chloroform
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
PDCB	Para-dichlorobenzene
PMMA	Poly (Methyl Methacrylate)
SEM	Scanning Electron Microscope
SS	Sublimating Substance
STM	Scanning Tunnelling Microscope
TM	Target Material

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**FABRICATION AND CHARACTERIZATION OF NANOSTRUCTURES  
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Department of Chemical Engineering

MSc. Thesis

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With the increasing demand of nano-scale material, studies on effective nanotechnology techniques show a progressive raise in interest from the industrial area, which needs fast, low-cost and practically applicable nanofabrication processes. In this frame, a self-assembly method, ASB-SANS (Auxiliary Solvent-Based Sublimation-Aided Nanostructuring) has been studied. Basically, this method involves a ternary solution composed by a target material (the material to be nanostructured; in this case PMMA), a sublimating substance (PDCB) and a proper solvent ( $\text{CHCl}_3$ ); then, drop-casting on Si/SiO<sub>x</sub> substrates and evaporation and sublimation processes. the crystal structure of sublimating substance gives the desired nanostructure to the target material.

Sixteen different concentration ratio has been prepared and examined by their effect on the morphology as dotted/fibre alignments. Fundamentally, ternary solution prepared on different concentrations of auxiliary solvent and sublimating substance. Furthermore, obtained morphologies have been examined by their width and distance and grouped as primary, secondary, tertiary patterns. And the reasons of difference have been searched. Basically, sixteen different ternary concentrations have been prepared based on auxiliary solvent and sublimating substance concentration variations.

In conclusion, the analysis and findings of this study supports our claim that ternary solution composition values play an important role to achieve desired structure. Despite

to the fact that the method is easy applicable and fast, it requires well-preparation and precision work. However, environmental control and surface treatment are rather important to gain uniform, anticipated pattern. Besides those, used method allows to fabricate nano-micro structures in big areas (several cm<sup>2</sup>) and a way that is low-cost, in short time (several seconds).

**Key words:** Nanofabrication, Self-assembly, ASB-SANS, Poly (Methyl methacrylate), nanostructure



## NANOYAPILARIN SELF-ASSEMBLY YÖNTEMİ İLE FABRİKASYONU VE KARAKTERİZASYONU

İLKNUR HATİCE ERYILMAZ

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Artan spesifik nano boyutlu ürün ihtiyacı ile birlikte, etkin nanofabrikasyon teknikleri üzerine yapılan çalışmalarda da artış yaşanmaktadır. Bu doğrultuda bir “Down-to-Up” Kendiliğinden oluşum metodu olan ASB-SANS (Auxiliary Solvent-Based Sublimation-Aided Nanostructuring) üzerinde çalışılmıştır. Bu yöntem, ana madde (PMMA) ve süblimleşen maddenin (PDCB) ortak çözücü (CHCl<sub>3</sub>) içerisinde çözünmesi ve Drop-Casting yöntemi ile Si/SiO<sub>x</sub> yüzeylere damlatılması işlemidir. Daha sonrasında, evaporasyon ve süblimasyon gerçekleşerek istenilen yapılar substrat üzerinde elde edilir. Süblimleşen maddenin kristal yapısı ana maddeye istenilen deseni kazandırır.

Oda sıcaklığı (Sıcaklık sabit tutularak), ortam basıncında yapılan çalışmada farklı üçlü bileşen konsantrasyonların elde edilen desen üzerindeki noktasal/sürekli gibi morfolojik etkisi incelenmiştir. Ayrıca, elde edilen birincil, ikincil, üçüncül desenlerin kalınlık ve uzaklıkları ölçülmüş, buna göre gruplandırılmış ve oluşan farklılıkların ardındaki nedenler araştırılmıştır. Temelde, çözücü konsantrasyonu ve süblimleşen madde konsantrasyonları değişimi şeklinde iki farklı yönde ilerlenmiştir ve sonuçta 16 farklı durum ortaya çıkmıştır.

Sonuç olarak elde edilen veriler üçlü bileşen konsantrasyonunun istenilen yapıyı elde etmekte oldukça önemli olduğunu göstermektedir. Yöntem uygulanabilirliği açısından oldukça kolay olmasının yanında iyi bir hazırlık ve hassasiyet gerektirmektedir. Difüzyon,

evaporasyon, süblimasyon prosesleri, yüzey kimyası ile çevresel faktör (sıcaklık, nem vb.) kontrolünün yüksek öneme sahip olduğu görülmüştür. Bunun yanında, çok kısa surede (Birkaç saniye), geniş alanlarda (birkaç cm<sup>2</sup>) istenilen şekilde nano-mikro yapıların düşük maliyetle üretimine olanak vermektedir.

**Anahtar Kelimeler:** Nanofabrikasyon, Self-Assembly, ASB-SANS, Polimetilmetakrilat, nanoyapı



### INTRODUCTION

#### 1.1 Literature Review

Materials in the nanoscale show different chemical, physical, electronic, optic properties than their macroscale properties [1]. Thanks to these beneficial properties, materials gain new application areas in numerous industry such as catalyst, medicine, electronic, ceramic, cosmetic etc. [2], [3], [4]. PMMA, also known as acrylic or acrylic glass is mostly used in sheet form as a lightweight and shatter-resistant alternative to glass thanks to its transparency, easy handling, low cost, durability, biocompatibility and thermoplastic properties. It is used in the lenses of exterior lights of automobiles [5], rigid intraocular lenses which are implanted in the eye in case of cataract problem [6], soft contact lenses where acrylate monomers containing one or more hydroxyl groups make them hydrophilic[7]. It has a lot of application area in medicine thanks to its biocompatibility such as bone cement in orthopaedic surgeries [8]. In the area of regenerative medicine and also controlled release devices for pharmaceutical products [9] are another examples of tissue engineering applications.

When considered nanofabrication techniques based on “Down-to-Up” methods, auxiliary solvent-based sublimation-aided nano structuring (ASB-SANS) has advantages over other methodologies about cost, time efficiency, and higher versatility for the creation of large-area, ordered arrays of organic-material-based filamentary nanostructures [10]. On the other hand, it is the method which requires critical environmental control to have a uniform pattern.

## **1.2 Objective of the Thesis**

PMMA can be formed in nanostructures using the ASB-SANS method, which exploits a ternary solution for growing nanostructures onto a surface. These nanostructures can be used in tissue engineering applications, using either PMMA or other biocompatible polymers as scaffolds for cell growth.

Objective of this research thesis is to study the effect of different ternary solution (TS) composition on the nanostructures developed onto a Si/SiO<sub>x</sub> surface after having deposited such a solution onto the surface, and to find correlations between the TS composition and the topological/morphological parameters of the developed nanostructures. The work considers how it is possible to control the transition from continuous nanofibers to aligned nanodots simply changing the composition of the TS on which ASB-SANS is based. This study has been carried out realizing a ternary diagram relating the various TS compositions and the resulting nanopatterns morphologies has been realized. Moreover, the fibres/dots lines width and inter-pattern distance variations have been analysed with respect to the TS composition, showing consistency with currently accepted models for macromolecular chains mobility in a medium.

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## **1.3 Hypothesis**

In this study, an extensive investigation over the parameters controlling the morphology and the size of ASB-SANS-generated patterns (nanofibers and aligned dots) is reported. In this study, one of the self-assembly methods based on “Bottom-Up”, ASB-SANS, is used and we focused on to understand the distinction between different concentration ratios as it relates to nanostructures.

As a simple method to achieve desired structures all experiments have been carried out at the room temperature and under ambient pressure. PMMA structures are controlled via alteration of the ternary solution composition which consists of target material



(PMMA), sublimating substance (SS) and auxiliary solvent (AS). According to experiments and examination of obtained structures, it was seen that desired morphological properties may be envisaged by changing these three-component concentrations.



### GENERAL INFORMATION

In this chapter, nanotechnology, nanomaterials and outstanding nanofabrication techniques will be discussed.

#### 2.1 Nanotechnology and Nanomaterials

Nanotechnology is a combination which includes science, engineering and technology at the nanoscale. This term refers to very tiny features, within sizes ranging between 1 to a few hundred nanometres. Nanotechnology joins different research fields as surface science, organic chemistry, molecular biology, solid physics, microfabrication, nano-thermodynamics etc. Nanoscale materials were used for centuries even though it seems a modern technology. Nano-sized gold and silver particles gave colours in the stained-glass windows of medieval churches hundreds of years ago. The artists back then just didn't know that the process they used to create these beautiful works of art.

Under micro level has become a scientific discussion first time at an American Physical Society meeting at the California Institute of Technology on December 29, 1959, by physicist Richard Feynman. In the discussion, Feynman presented a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, in his explorations of ultraprecision machining, Professor Norio Taniguchi coined the term nanotechnology. In the '80s the development of the scanning tunnelling microscope (STM) and the atomic force microscopy (AFM) (see figure 1 for their working principles) allowed to "see" individual atoms, starting the field of modern nanotechnology [11].

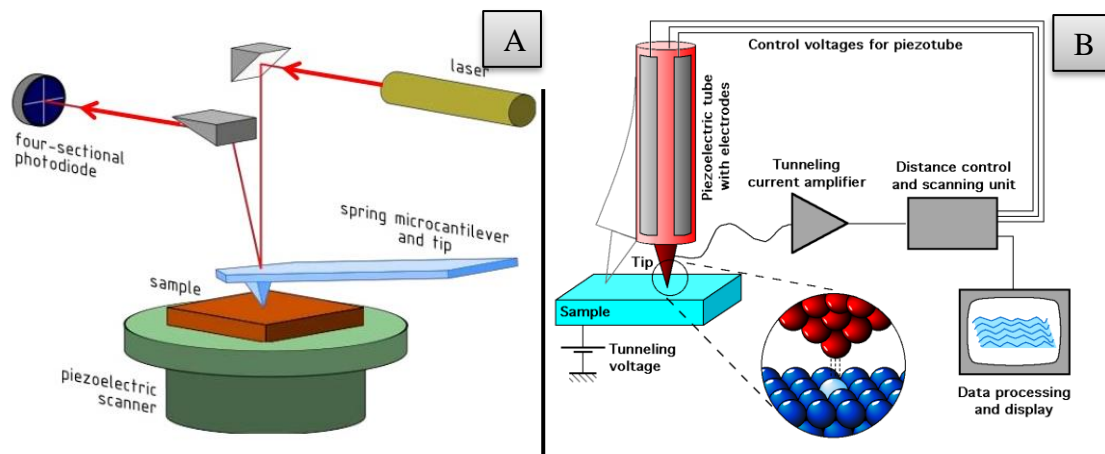


Figure 2.1 Schematic view of A) Atomic Force Microscope [12] and B) Scanning tunnelling microscope [13]

Nanoscale properties of materials are significantly different from their macroscale properties. For example, gold is yellow the colour at the macro scale, meanwhile it is red/purple at the nanoscale [14]. Nanomaterials provide unique properties such as physical, chemical, mechanical, optical, etc. Furthermore, decreasing the characteristic dimension increases the surface area/volume ratio. Thus, the smaller the characteristic dimensions, the more pronounced become the surface-related effects. For example, sensing materials on the surface would react with the detection gas, which accomplish high sensing sensitivity and rapid response speed [15]. At the nanometre scale (1–100 nanometres), quantum effects rule the behaviour and properties of particles. Thus, when particle size is made to be nanoscale, properties such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of the size of the particle. A fascinating and powerful result of the quantum effects of the nanoscale is the concept tenability properties of material. That is, by changing the size of the particle, a scientist can literally fine-tune a material property of interest. Another potent quantum effect of the nanoscale is known as “tunnelling,” which is a phenomenon that enables the scanning tunnelling microscope and flash memory for computing. Basically, STM working principle relies on penetrability of very small masses (tunnelling); while small masses such as electron pass the barrier, other objects can’t pass.

Ever since nanotechnology provides nanometre-scale processing and production of unique materials through controlling their size and shape, they received much attention

in different industrial areas such as renewable energy, electronics, textile, medicine, environment, etc. Such nanomaterials are designed to be stronger, lighter, more durable, water-repellent, anti-reflective, self-cleaning, ultraviolet- or infrared-resistant, anti-fog, antimicrobial, scratch-resistant, or electrically conductive, among other possible applications. For instance, industrial materials include protective clothing against chemical and biological warfare agents, sound absorption materials. Sensor applications for detecting chemical agents, highly sensitive chemical gas sensors which detect the presence of different gas in an area are important for humans and animals about environmental pollution [16].

