

Chapter 2

Background

This work is based on the combination of two distinct subjects: the self-assembly of block copolymers in thin films and optical metamaterials.

In this chapter I will give a brief introduction of these two fields and of their recent research progress.

2.1 Block Copolymers

Polymers are a class of macromolecules composed of many repeating subunits, defined as monomers, linked by covalent bonds. Polymers can be classified into two types: homopolymers composed of only one repeating monomer unit, and copolymers derived from two or more types of monomer units. In turn, copolymers can be classified based on how these units are arranged along the chain. The arrangement can generate: alternating copolymers with regular alternating A and B units (e.g. A-B-A-B-...), periodic copolymers with A and B units arranged in a repeating sequence (e.g. (A-B-B-A-B)_n), statistical copolymers in which the sequence of monomer residues follows a statistical rule, and block copolymers [1]. In the block copolymer subclass, two or more homopolymers are covalently arranged into distinct blocks [2]. The simplest example is an A-B block copolymer with two covalently tethered homopolymers. Block copolymers with two or three distinct blocks are called diblock copolymers and triblock polymers, respectively (Fig. 2.1).

Block copolymer can be synthesized by living polymerization [3], a technique that enables the sequential addition of monomers and the synthesis of functional-ended polymers by selective termination allowing the additive synthesis of additional blocks.

An important property of block copolymers is their ability to self-assemble into periodic nanostructures. To understand the block copolymer self-assembly let us first consider a mixture of two separate immiscible homopolymers A and B. The minimization of unfavourable interfaces drives the homopolymers to blend to macrophase separation into coexisting bulk phases, similarly to water and oil mixtures. When two

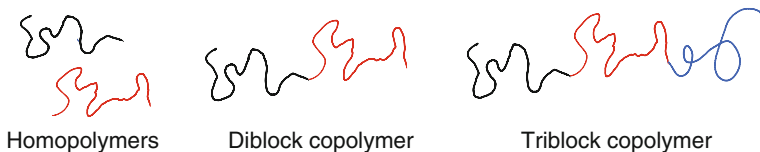


Fig. 2.1 Homopolymers and block copolymers architectures. Polymers are a class of macromolecules that are composed of many repeating subunits. Homopolymers consist of a single type of monomer, while linear block copolymers are chains containing sequences of different homopolymers

immiscible homopolymers are covalently bonded to form an A-B block copolymer, the length scale of the phase separation is limited by the polymer chain length, leading to microphase separation.

In the block copolymer melt, the enthalpic forces, driving the interface minimization, are counterbalanced by entropic forces that encourage the reduction of chain stretching [4]. The affinity between two polymers is defined by the Flory-Huggins interaction parameter χ . In addition to the Flory-Huggins parameter, the phase behaviour of block copolymers is controlled by the degree of polymerization N and the volume fraction of each block (f_a and f_b in a diblock copolymer).

For volume fractions $f_a \simeq f_b$, the interface minimization drives the phase separation to lamellae containing alternating the A and B blocks. For volume fractions $f_a \gg f_b$ the best geometrical solution to minimize the polymer interface leads to the formation of spheres containing the polymer with the lower volume fraction, embedded in a major phase of the other polymer.

The equilibrium phases can therefore be mapped as a function of the volume fraction f_a and the χN parameter in a phase diagram, shown in Fig. 2.2.

2.1.1 Triblock Copolymer Morphologies

The addition of a third block to a linear block copolymer gives rise to several new potential architectures, some of which are shown in Fig. 2.3, with many others still under investigation [6–8].

In the gyroid morphology, the blocks forming the two interwoven networks are composed of distinct polymers, denoted as minority phases, each forming a so-called single gyroid. The largest part of the work presented in this dissertation focuses on gyroid formed by triblock copolymers, where one of the minority phases was selectively etched and backfilled by electrodeposition, producing a metal single gyroid.

The single gyroid has strong chirality in certain directions, with helices visible in the [111] and [100] orientations as shown in Fig. 2.4. In these directions we can distinguish two helices with opposite chirality and different radii.

The phase map of a triblock copolymer composed of polyisoprene (PI), polystyrene (PS) and polyethylene oxide (PEO), commonly named ISO block copolymer, is

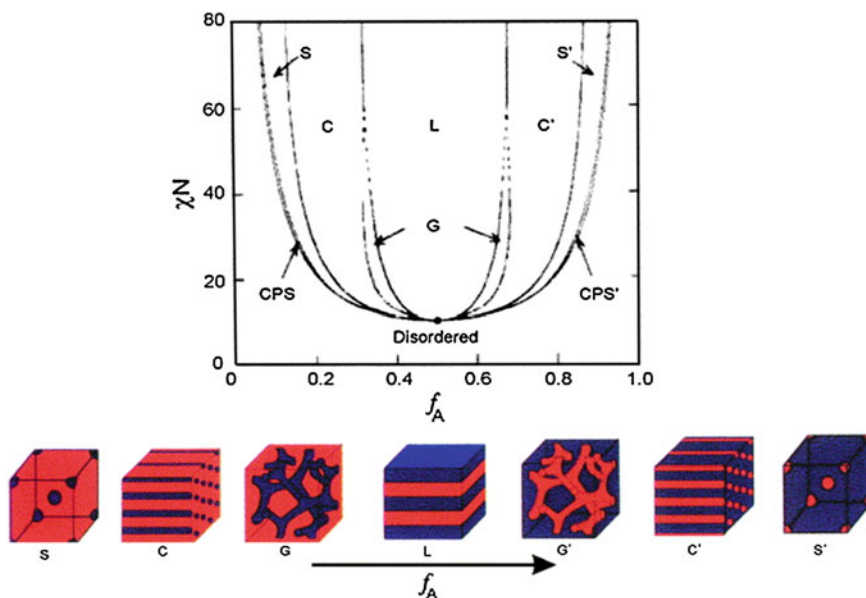


Fig. 2.2 Phase diagram for linear AB diblock copolymers with the regions of stability for cylinders (C), spheres (S), lamellae (L), gyroid (G), close packed spheres (CPS), and disordered phase. Adapted from [5]

displayed in Fig. 2.5. As it will be discussed in the next chapter, the metal single gyroid will be fabricated from the ISO triblock copolymer with the alternating gyroid morphology. This morphology is generated in a narrow area of the phase diagram as displayed in Fig. 2.5.

2.1.2 Gyroid Morphology

The gyroid phase observed in diblock copolymers is a structure consisting of two interwoven continuous networks, containing the polymer with lower volume fraction, embedded in a matrix formed by the majority block. Since both minority and majority phases are continuous in all three dimensions the structure is termed bicontinuous.

The term “gyroid” was coined in 1970 by Alan Schoen [12], a mathematician who discovered the family of triply periodic minimal surfaces (i.e. with zero mean curvature everywhere), which are now named after him. The “Schoen G” or “gyroid surface” is a triply periodic minimal surface that divides the space into two separate twisting volumes as shown in Fig. 2.6a.

The majority phase of the gyroid block copolymer is equivalent to the gyroid surface with a given finite thickness, by simultaneously expanding of the two surfaces on both sides. Space is consequently divided into three non-intersecting volumes. The

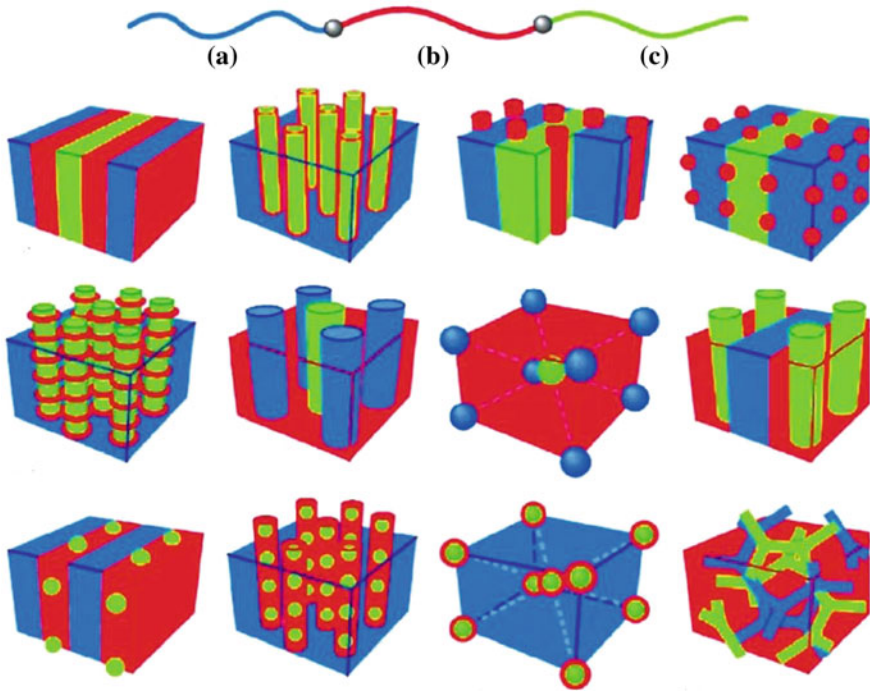


Fig. 2.3 Morphologies for linear ABC triblock copolymers. The phases are coloured as shown by the copolymer blocks at the *top*, with block types A, B and C confined to regions colored *blue*, *red* and *green*, respectively. Adapted from [9]