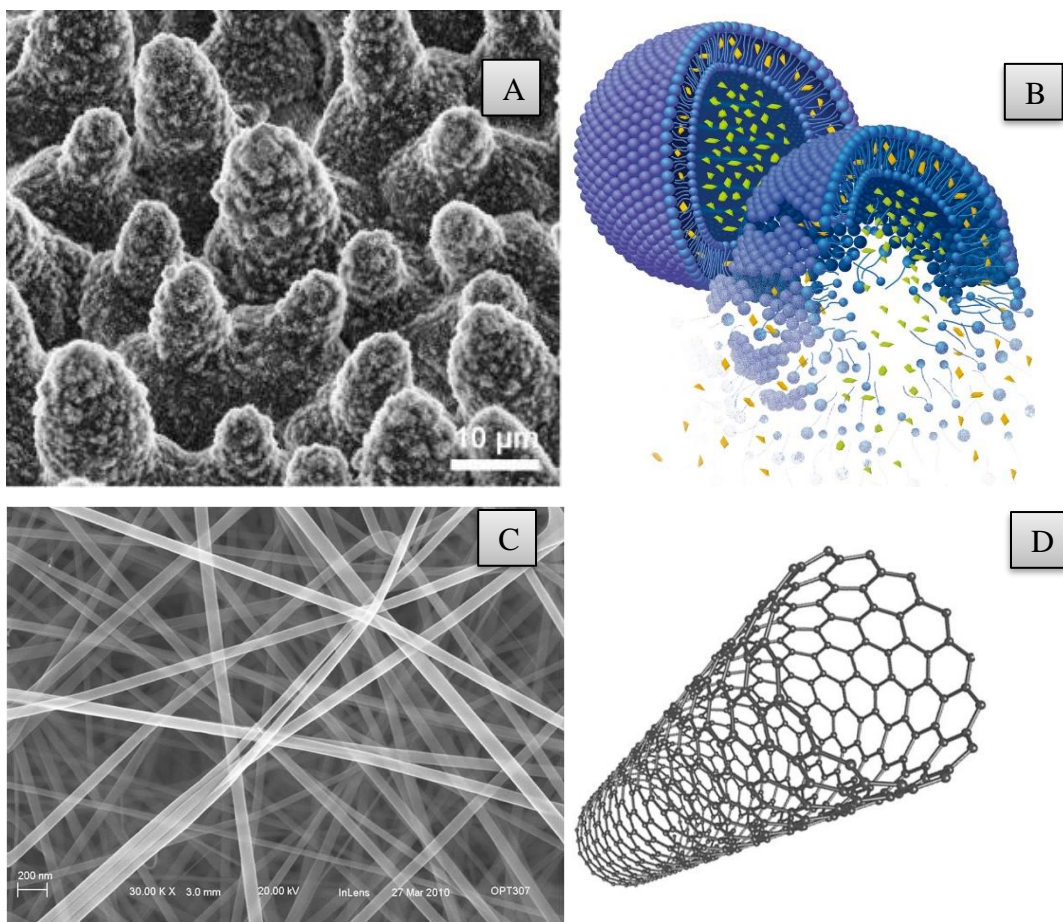


Figure 2.2 Different nanostructures used in different field of industries A) Nanowires to be used in Polymer Electrolyte Membrane(PEM) fuel cells, B) Nanospheres to be used in drug delivery[17], C) Natural nanostructure of Lotus which provide super hydrophobic surface [18] D) CNTs, to be used in military applications [19]

Nano applications in medicine includes drug delivery and tissue engineering mainly. Tissue engineering or artificial organ applications may include the realization of proper nanostructured scaffolds which will allow cell attachment and migration, deliver and

retain cells and biochemical factors, enable diffusion of vital cell nutrients and expressed products, exert certain mechanical and biological influences to modify the behaviour of the cell phase. For cardiac tissue engineering applications, scaffold design requires special scaffold alignment, structure, porosity, stiffness. [20] [21]. Nanofabrication of microelectronic devices and information technologies are also a big area which is currently under intense development. It requires improvement in terms of large-scale, commercial implementation of nanofabrication, to increase the density of components, lower their cost, and increase their performance per device and per integrated circuit. [22].

Nanofabrication focuses on the process of making desired special structures with arbitrary patterns having minimum dimensions currently defined at the nanoscale. There are various ways to fabricate nanomaterials such as “Top-Down” and “Bottom-Up” which will be presented in the following section, “General trends in the fabrication of nanomaterials”. These methods are chosen based on the usage target of material, fabrication cost, energy and time consumption, etc.

Methods to produce conventional polymer fibres smaller than 10  $\mu\text{m}$  diameter is a very active research area in nanotechnology. In particular, in tissue engineering, three techniques have proven successful: self-assembly, phase separation, and electrospinning [23] [24].

Morphological properties of nanostructures play an important role in the functionality of material, especially for biological applications. Their size, shape and spatial organization (aggregate structure) identify these functions. Essentially, it relies on their material composition, crystal structure and fabrication method. In case of nanofabrication with the organic molecules, result morphologies may show infinite variation depend on organic chemistry. Physical, chemical and thermodynamic properties of organic compounds are generally connected to their structures and vary with them in a systematic way [25].

The aim of this thesis is to create ladder-like nanostructures which can play role as scaffold in tissue engineering. For this purpose, one of the self-assembly method, ASB-SANS, is used. Different patterns achieved by different concentrations and morphological diversity is examined by their width and inter pattern distance. It is clearly

seen this method may be applied more than tissue engineering such as gas sensing, renewable energy, coating applications.

## **2.2 General Trends in the Fabrication of Nanomaterials**

A numerous technique can create nanostructures. Because of commercial applicability, sometimes these techniques are grouped as conventional or unconventional. Hence the name, conventional techniques are commercially available and widely implemented in different fields of industry. For instance, lithography is highly developed and widely used for fabricating microelectronic circuits. Conventional techniques have relatively high cost and low throughput; they are also largely restricted to planar fabrication in semiconductor materials and are incompatible with many problems in nonstandard fabrication [22].

Sometimes conventional methods are not enough to have specific properties such as patterning relatively fragile materials, such as organic materials (especially biological materials) other than photoresist. In these times, unconventional methods are being in demand. Unconventional routes to nanofabrication are often appears in research. These techniques create opportunities for fabrication on nonplanar surfaces (particularly smooth, curved surfaces) and over large areas and may offer competition in nanofabrication where cost and materials make photolithography difficult. For instance, tools for moulding on the nanometre scale are already in commercial production. Furthermore, they are probably the only techniques that are applicable to biological materials and to sensitive organic and organometallic materials. The ability of any techniques conventional or unconventional to prototype nanoscale structures rapidly and inexpensively will be a factor that influences the acceptance of that technique. Unconventional techniques have the potential to be the ultimate, low-cost method for nanofabrication. Unconventional approaches are also operationally much simpler to use than are conventional techniques and thus help to open nanoscience and nanotechnology to exploration by a wide range of disciplines, especially those historically weakly connected to electrical engineering and applied physics [22].

Table 2.1 compares the capabilities of conventional and unconventional techniques for patterning nanostructures for 2004. This table summarizes the current minimum feature

size (minimum lateral dimension), the highest resolution (pitch), and the types of patterns that can be generated reproducibly by each technique [22].

Table 2.1 Capabilities of Conventional and Unconventional Nanofabrication Techniques (2004) [22].

Technique	Minimum Feature <sup>a</sup>	Resolution	Pattern
<b>Photolithography</b> <sup>1</sup>	37nm	90 nm	Parallel generation of arbitrary patterns
<b>Scanning beam lithography</b> <sup>88, b</sup>	5nm	20 nm	Serial writing of arbitrary patterns
<b>Moulding, Embossing and printing</b> <sup>116,123,168, c</sup>	≈ 5 nm	30 nm	Parallel formation of arbitrary patterns
<b>Scanning probe lithography</b> <sup>28,52</sup>	< 1nm	1 nm	Serial positioning of atoms in arbitrary patterns
<b>Edge lithography</b> <sup>39, d</sup>	8 nm	16 nm	Parallel generation of non-crossing features
<b>Self-Assembly</b> <sup>353-357</sup>	> 1 nm	> 1nm	Parallel assembly of regular, repeating structures

<sup>a</sup> Refers to the minimum demonstrated lateral dimension. <sup>b</sup> Obtained with a focused ion beam. Limited by photoresist sensitivity and beam intensity. <sup>c</sup> Limited by available masters and, ultimately, van der Waals interactions. <sup>d</sup> Potentially smaller sizes could be obtained using atomic layer deposition.

When nanofabrication methods examined in respect to process, formation; “top-down” and “bottom-up” would be better to describe and understand the way of generation nanoscale structures and nanostructured materials. The top-down approach uses various methods of lithography to pattern nanoscale structures. And the bottom up approach uses interactions between molecules or colloidal particles to assemble discrete nanoscale structures in two and three dimensions.

Table 2.2 Top-Down and Bottom-Up Methods of nanofabrication

TOP-DOWN METHODS (DESTRUCTION)	BOTTOM-UP METHODS (CONSTRUCTION)
<ul style="list-style-type: none"> <li>• Lithography                             <ul style="list-style-type: none"> <li>• Photolithography</li> <li>• Scanning Beam Lithography</li> <li>• Scanning Probe Lithography</li> <li>• Soft Lithography</li> </ul> </li> <li>• Chemical Etching</li> <li>• Dry Etching</li> <li>• Ball Milling</li> </ul>	<ul style="list-style-type: none"> <li>• Self-Assembly                             <ul style="list-style-type: none"> <li>• Nontemplated Self-assembly</li> <li>• Templated Self-assembly</li> </ul> </li> <li>• Sol-gel Technique</li> <li>• Spray Pyrolysis</li> <li>• Chemical/ Physical Vapour Deposition</li> <li>• Atomic Layer Deposition</li> <li>• Pulsed Laser Deposition</li> <li>• Molecular Beam Epitaxy</li> <li>• Electrodeposition</li> <li>• Metal Organic Vapour Phase Epitaxy</li> </ul>

Top-down and bottom-up terms were first applied to the field of nanotechnology by the Foresight Institute in 1989 in order to distinguish between molecular manufacturing and conventional manufacturing. Bottom-up approaches seek having smaller as molecules components built up into more complex assemblies, while top-down approaches seek to create nanoscale devices by using larger, externally controlled ones to direct their assembly [26].

Both approaches play very important role in the nanotechnology industry. There are advantages and disadvantages in both approaches. Firstly, all the tools we have possessed are too big to deal with such tiny subjects. The biggest problem with top down approach is the imperfection of surface structure and significant crystallographic damage to the processed patterns. However, this approach leads to the bulk production of nanomaterial. Furthermore, top down approach most likely introduces internal stress. Regardless of the defects, they have always an important role in the synthesis of nanostructures.

When the desired structure is on the nanometre scale, there is a little chance for top down approach. Bottom up approach shows a greater chance to obtain nanostructures with less defects, more homogeneous chemical composition. [27].



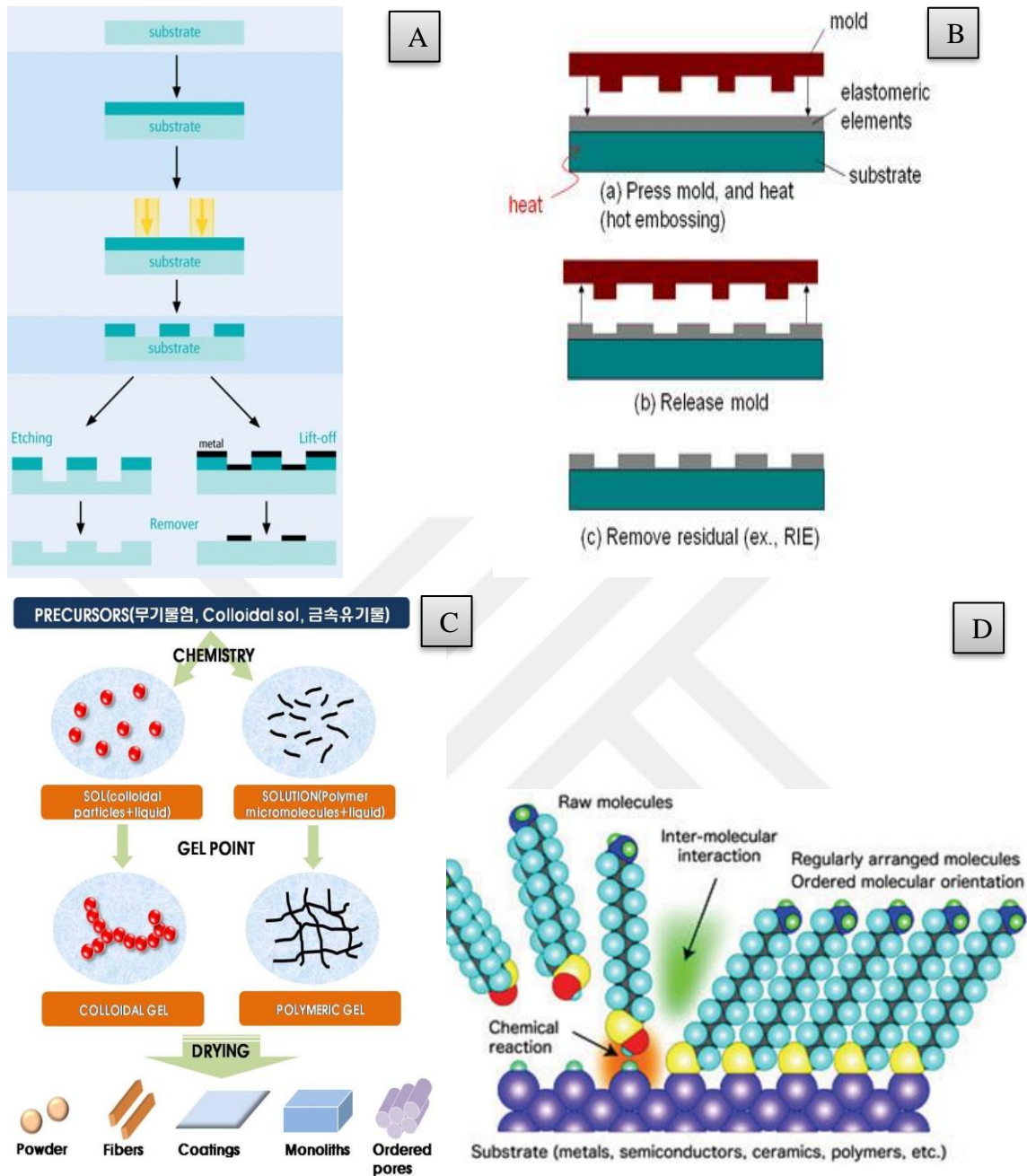


Figure 2.3 A) Electron beam lithography, B) Soft lithography, C) Sol-gel, D) Self-Assembly techniques (Example of self-assembling set to occur on previously chemically-functionalized surfaces) [28] [29]

### 2.2.1 Top-Down Methods

The top-down approach mostly uses the traditional workshop or microfabrication methods where externally controlled tools. This tools play a role to achieve desired nanostructures such as cutting, milling processes. In this process, required material is protected by a mask and the exposed material is etched away. Etching of the base material can be done chemically using acids or mechanically using ultraviolet light, x-

rays or electron beams depends on the level of resolution required in the final product. This is the technique commonly applied to the manufacture of computer chips [30]. Nanotechnology techniques for top down fabrication vary but can be split into mechanical and chemical fabrication techniques.

The most used top down fabrication technique is nanolithography. Although the concept of photolithography is simple, the actual implementation is very complex and expensive [31]. Electron-beam lithography and X-ray lithography techniques have been developed as alternatives to photolithography. With the electron beam lithography, the pattern is written in a polymer film with a beam of electrons. But, since diffraction effects are largely reduced due to the wavelength of electrons, so the resolution is greatly improved. Furthermore, the electron beam technique is very expensive and very slow. With the X-ray lithography, diffraction effects are also minimized, but conventional lenses are not capable of focusing X-rays and the radiation damages most of the materials used for masks and lenses.

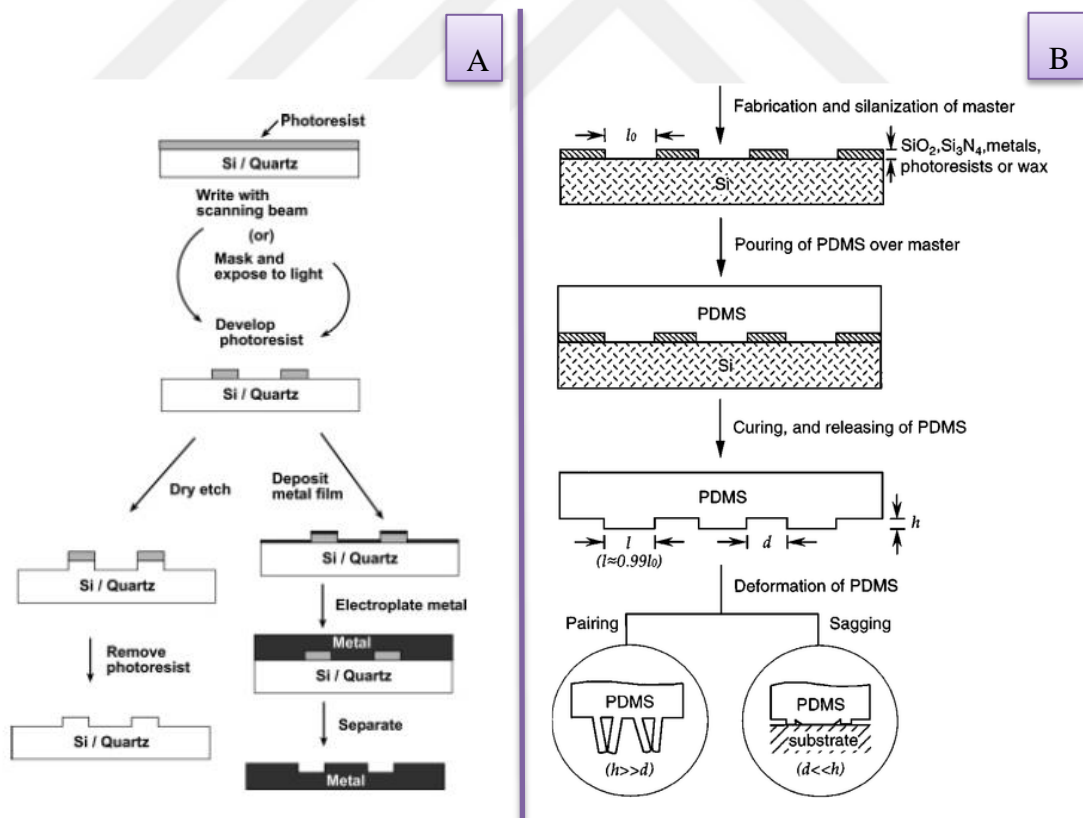


Figure 2.4 Schematic illustration of the fabrication of topographically patterned surfaces (A) Conventional photolithography and electroplating. [22]. (B) The process of fabricating a PDMS stamp from a master mold. This allows for the creation of many stamps [32]

Printing, stamping, and molding use mechanical processes instead of photons or electrons. These methods are normally called soft lithography methods because they involve the use of polymers; through the use of a stamp/mould made from a "soft" material (referring to elastomers, typically PDMS), transfer a pattern to a substrate [33]. Although lithography techniques have been quite popular in high-tech industries, soft-lithography offers several advantages. Because, once the master template has been made, no special equipment is required for soft lithography. So, significantly lower cost for mass production compared to lithography. Furthermore, soft lithographic methods are capable of producing nanostructures in a wide range of materials and can print or mold on curved as well as planar surfaces.

Some fabrication techniques have also used the combination of the two forms of lithography (soft-lithography and photolithography) to develop hybrid methods that utilize a PDMS photomask in addition to a Chromium photomask to create novel structures [34].

### **2.2.2 Bottom-Up Methods**

Bottom up is another approach to achieve nanoscale materials. Basically, it is the process from the lowest level of a hierarchy to the top. It has been always in the nature and all the living beings observe growth by this approach only. Also, it has been in industrial use for over a century such as the production of salt and nitrate.

Bottom-up approaches use the chemical properties of single molecules to cause single-molecule components to (a) self-organize or self-assemble into some useful conformation, or (b) rely on positional assembly. These approaches utilize the concepts of molecular self-assembly and/or molecular recognition can thus be viewed as a synthesis approach where the building blocks are added onto the substrate to form the nanostructures. Such bottom-up approaches are able to produce devices in parallel and much cheaper, but could potentially be overwhelmed as the size and complexity of the desired assembly increases [35]. Spontaneous organization of molecules into stable, structurally well-defined aggregates and molecules can be transported to surfaces through liquids.

Bottom-up methods driven mainly by the reduction of Gibbs free energy, therefore closer to a thermodynamic equilibrium state and at the end material has less defects, homogeneous chemical composition and short-long range ordering. Furthermore, different synthesis and processing approaches often result in appreciable differences in chemical composition, crystallinity, and microstructure of the material due to kinetic reasons [36].

Atomic layer deposition (ALD) is an industrial process that is capable of coating any material, regardless of size, with a monolayer or more of a thin film. A relatively pure bottom-up process starting with gas-phase constituents. Molecular beam epitaxy (MBE), a technique for epitaxial growth via interaction of one or more molecular or atomic beams that occur on a surface of a heated crystalline substrate, is other industrialized processes that are considered to be bottom-up. The term “beam” means that evaporated atoms do not interact with each other or any other vacuum chamber gases until they reach the substrate, due to the long mean free paths of the beams [37]. It takes place in high vacuum or ultra-high vacuum ( $10^{-8}$ ,  $10^{-12}$  Torr). The most important aspect of MBE is the deposition rate (typically less than 3000 nm per hour) that allows the films to grow epitaxial.

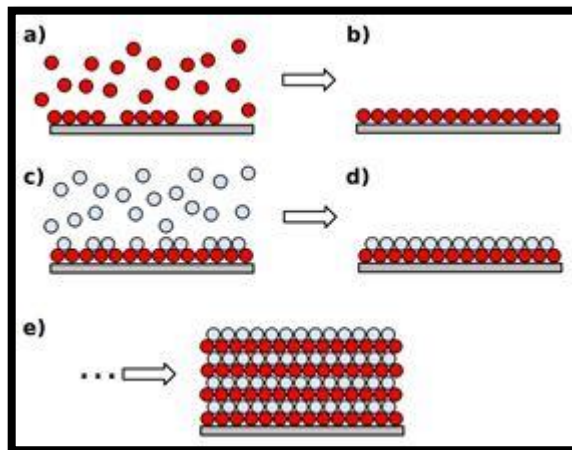


Figure 2.5 An idealized ALD process. Introduced precursor 1 (red circles) and precursor 2 (white circles) repeated until the desired thickness is reached (e) by step by step self-limiting monolayers. [38]

Chemical vapour deposition (CVD) is a gas-phase process by which reactive constituents react over a catalyst or pre-templated surface to form nanostructured materials [39] It is the low-cost synthesis of carbon nanotubes is by CVD. And it is a process in which a

solid material is deposited on a substrate by creating reactive species in the gaseous phase. These reactive species are produced when precursor gases travel over the heated substrate.

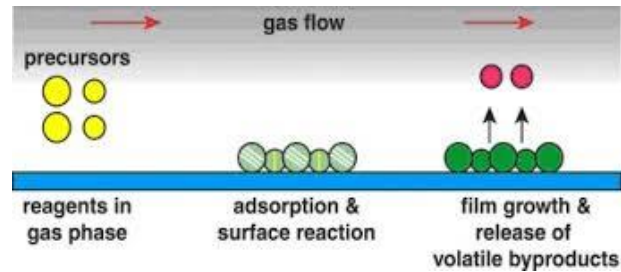


Figure 2.6 Illustration of metal-organic chemical vapor deposition (MOCVD) mechanism [40]

Electrodeposition is an essential way to deposit metal layers on a conducting wafer. The process is relatively cheap and fast, also allows complex shapes [37]. The layer thickness simply depends on the current density and the time for which the current flows. Electrodeposition is relatively cheap and can be performed at low temperatures. The film thickness can be controlled by monitoring the amount of charge delivered, whereas the deposition rate can be followed by the variation of the current with time. The composition and defect chemistry can be controlled by the magnitude of the applied potential. Pulsing or cycling the applied current or potential in a solution containing a mixture of precursors allows the production of a multi layered material [41].

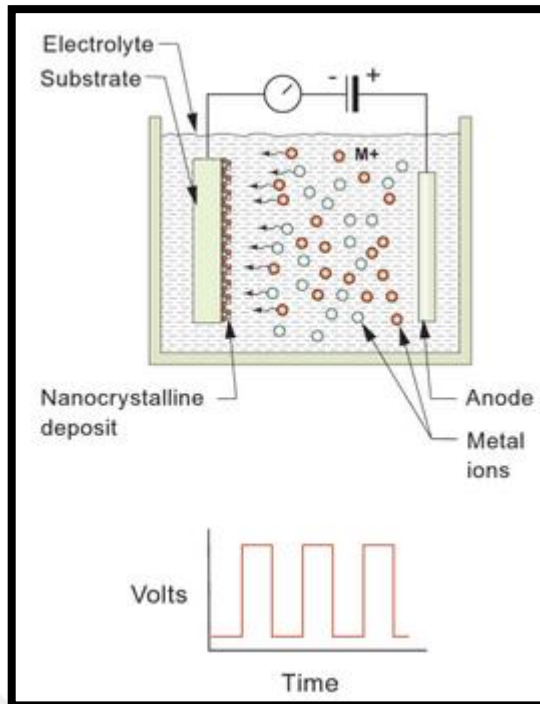


Figure 2.7 Pulsed electrodeposition. The pulsed potential nucleates many nanoscale crystals that build to form a layer up to 5 mm thick [41].

Sol-gel technology is a well-known colloidal chemistry technology, which offers possibility to fabricate various materials with novel, predefined properties in a simple process. The sol-gel process is a low-cost and low-temperature method for producing transparent and homogenous solid materials with high purity. The sol is a name of a colloidal solution made of solid particles, suspended in a liquid phase. The gel can be considered as a solid macromolecule immersed in a solvent. Sol-gel process consists in the chemical transformation of a liquid (the sol) into a gel state and with subsequent post-treatment and transition into solid oxide material [42]. Compounds produced by the sol-gel process have many applications in super hydrophobic surfaces [43], electrolyte [44], biosensors [45], corrosion protection [46], etc.

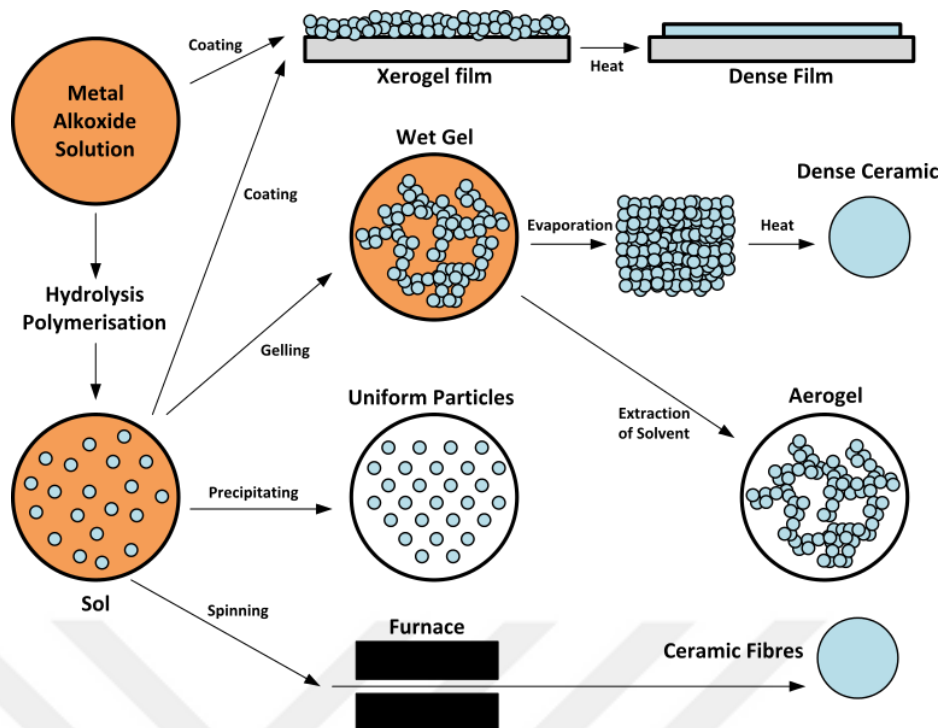


Figure 2.8 Schematic representation of the different stages and routes of the sol-gel technology[47]

In the “bottom-up nanofabrication” outline, synthetic chemistry, self-assembly has provided a powerful way of producing materials and organizing them into functional structures designed to be used a specific area. Self-assembly, as a fundamental building principle, exemplified by atoms and molecules, colloids and polymers, can undergo spontaneous organization to a higher level of structural complexity.