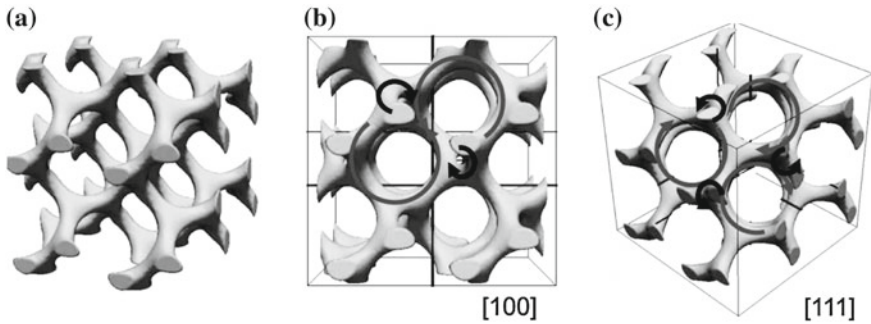


Fig. 2.4 **a** Perspective view of the gyroid structure with 10% filling fraction. **b** View of the chiral [100] direction with the two opposite helices indicated by the *black* and *red* arrows. **c** View of the chiral [111] direction. Adapted from [10]

“central volume” forms the majority phase, embedding two distinct non-intersecting gyroid networks. The two gyroid network morphology will be hereafter called double gyroid.

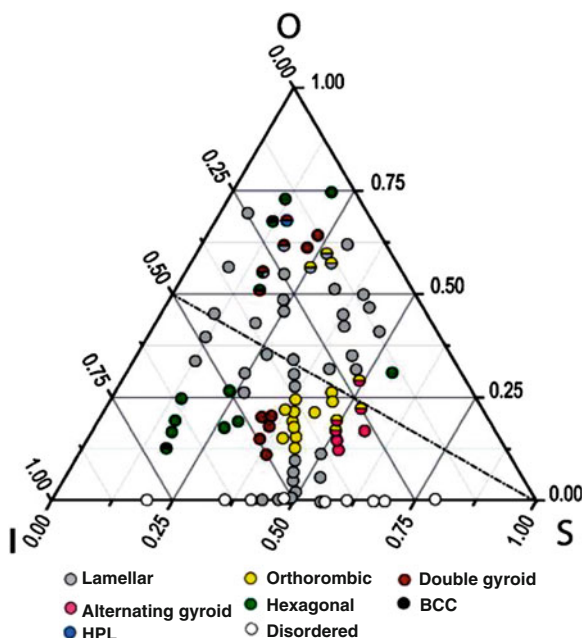


Fig. 2.5 Experimental phase map of the triblock copolymer systems composed of polyisoprene (*I*), polystyrene (*S*) and polyethylene oxide (*O*) at a set value of χN [11]. The axes identify volume fractions of each block. The phase morphologies are identified by colours and labeled below the diagram with abbreviations defined as: LAM (lamellar), HEX (hexagonal), BCC (body-centered cubic), HPL (hexagonally perforated layers). The schematic representations of these morphologies are described in [11]

Why polymers select this non trivial morphology is an interesting issue that can be addressed by examining the concept of minimal surface. A minimal surface is a surface that minimizes the total surface area under some constraint. For example,

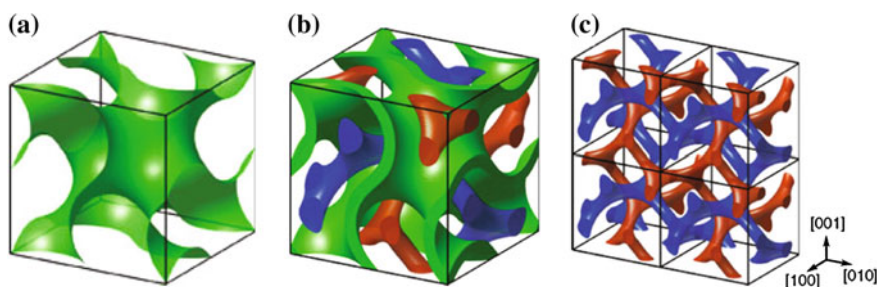


Fig. 2.6 a "Schoen G" or "gyroid surface". b A schematic of the the double gyroid unit cell showing the majority phase equivalent of the gyroid surface (*green*) and the two gyroid networks (*blue* and *red*). c Four cubic unit cells of the double gyroid network with a volume fraction of 12 %. Adapted from [13]