The self-assembly of alkane thiol monolayers on gold for a myriad of soft-lithography is an important example for its nanofabrication potential [48], [49], layer-by-layer electrostatic self-assembly of polyelectrolytes of alternating charge for smart drug delivery vehicles[50][51][52], bio-conjugated self-assembled nanocrystals for medical diagnostics[53], [54], self-assembled semiconductor nanowires for flexible electronics[55], [56] self-assembled microspheres for opal optics[57], periodic mesoporous carbons for lithium solid state battery anodes[58], and micro phase separated block copolymers as nano-lithographic masks for silicon-based flash memories[59]. These examples show high profile of how self-assembly has been an enabler of nanofabrication and a facilitator of nanotechnology. Self-assembly will be mentioned in the following section in detail.

However broad the range of synthesis approaches, the critical control points fall into two categories:

- (1) Control of the size and composition of the nanocluster components, whether they are aerosol particles, powders, semiconductor quantum dots, or other nanocomponents
- (2) Control of the interfaces and distributions of the nanocomponents within the fully formed materials [60]

These two aspects of nanostructure formation are inextricably linked; nevertheless, it is important to understand how to exercise separate control over the nucleation of the nanostructure building blocks and the growth (for example, minimizing coagulation or agglomeration) of those components throughout the synthesis and assembly process.

This latter issue is related to the importance of the following:

- The chemical, thermal, and temporal stability of such formed nanostructures
- The ability to scale-up synthesis and assembly strategies for low-cost, large-scale production of nanostructured materials, while at the same time maintaining control of critical feature size and quality of interfaces (economic viability is a compelling issue for any nanostructure technology) [60]



### SELF-ASSEMBLY

In this chapter, self-assembly method and applications will be explained.

#### 3.1 Self-Assembly Method at the Molecular Level

Self-assembly occurs in the nature spontaneously in different biological systems such as the self-assembly of the lipid bilayer membrane in cells or cell membranes which shows which shows hydrophilic-hydrophobic interactions. As every innovation of new material and process is the reflection of nature, self-assembly method has been also found a place in research and development area in technology. In nanotechnology, this method is important to achieve final desired structure to gain new properties to the material. Compared to the lithography method which is “Top-Down”, self-assembly is referred to as a “Bottom-Up” method.

Molecular self-assembly is the process where molecules organize a defined structure without any outside management, either mediated by physicochemical pathways or assisted by biomolecules to promote molecular selectivity and specificity. It happens in two different ways; intramolecular or intermolecular self-assembly. When assembling happens to complex polymers from a random coil formation, this case defines as intramolecular self-assembly. Even though intramolecular self-assembly is not considered as a self-assembly, it has examples such as protein folding etc. Besides that, intermolecular self-assembly means the assembly ability of molecules to form supramolecular structure. It is possible to see this self-assembly in the formation of a micelle by surfactant molecules in solution.

Self-assembly has an important role in technology for several reasons; it provides routes to a range of materials with regular structures, it has possibility to occur larger components than molecules. Thus, it has high potential to be used in material science and different field such as physic, chemistry, biology.

### **3.2 Principles of Molecular Self-Assembly**

Molecular self-assembly depends on surface functionalisation, assembly, patterning, orientation and alignment into functional networks. Among the bottom-up strategies, self-assembly procures a promising route to build up complex systems with endless flexibility in terms of nanoscale building blocks and resulting functionalities and properties.

Surface functionalisation is for tuning the properties of nanostructures (i.e. biocompatibility, biodegradability, charge injection/separation for optoelectronics, water-solubility, stability, multifunctional ability (targeting, probing, drug delivery).

For self-assembling a system, it all requires four characteristics; components, interactions, adjustability and environment. Components may be molecules or molecular segments and their interactions with each other lead from disordered state (A solution, disordered aggregate, random coil) to a final ordered structure (A crystal, folded macromolecule).

Self-assembly interactions occur based on two key factors which depend on a balance of attractive and repulsive forces: motion and stickiness. Motion of molecules happens due to their heat energy and when two molecules move and find the right orientation they stick eventually. Stickiness is more about intermolecular attractions from small Van der Waal's forces, hydrophobic interactions to stronger hydrogen bonds and Coulomb forces. Although these attractions are weak individually, when the all molecules gain this property material achieves strength and flexibility.

To generate ordered structures, unification must be reversible or allow components to adjust their positions within in aggregate. So, the strength of bonds must be comparable with the thermal motion. Irreversible collision between molecules generate glasses, not crystals.

Another factor is environment; self-assembling molecules needs to be mobile in some environment to have flexibility to move and orientation. Environment can be either solution or an interface and interaction between environment and components effect the all process.

### **3.3 Self-Assembly Process**

Basically, self-assembly can occur with two different processes: static self-assembly and dynamic self-assembly. With the absence of external influences, building block static self-assembly is driven by energy minimization to form static equilibrium structures. Other case, in the presence of outside influences, a dynamically self-assembling system may adjust to its environment [61]. Thus, the system resides on a minimum energy case that caused by the influx of energy in the system. In case of any energy flows into the system, the minimum disappears and so the system disassembles. For instance, every living organism is a perfect example to dynamic self-assembly.

Dynamic self-assembly is not considered as “self-assembly system” by some scientists. This is because of the patterns of pre-existing components organize by specific local interactions. It reduces entropy by absorbing energy from the environment. This gradient in entropy between the organism and the environment can be maintained only if energy is driven from the environment into the organism in the form of food and heat. Once that flux ceases, the organism disassembles.

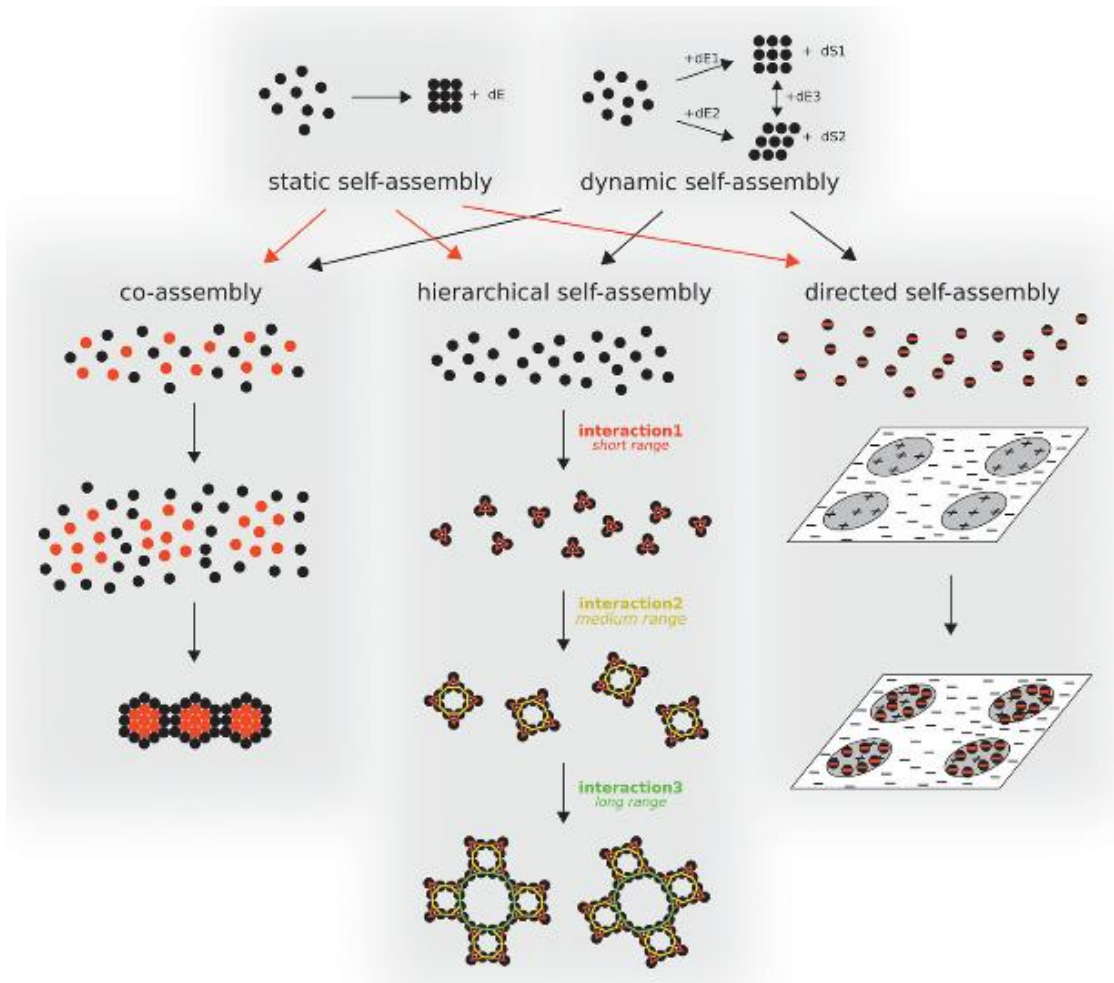


Figure 3.1 Static and dynamic self-assembly and how they relate to co-assembly, hierarchical assembly and directed assembly [62].

Co-assembly, directed self-assembly, hierarchical self-assembly may be considered as under title of static and dynamic self-assembly. Co-assembly is the case when the different building blocks self-assembling spontaneously in the same system. Generation of mesoporous silica by surfactant micelle templating of silicate building blocks may be example of this case [63].

Hierarchical self-assembly is the organisation of single building block over multiple length scales step by step. This process can be seen to create large functional structures in biological systems [64].

Directed assembly is a case where the self-assembly is directed by external forces. This is the typical case for bottom-up-meets-top-down approaches. For example, a lithographic pattern can be used to direct the self-assembly of colloids from solution on a substrate [65]. Even though the dynamic self-assembly is not so outstanding method, potentially it is far more powerful than the static self-assembly [66].

### EXPERIMENTAL PART

In this chapter, used materials and method, experimental process (Preparation of substrate, compositions, drop-casting etc.) will be shown. Also, the SEM pictures of different ternary composition will be placed and examination of samples will be shown.

#### 4.1 Materials

Poly (methyl methacrylate) (PMMA) (number-averaged molecular weight,  $M_n = 15\ 000$  Da), para-dichlorobenzene (PDCB) (99 + %),  $\text{CHCl}_3$  (99,9 + %) were purchased from Aldrich and used as received. p-Doped Si/SiO<sub>x</sub> substrates (100) were purchased from ITME (Poland). SEM photos were taken with a Carl Zeiss Supra 40 Scanning Electron Microscope. An Olympus BH2 optical microscope, equipped with an Olympus video camera and connected to a PC, was used for video recording. The experimental procedures were carried out at room temperature and pressure, under a fume hood when needed.

The stock solution was prepared with 1 mg PMMA which dissolved in 1 mL of  $\text{CHCl}_3$  in a closed vial. It was left on stirring for a day until a homogeneous solution was obtained after sonication about 5 min. Solution has been filtered with the intent of obtaining the most possible purified solution. Different amount of PDCB is added to the stock solution to prepare a mixture at different concentrations.

In order to achieve desired pattern, PDCB is used as a sublimating substance. In consideration of that polymorphic PDCB shows different crystal structures over broad temperature and pressure ranges [67].

PDCB represents a versatile system for studying weak intermolecular interactions in organic systems. Crystallization of PDCB happens in three different phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) and one discussion phase ( $\delta$ ) [67]. It depends on temperature and pressure. When we have carried out our experiments, we have achieved monoclinic phase in the most of situations. However, sometimes triclinic phase has been seen on the surface, but this structure was undesirable so it hasn't been counted.

1.  $\alpha$ -phase (I-monoclinic)

At the ambient pressure in a rather narrow temperature range around room temperature ( $\sim 303$  K)

2.  $\beta$ -phase(II=triclinic)

At the ambient pressure from  $\sim 303$  K until the melting point at  $\sim 326$  K.

3.  $\gamma$ -phase(III-monoclinic)

Exists below  $\sim 270$  K at high pressure. At ambient pressure, it can exist below  $\sim 248$  K.

4.  $\delta$ -phase (Termed phase IV, Orthorhombic)

This phase is on discussion. Researches show it exists at ambient pressure above 3 kbar.

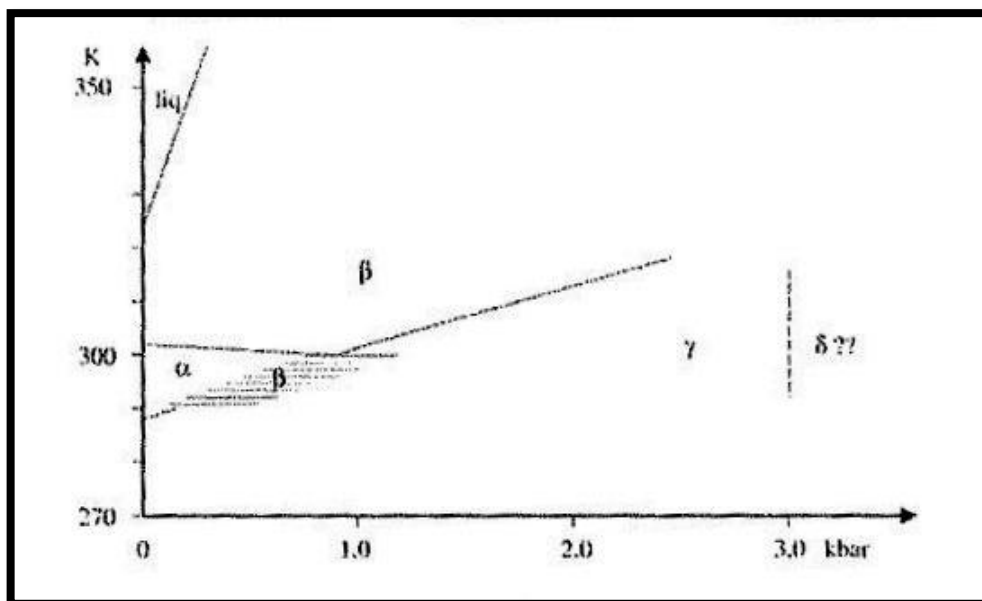


Figure 4.1 Polymorphic phases of PDCB at the different temperature and pressure

We used the  $\alpha$ -phase (I-monoclinic; Estop et al (1977) [68]) which exists at ambient pressure and in a rather narrow temperature range around room temperature. It is a simple aromatic molecule, which forms beautiful needle-like crystals in normal conditions (monoclinic  $\alpha$ -phase, space group P21/a ; number of molecules per unit cell,  $Z = 2$  [69] ), with a melting point of about 53°C and a vapour pressure of 1.76 mm Hg at 25°C. PDCB is fully miscible with many organic solvents, including chloroform ( $\text{CHCl}_3$ , bp: 62°C). Doped Si/SiO<sub>x</sub> substrates were used to facilitate the subsequent scanning electron microscopy (SEM) investigation [70].

Sixteen different ternary solutions were prepared with the following general procedure. To see the effect of  $AS/[SS + TM]$  four series have been created ( $AS/TM$  ( $\mu\text{l}/\mu\text{g}$ ): 10, 4, 2, 1.33) and to examine  $SS/[AS + TM]$  effect, for each  $AS/(TM + SS)$  series a set of  $SS/(TM + AS)$  sub-series ( $SS/TM$  ( $\mu\text{g}/\mu\text{g}$ ): 100, 200, 400, 1000) have been prepared. The TS composition was varied in order to explore the effect of the composition changes on the developed TM patterns, as for Table 4.1

Table 4.1 Experimental Amounts of Materials

Stock: 1mg TM + 1 ml AS	100 SS/TM ( $\mu\text{g}/\mu\text{g}$ )			200 SS/TM ( $\mu\text{g}/\mu\text{g}$ )			400 SS/TM ( $\mu\text{g}/\mu\text{g}$ )			1000 SS/TM ( $\mu\text{g}/\mu\text{g}$ )		
1.33 AS/TM ( $\mu\text{l}/\mu\text{g}$ )	Stock	AS	SS	Stock	AS	SS	Stock	AS	SS	Stock	AS	SS
	$\mu\text{l}$	$\mu\text{l}$	mg	$\mu\text{l}$	$\mu\text{l}$	mg	$\mu\text{l}$	$\mu\text{l}$	mg	$\mu\text{l}$	$\mu\text{l}$	mg
	75	25	7.5	75	25	15	75	25	30	75	25	75
2 AS/TM ( $\mu\text{l}/\mu\text{g}$ )	50	50	5	50	50	10	50	50	20	50	50	50
4 AS/TM ( $\mu\text{l}/\mu\text{g}$ )	25	75	2.5	25	75	5	25	75	10	25	75	25
10 AS/TM ( $\mu\text{l}/\mu\text{g}$ )	10	90	1	10	90	2	10	90	4	10	90	10

#### 4.2 Preparation of Ternary Solutions and Drop Casting

The TS have been carefully drop-cast onto the substrate by means of a Pasteur pipette, taking care for constantly dropping ( $10 \pm 1$ ) mg of solution onto an approximately  $1 \text{ cm}^2$  surface. The drop casting was carried out at room temperature ( $23^\circ\text{C}$ , controlled via vibration-free thermostatic water bath coupled to a thermocouple, see the Fig 4.2) and ambient pressure. PDCB can exist in different crystalline phases.



Figure 4.2 Drop-casting mechanism



For the described experiments, we used the PDCB monoclinic  $\alpha$ -phase, (space group P21/a; number of molecules per unit cell,  $Z = 2$ ; [68] [71] which forms beautiful needle-like crystals in normal conditions (i.e., ambient pressure and room temperature of 25°C).

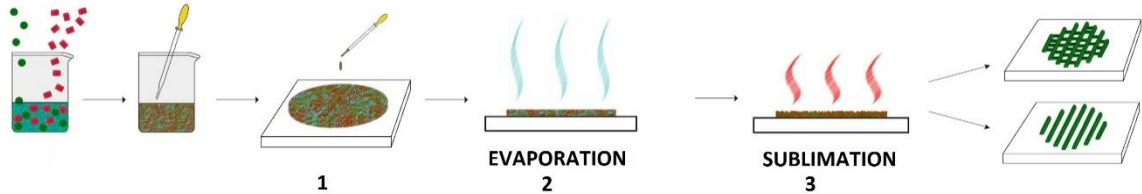


Figure 4.3 ASB-SANS technique stages

After drop-casting the AS was allowed to evaporate completely, and the resulting film (SS incorporating the TM, see step 3 of Fig. 4.3) was capped with a small Petri dish to establish sublimation conditions as close as possible to equilibrium (i.e., to saturate the atmosphere surrounding the substrate with SS vapours). Substrates were then left to rest 4 hours to ensure the complete removal of SS. For each TS composition from 20 to 50 different samples have been prepared.

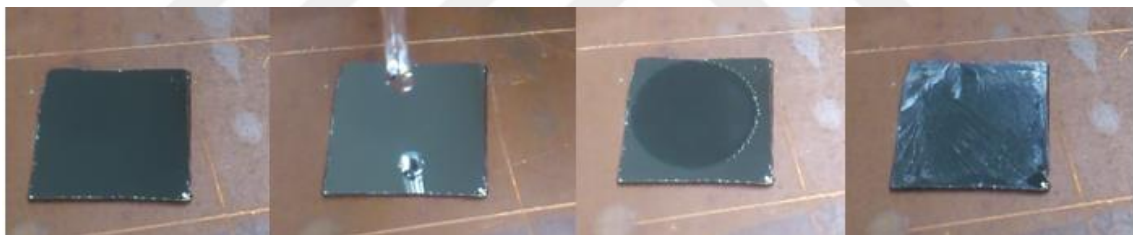


Figure 4.4 Drop-casting and evaporation process; after  $\text{CHCl}_3$  left, the sample is capped  
To follow up the results better, experimental design is created as four group (sublimating substance/target material). Group properties and obtained visual details will be discussed in the following parts.

#### 4.2.1 Group 1 (PDCB/PMMA=100 ( $\mu\text{g}/\mu\text{g}$ ))

Sub-grouped as;

- $\text{CHCl}_3/\text{PMMA}=10, 4, 2, 1.33$  ( $\mu\text{l}/\mu\text{g}$ )

This group has lowest amount of sublimating substance and target material ratio is highest on the 1.33 ( $\mu\text{l}/\mu\text{g}$ )  $\text{CHCl}_3/\text{PMMA}$  ratio. Evolution of patterns from dotted to the lineal is seen clearly in the following figure. In the drop-casting section,

solution was very diluted and expanding fast on the substrate and very thin material has been left on the substrate. Here, the smallest nanostructures have been found. Morphology of substrate is highly ordered and uniform. SEM pictures from A to D describes the decrease in  $\text{CHCl}_3$  not also for Group 1 but also Group-2, 3, 4.

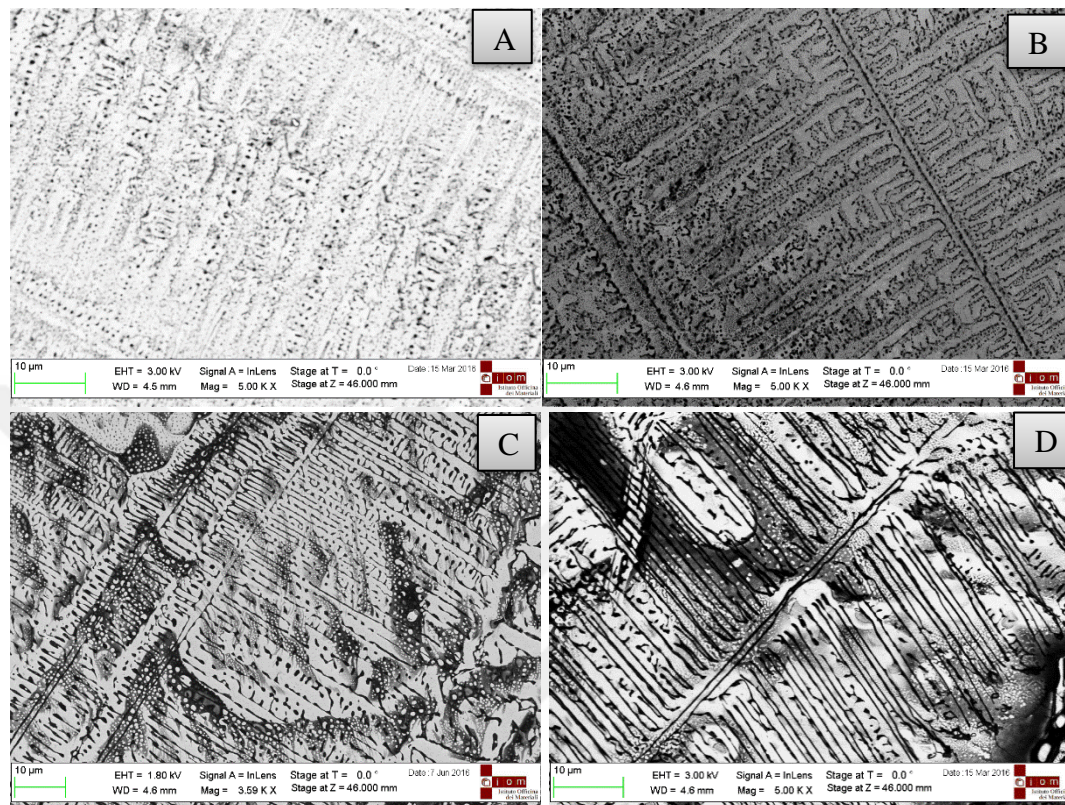


Figure 4.5 Transformation from aligned dots to fibers for PDCB/PMMA=100 ( $\mu\text{g}/\mu\text{g}$ )

#### 4.2.2 Group 2 (PDCB/PMMA=200 ( $\mu\text{g}/\mu\text{g}$ ))

Sub-grouped as;

- $\text{CHCl}_3/\text{PMMA}=10, 4, 2, 1.33$  ( $\mu\text{l}/\mu\text{g}$ )

Sublimating substance ratio is higher than first group. When sublimating substance ratio rises, patterns start to become disrupted by sublimating substance. Accordingly, they start to lose their alignment and order. Also, solution becomes dense depends on the concentration increase of  $\text{CHCl}_3$ .

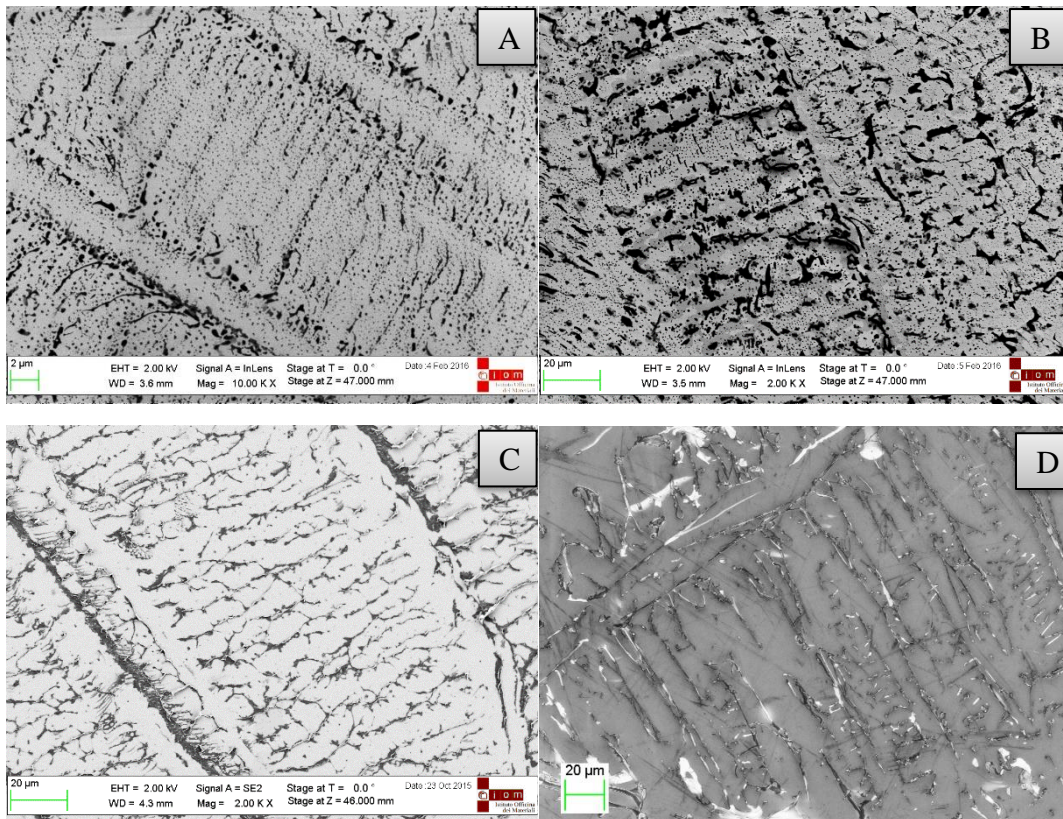


Figure 4.6 Transformation from aligned dots to fibers for PDCB/PMMA=200 ( $\mu\text{g}/\mu\text{g}$ )

#### 4.2.3 Group 3 (PDCB/PMMA=400 ( $\mu\text{g}/\mu\text{g}$ ))

Sub-grouped as;

- $\text{CHCl}_3/\text{PMMA}=10, 4, 2, 1.33$  ( $\mu\text{l}/\mu\text{g}$ )

The denser solution causes to be harder to do drop-casting, at the edge of pipette solution crystallises fast. So, experiments have been done very carefully and quickly. Sublimation is slow on the surface and material is thicker on the silicon surface. Drop expands slowly depends on viscosity. As seen in the fig. 4.5, here, structures are disrupted, they lose ordered pattern.

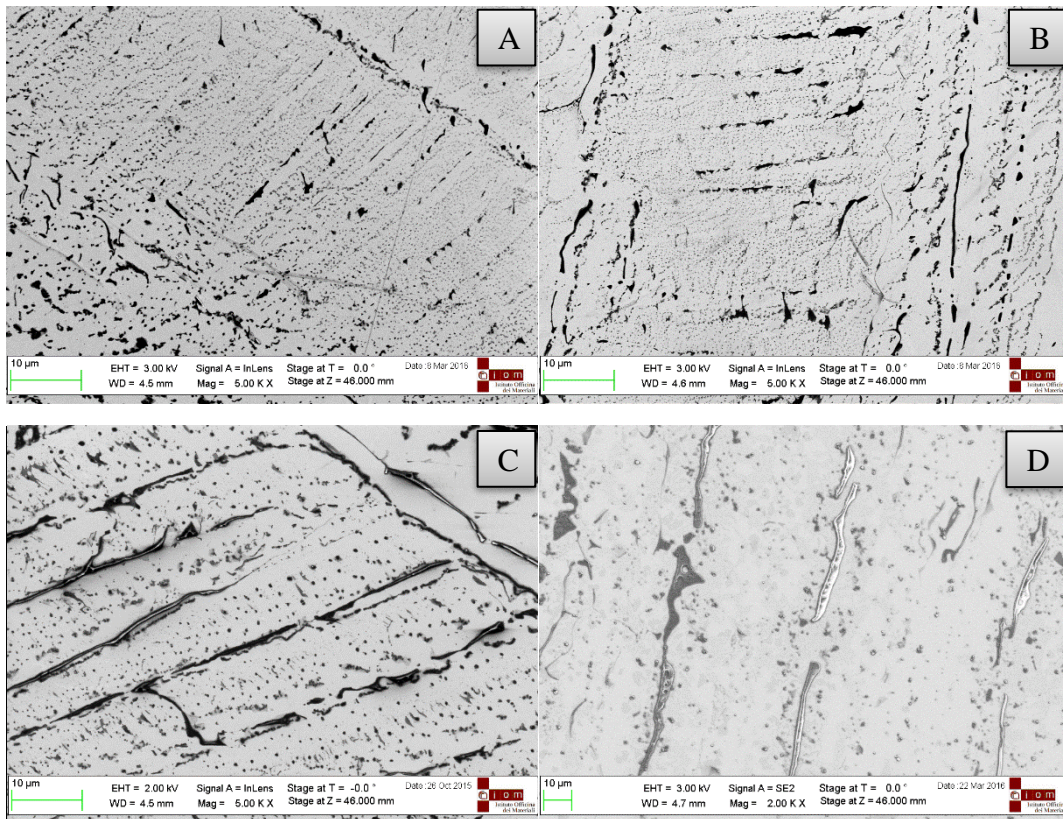


Figure 4.7 Transformation from aligned dots to fibers for PDCB/PMMA=400 ( $\mu\text{g}/\mu\text{g}$ )

#### 4.2.4 Group 4 (PDCB/PMMA=1000 ( $\mu\text{g}/\mu\text{g}$ ))

Sub-grouped as;

- $\text{CHCl}_3/\text{PMMA}=10, 4, 2, 1.33$  ( $\mu\text{l}/\mu\text{g}$ )

The solution is in highest level because of highest PDCB ratio. Sublimation is rather slow; it takes longer time to disappear from surface. Target material motion in the PDCB causes material to merge. Structures are greater and far from each other. General view of pattern is rather disordered.

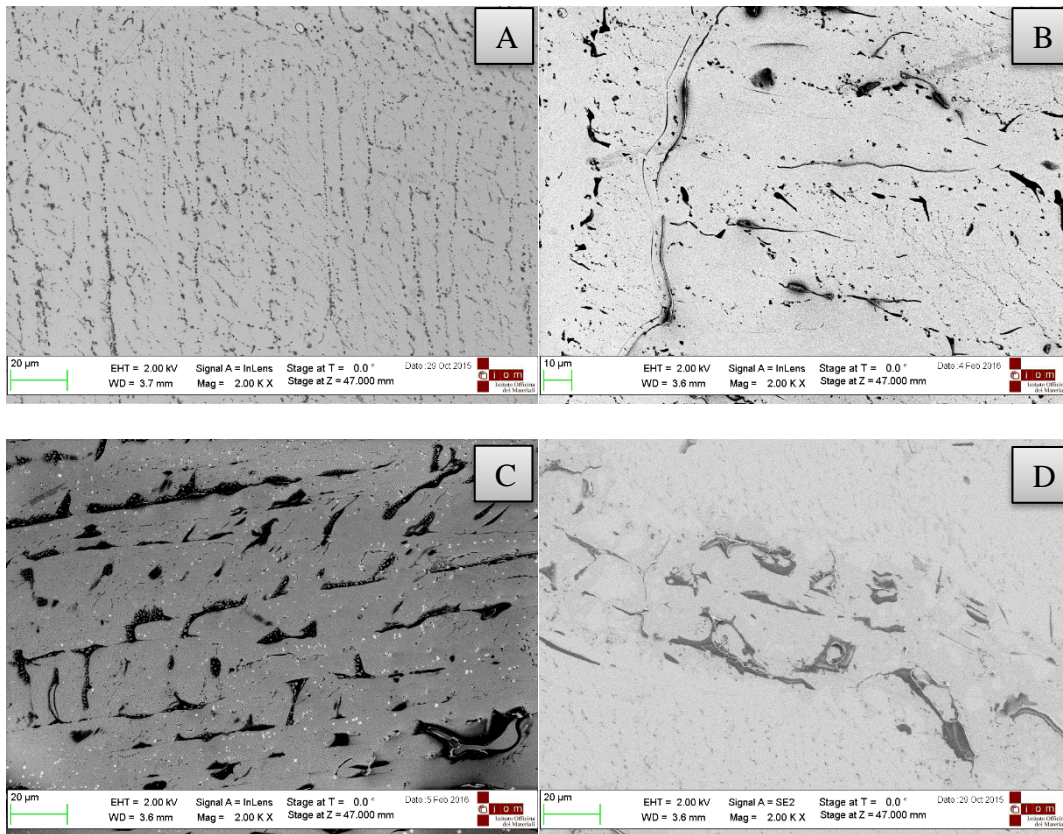


Figure 4.8 Transformation from aligned dots to fibers for PDCB/PMMA=1000 ( $\mu\text{g}/\mu\text{g}$ )

### 4.3 Determination of the Morphological Parameters

Each concentration experiment had been repeated at least 20 times before results were compared and examined. Once the substrates are ready after evaporation and sublimation process, pictures were taken via microscope and SEM. Pattern morphologies was analysed with the Gwyddion program [72] in terms of fibres' width and inter-patterns distance from SEM images. Based on the data similarity, patterns are grouped as primary, secondary and tertiary.

### 4.4 Experimental Results and Comparison of Different Ternary Solutions

After a lot of time repeating experiments, we have achieved a result that ternary composition variations made a big impact on the final structure rely on changing the process of evaporation and sublimation. When the liquid mixture is deposited on the substrate, at first the AS and then the SS leave the TS (See Fig. 4.3, experimental part), leaving on the substrate a well-defined pattern, whose topology is dictated by the TS composition.

The typical patterns found on the Si/SiO<sub>x</sub> plate after the ASB-SANS procedure are shown as a cartoon in Fig. 4.9 (A). For a better clarity, the cartoon is reported in the frame of a Cartesian diagram showing different topologies at varying AS/SS/TM ratios.

In the upper left of the diagram a typical pattern deriving from relatively concentrated TM is visible, with aligned and orthogonally arranged fibres of primary, secondary and tertiary order, already found in previous studies [70]. The orthogonal arrangement is given by the monoclinic nature of the PDCB crystallites, that, acting as template for the TM, originate patterns aligned with crystallites [73]. When the amount of SS is increased with respect to that of both TM and AS (direction 1 in the cartoon) a number of morphological changes are observed: i) the higher orders of patterns are almost suppressed (tertiary patterns) or greatly diminished in occurrences (secondary patterns), for both fibrillary (A, B) and dotted (C, D) patterns; ii) the size of the patterns evolve from smaller (patterns A, C) to larger (B, D) structures. Again, this is verified for both fibrillar and dotted patterns; iii) inter-pattern distances tend to become greater, once more irrespectively of fibrillar or dotted patterns (compare A, C with B, D). When the amount of AS with respect to SS and TM is increased (direction 2), a transition from continuous patterns (A, B) to dotted patterns (C, D) is found, independently from their lateral size. Along the dotted patterns, dots conserve a notable degree of alignment, even across several microns' lengths, and a similarly remarkable small dispersion of the dots' size, at all levels of the patterns (i.e., primary, secondary and tertiary). Moreover, the inter-patterns distance decreases.

In Figure 4.9 (B) pictures of all cases are shown in Fig. 4.9 (A), arranged in a 4 x 4 equal size SEM photos matrix of morphologies of patterns derived from the ASB-SANS of the sixteen starting TSs. For a better understanding of the images, the orientations of the primary, secondary and tertiary PMMA patterns in these SEM photos are aligned with those of the cartoon 4.9 (A). As it can be seen along the horizontal diagram direction, the transition from continuous, hierarchically organized patterns (panels A, E, I, M) to disrupted patterns with increased feature size and increased inter-pattern distance (D, H, L, P) is progressive, higher SS concentrations (with respect to the TM+AS amounts) are reached. Similarly, upon increase of the AS concentration (vertical direction), a progressive transition from continuous patterns to disrupted ones leads to well defined

dotted morphology. Interestingly, the dotted morphology can be developed over extremely long lines, up to several tens of microns, still conserving very little dispersed dots diameters, well below one micron (Fig. 4.10 (A), obtained from a TS of type M). This is verified at each level of the patterns hierarchy. This type of PMMA morphology can be useful in fields like lithography, for example for obtaining large arrays of microlenses or for realizing large arrays of nanostructured scattering surfaces (which in turn could be useful for photovoltaic applications). In some samples the developed patterns presented a mixed morphology, combining continuous and disrupted fibers with aligned dots structures (Fig. 4.10 (B)). These findings are attributed to local variations of TM concentration or inhomogeneous SS/TM layer thicknesses, in turn due to non-equilibrium mass transport phenomena occurring inside the drop cast TS, most likely due to the fact that the ASB-SANS procedure has been conducted in non strictly controlled conditions (i.e., no particular equipment for controlling the environmental humidity or, more in general, the gas pressure). On the other hand, the robustness of the ASB-SANS is testified by the reproducible possibility to obtain very homogenous patterns over thousands of  $\mu\text{m}^2$ , as exemplified by Figure 4.10 (A).

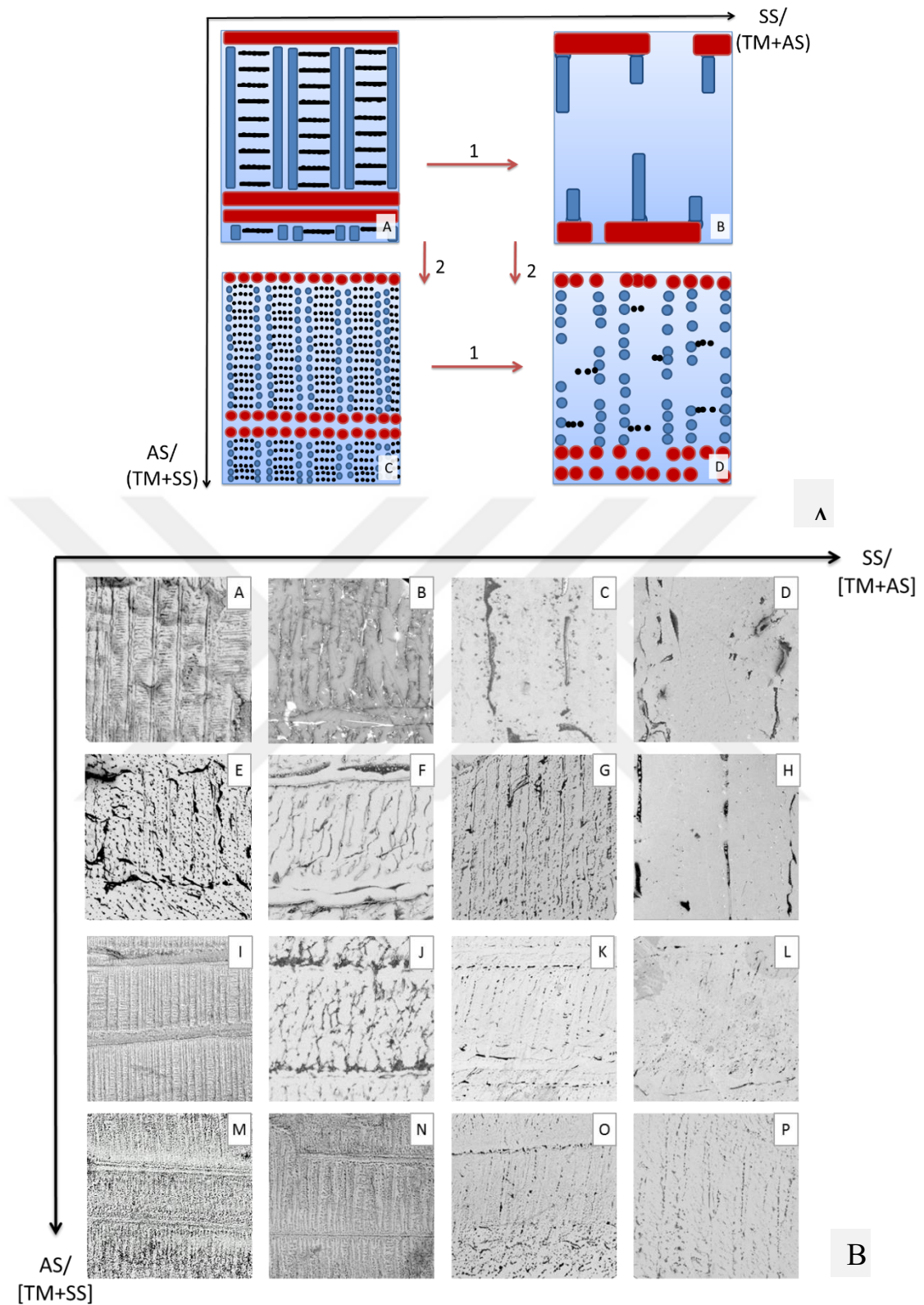


Figure 4.9 (A) Schematic illustration of morphological evolution in the terms of width and distance of primary (red), secondary (blue), tertiary (black) patterns. In parallel to Fig (A). Fig (B) presents SEM photos of each ternary composition sample (Each square 91.8  $\mu\text{m}$  x 91.8  $\mu\text{m}$ ).



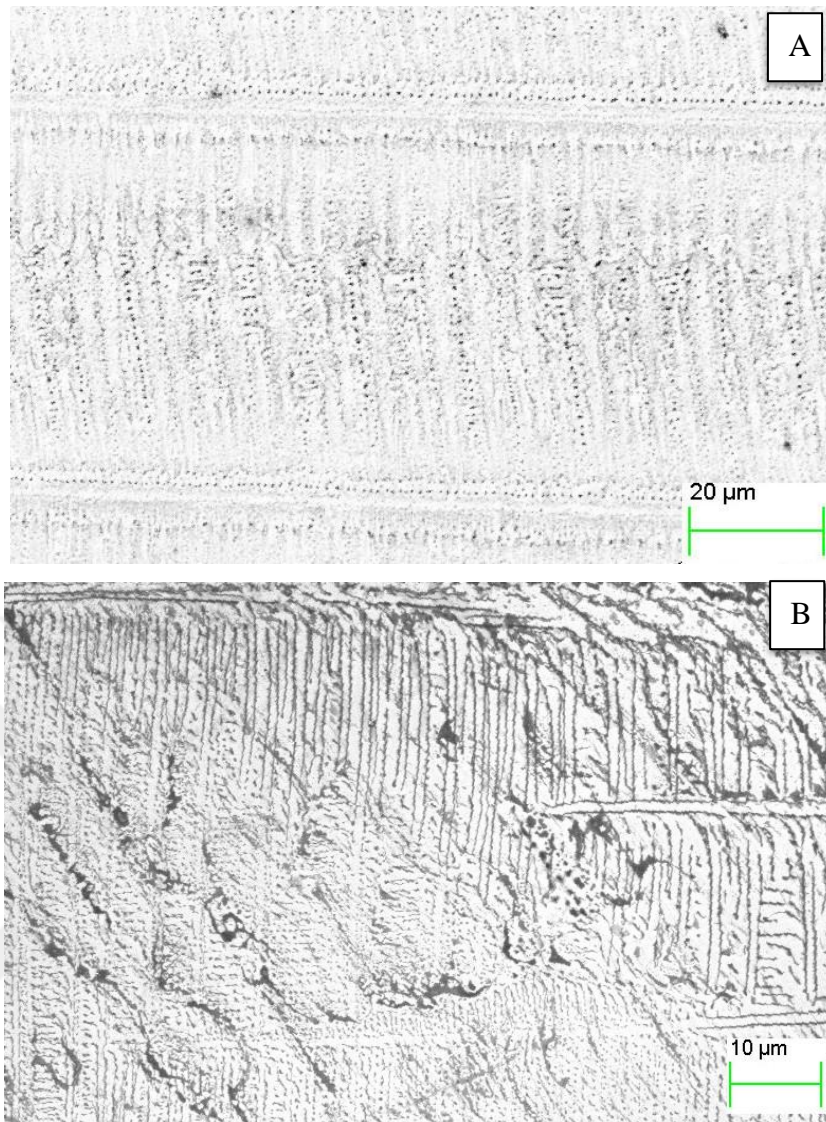


Figure 4.10 (A) In case of highest AS, parallel to Fig 2 (B)-M, ordered alignment of the nanostructures; Image (B) mixture of patterns dotted to lineal.

The influence of the relative TS components concentrations on the developed patterns can be better visualized on a ternary diagram (Figure 4.11). In the figure, 1. Diagram is a real diagram with the real numerical value, but it is not possible to see the difference by eyes because of TM's very low percentages, so 2. diagram is prepared by editing the real values in an attempt to understand the relation between component concentrations presents the evolution of concentration change with the exaggerated values and helps to understand the effect of different TSs. As the prepared TSs cover just a small part of the full ternary diagram, i.e. the concentrations of AS - w/w - range from 99.33 to 66.48% and those of SS from 0.66-33.48%, just the relevant part of the diagram is shown).

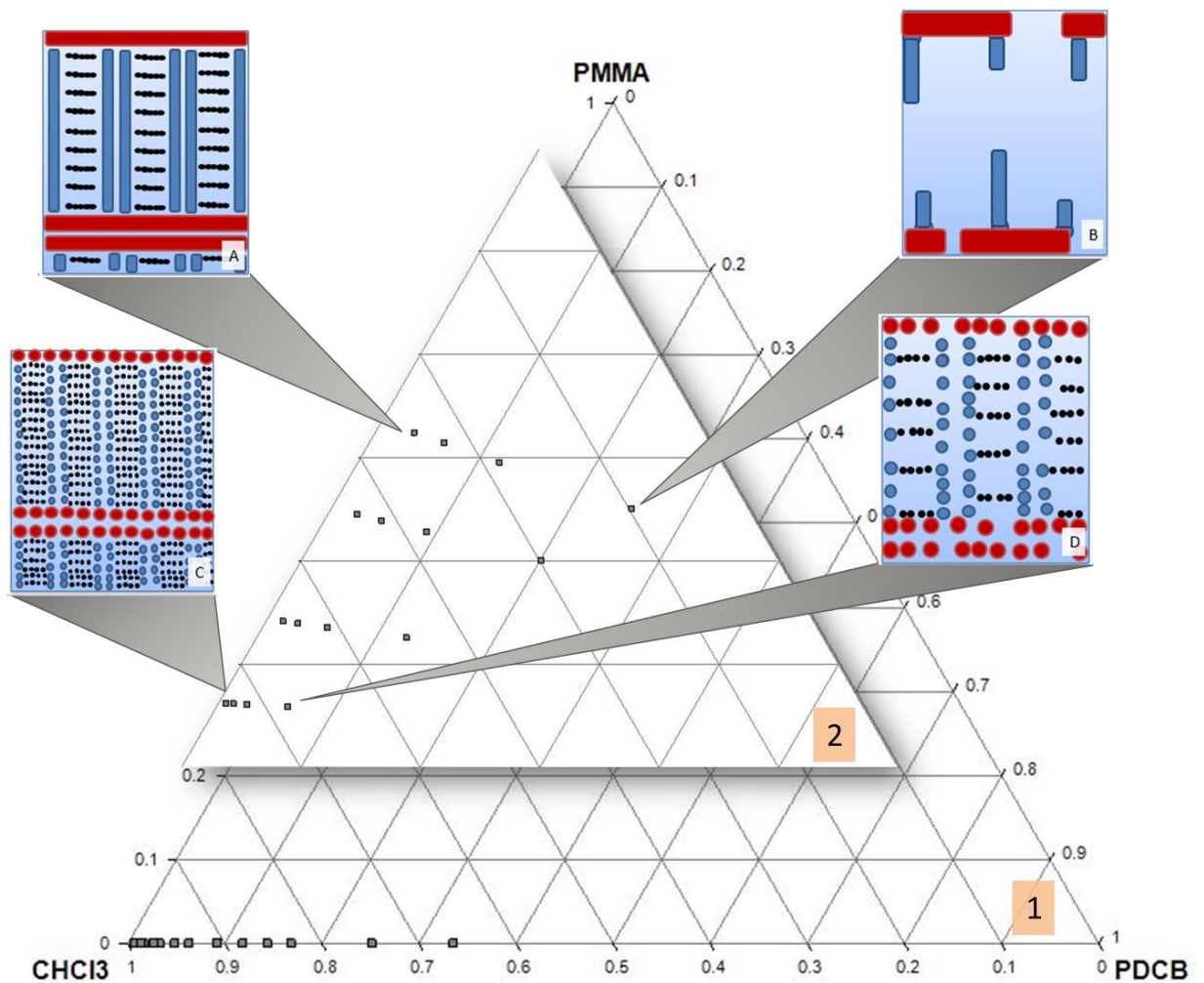


Figure 4.11 The ternary diagram shows the percentages of components (weight %) and its effect on topology (Figures belongs to extreme concentration ratios which explained before.)

As is visible, the most continuous patterns are found at relatively high concentrations of TM (upper left part of the diagram), and going towards progressive dilution of the TM the patterns are disrupted, originating either discontinuous fibres (upper-right part of the diagram) or aligned dots (lower part of the diagram). This behaviour is reasonable in view of the procedure used for obtaining the described patterns. In fact, a similar amount of TS has been deposited for all the realized samples, and the progressive dilution of the TM within the TS leads to less and less TM to be arranged within the solid matrix that is left on the substrate upon evaporation of the AS (vide infra). Remarkably, the increase of AS content in the TS led to very well aligned PMMA dots of little dispersed size (Fig. 4.10 (A)). This suggests that the self-assembly phenomena at work in the

considered systems are effective enough to overcome the relatively poorly controlled fabrication conditions.

Two distinctive morphological features of the observed patterns have been analysed in order to better understand the behaviour of the system, i.e. the patterns' width and the distance between the pattern structures, dividing these measurements for each pattern level (i.e., primary, secondary and tertiary patterns; where the pattern level was not present, as in the most TM-diluted TSs, these calculations have not been carried out). The results of this analysis, carried out for 20 to 50 different samples per each considered pattern type, are reported in Table 5.1.

Table 5.1 Average width and distance values of primary, secondary and tertiary lines

	<i>Min- Max Width(<math>\mu\text{m}</math>)</i>	<i>Min-Max Distance(<math>\mu\text{m}</math>)</i>
<i>Primary Patterns</i>	0.358-2.925	27.730-571.000
<i>Secondary Patterns</i>	0.207-1.375	3.243-58.780
<i>Tertiary Patterns</i>	0.068-0.588	0.473-7.570

The typical size of the primary patterns is in the range of 0.5-3  $\mu\text{m}$ ; for the secondary one, 0.2-1.4  $\mu\text{m}$ ; for the tertiary (when present) in the range 0.07-0.6  $\mu\text{m}$ . With respect to the inter-pattern distance, for primary patterns the range is 27-571  $\mu\text{m}$ ; for secondary ones, 3-60  $\mu\text{m}$ ; for tertiary ones, 0.5-8  $\mu\text{m}$ . While in each case one can observe some overlap between different hierarchical levels, the different ranges are rather well defined, and confined within about one order of magnitude.

The obtained results have been plotted in function of the growing amount of AS in the TS (Figure 4.12). As is visible, the pattern widths (being them continuous or disrupted fibres, or dots) decrease with the increase in AS/(TM+SS), at each considered hierarchical level (Fig 4.12 A, C, E). Similarly, the inter-pattern distances decrease upon increasing AS/(TM+SS), again at each considered hierarchical level (Fig 4.12 B, D, F).

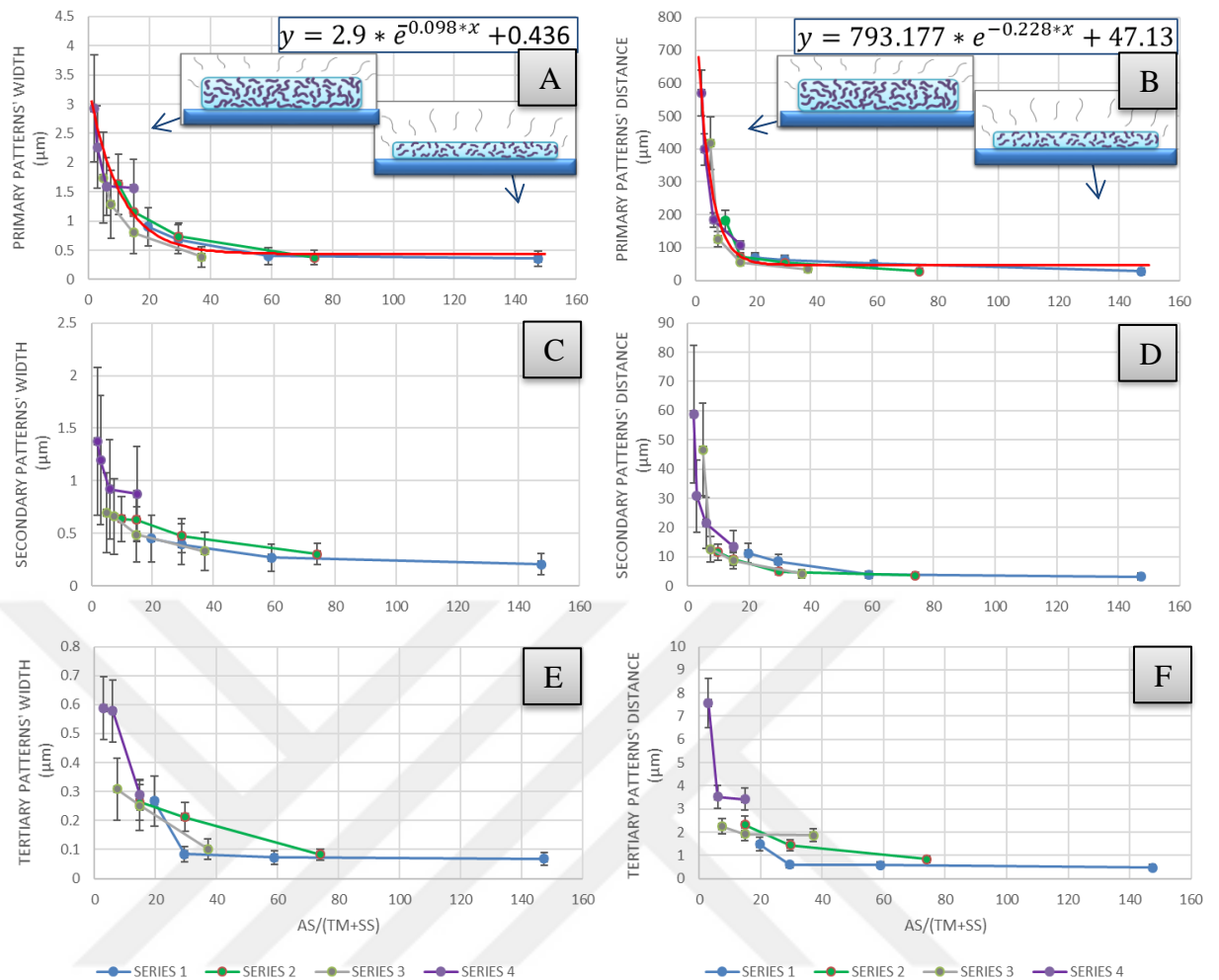


Figure 4.12 Graphs shows the pattern's average widths and inter-patterns' distances with the standard deviation based on AS/(TM+SS) ratios (weight %). Coloured lines specify on SS/TM ratios respectively from the lowest SS ratio (Series 1) to highest SS ratio (Series 4).

For both the linear and the dotted patterns, and at each hierarchical level, it is possible to fit the data points with a first order exponential decay curve (Fig. 4.12 A, B, red curves), which suggests that the underlying phenomenon at work at all the considered dimensional scales is similar in the two cases. Interestingly, many of models describing the diffusion of diluted polymeric chains within liquid solutions, like the Zimm model, foresee an exponential decay dependence of the distance travelled by two ends of the chain with respect to the time elapsed between one discrete step movement of a chain segment and the subsequent one [74]. In our case, a number of occurrences suggest a parallel between Zimm-like models and the found patterns width and the inter-patterns distances: i) both the patterns width and the inter-patterns distance can be viewed as proxies of the PMMA chains mobility within the SS matrix; ii) the PMMA (TM) diffusion

proceeds within an extremely diluted solid matrix constituted by the SS left on the substrate after the AS evaporation in each considered TS; iii) since we deal with a TS with fixed relative concentrations in SS, TM and AS, the  $AS/(SS+TM)$  parameter can be seen as a measure of the time available to the PMMA to travel through the SS matrix once the AS has left the system (the more AS is present in the TS, the less SS there is, meaning that the SS/TM layer left on the substrate after the AS evaporation will be thinner; see Fig. 4.13 and related text for more detail). Therefore, we are tempted to draw a parallel between Zimm-like models for macromolecular motion within liquid, diluted solutions and our case of highly diluted TM (PMMA) incorporated within SS (PDCB) matrices, although in our case the matrix is solid rather than liquid.

Overall, on the basis of these observations we propose the following tentative explanation of the above reported findings.

As has been verified in the study of Morgera, the TM patterns are found exactly where the SS crystallites leave the substrate [73, see video uploaded as Supplementary Material]. This indicates that the TM diffuses through the SS solid matrix as the latter gradually disappears by sublimation, and hence it precipitates forming the observed patterns. The very precise alignment of the found fibres with the crystal habit supports the view that in this phenomenon the SS crystal acts as a template for the TM. Particularly, it is believed that the nano9patterns formation proceeds by self-assembly mechanisms mediated by inter-macromolecular forces, as pointed out by previous studies, where UV-Vis-responsive conjugated polymers used as TMs in ASB-SANS-generated fibres showed much stronger intermolecular interactions than the same polymer deposited from a similar solution missing the SS [69]. As it is well known, polymeric chains tend to self-assemble into spherical particles (coil-to-globule transition) when they are exposed to bad solvents [75] [76] and this has been verified also for PMMA [77]. Moreover, it has been proposed that solid substrates can enhance this transition via surface effects [78]. Since in our case the sublimation of the PDCB corresponds to the passage from a good solvent to a bad solvent (ambient atmosphere), we assume that the same phenomenon is driving the self-assembly phenomena leading to the formation of the observed nanostructures.

With respect to the difference found in the above reported patterns upon changes in the TS composition, it is clear that the transition from continuous patterns (Fibres, Fig. 4.9 A-A) to discontinuous ones (Fig. 4.9 A-B, C, D) occurs upon dilution of the TM in the ternary solution, independently from the fact that the dilution occurs upon increase of the SS or of the AS. However, the morphology found on the substrate after the ASB-SANS process completion depends dramatically over the specific composition of the TS. In fact, when the SS/AS ratio is high, the resulting patterns are fibrous (Fig. 2A-A, 2A-B). On the contrary, when the SS/AS is low, the resulting patterns are aligned dots (Fig. 2A-C, 2A-D). This difference is explained considering that when the SS is predominant over the AS, the solid layer resulting from the deposition of the corresponding TS on the substrate is thick (Fig. 4.12, insets at the top left of the upper graphs, and Fig. 4.13, left column). In this situation, the PMMA macromolecules have a relatively long time available for diffusing through the SS solid matrix before the latter disappears by sublimation, which allows them to self-assemble in well-defined nanofibers.

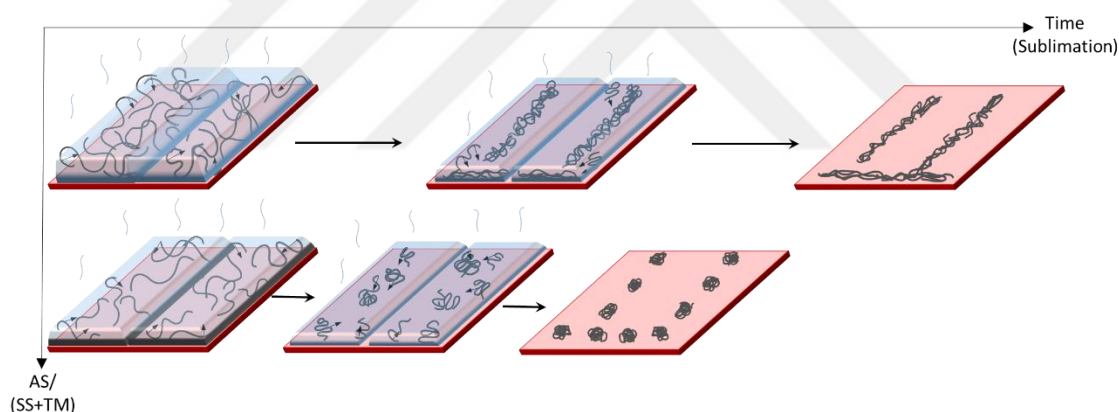


Figure 4.13 Chain motion and organization of TM in case of different amounts on the sublimation stage

The fibres length direction follows that of the PDCB crystallites (for the secondary patterns; for the primary patterns the relevant aligning surfaces are the domains borders) due to simple solvation energy balances. In fact, the long edges of the crystallites facilitate the solvation of the macromolecular chains along the length of the latter, rather than perpendicularly to it, creating nucleation centres with a very high aspect ratio parallel to the crystallite main axis, and acting as effective templates for the developed fibres (Fig. 4.13). The same applies to the crystallite domains borders.

### CONCLUSION

ASB-SANS takes advantage of the sublimation propriety of organic crystals an organic crystal able to sublimate (a sublimating substance, SS) as an easily removable templating matrix for the material to be structured/patterned (target material, TM) [72]. Both materials are dissolved in an appropriate auxiliary solvent (AS), able to dissolve both the TM and the SS, and with a low boiling point, so as to allow AS evaporation before the sublimation of the SS. In the here analysed ternary system, the SS is para-dichlorobenzene (PDCB), a simple aromatic molecule (one benzene ring bearing two symmetrically arranged chlorine atoms). PDCB is fully miscible with many organic solvents, including chloroform ( $\text{CHCl}_3$ ), that was hence used as AS. Poly-methyl methacrylate (PMMA) was used as TM, given its solubility in both  $\text{CHCl}_3$  and PDCB. The ternary mixture AS/SS/TM is formulated so to be liquid at room temperature, allowing easy handling.

We explain the tertiary patterns as originated by TM macromolecules that, while diffusing towards secondary patterns, have been "caught" in the middle of the travel by the final sublimation of the SS matrix, which caused their sudden precipitation on site. The perpendicularity of these tertiary patterns to the secondary ones, testifying the motion of the PMMA chains towards the latter, supports this view. Also, the almost complete absence of tertiary patterns at high SS concentrations in the TS (which means that the TM macromolecules had enough time to diffuse and self-assemble with secondary patterns) suggests this explanation.

On the contrary, when the SS/AS ratio is low the solid layer resulting from the TS deposition on the substrate is relatively thin, and due to the inherent formulation of the analysed solutions a lesser amount of TM is incorporated in it (Fig. 4.12, insets at the top

right of the upper graphs, and Fig. 4.13, upper row; see Experimental Part, Table 4.1, for details on the TS compositions). In this situation, the TM macromolecules have considerably less time than in the previous case for diffusing through the solid matrix and undergoing extensive self-assembly processes within the SS crystallites/crystal domains borders, resulting in very well-defined fibres, or, when the AS concentration is very high (which means that the SS/TM solid layer left on the substrate is extremely thin), in the simplest self-assembly the macromolecule can realize, i.e. in dots. As all the macromolecules present in the solid SS/TM layer undergo this process during the SS sublimation, the resulting dots become aligned, following the same hierarchy (primary/secondary/tertiary patterns) and crystallite-dictated templating effect found for the fibres. Notably, all the aligned dots belonging to the same hierarchical pattern order have very similar sizes, supporting the hypothesis that these formations occur upon local, well defined self-assembly processes

In conclusion, we have shown that it is possible to tune the topology of PMMA nanopatterns from continuous fibres to aligned dots by simple variation of the ternary solution composition, in a controlled way and over rather large areas (as wide as several thousands of  $\mu\text{m}^2$ ); in particular, the influence of the relative concentration of each TS component on the final pattern topology has been studied, allowing to create a ternary diagram that can be used as a reliable guide for rationally designing PMMA patterns over large areas.

The size of, and the relative distance between, the formed patterns is an exponential decay function of the relative concentration of the AS in the TS, suggesting that the self-assembly processes of PMMA occurring within the SS matrix can be described by well-known polymer chains diffusion laws (this hypothesis is currently being verified). A tentative explanation of the mechanism underlying the formation of the observed nanostructures has been given.

Relying on the above-mentioned findings, a qualitative explanation of the phenomena underlying the formation of the patterns have been given. Particularly, it is proposed that the SS crystallites exert an effective templating affect, and that the transition from continuous fibres to dots is governed by the SS/TM layer thickness left on the substrate after the AS has left the system.



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## CURRICULUM VITAE

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