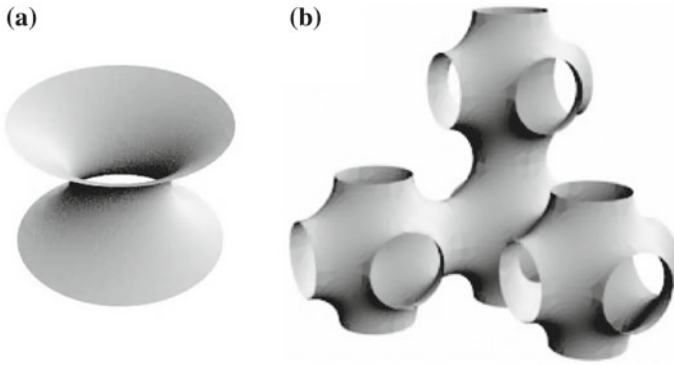


Fig. 2.7 **a** Catenoid minimal surface derived by minimizing the connecting surface of two parallel rings. **b** Schwartz P periodic minimal surface produced by connecting a cubic array of rings

under the constraint of connecting two parallel rings, the geometry that minimizes the surface area corresponds to the catenoid minimal surface. Similarly, the Schwartz P triply periodic minimal surface connects a cubic array of rings, as shown in Fig. 2.7. The gyroid surface can be seen as a tessellation of gyrating catenoids associated with the P-surface [14].

In the gyroid block copolymer system, the unfavourable interaction between polymers leads to the segregation of majority block in the the central matrix volume that, as a minimal surface, represents an optimized geometry which minimizes interface interactions.

Interestingly, the gyroid geometry is also found in nature in several systems in addition to block copolymers. In 1983 it was found in some surfactants, where lipid appeared to form a single bilayer continuous in three dimensions, separating two networks of water with a Schwartz G geometry [15].

Gyroids have been observed in biological structural coloration in butterfly wing scales [16, 17]. In these systems the gyroid structure has lattice size one order of magnitude higher than in the block copolymers, giving rise to photonic crystals. Gyroid structures are also occasionally found inside cells [18].

The gyroid surface can be trigonometrically approximated by the equation:

$$\sin\left(\frac{2\pi}{L}x\right)\cos\left(\frac{2\pi}{L}y\right) + \sin\left(\frac{2\pi}{L}y\right)\cos\left(\frac{2\pi}{L}z\right) + \sin\left(\frac{2\pi}{L}z\right)\cos\left(\frac{2\pi}{L}x\right) = t, \quad (2.1)$$

where L is the cubic unit cell and t is equal to 0.

For increasing t with $0 < |t| \leq 1.413$ the gyroid surface is monotonically reduced with an increase of volume of one of the two space regions divided by the gyroid surface, on the expense of the other. For $1.413 \leq t$ the gyroid surface is no longer connected and will be neglected in the following discussion.

Let us consider one of the two gyroid networks formed by the minority phase. Its surface can be described by Eq. 2.1. For $t = 0$, the single gyroid network occupies

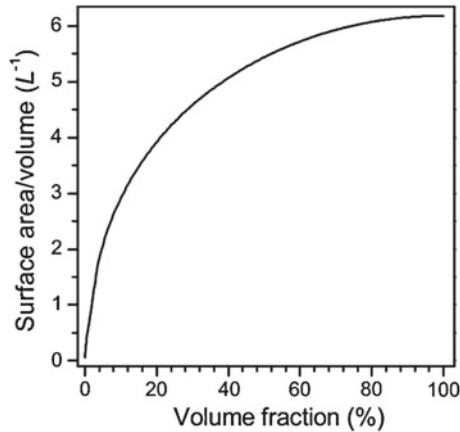


Fig. 2.8 Specific surface area to bulk volume ratio in units of the cubic unit cell dimension L of the double gyroid plotted versus the filling fraction. Adapted from [19]

exactly one half of the total volume, i.e. it has filling fraction $f = 50\%$. For $t > 0$ ($t < 0$) the filling fraction decreases (increases) monotonically and the surface of the gyroid network has no longer zero but an increasing (decreasing) constant mean curvature.

The surface area of the gyroid is related to its filling fraction. For the double gyroids the surface area per unit volume is plotted in Fig. 2.8. In the single gyroid the relation of surface area and filling fraction is analogous, with a maximum for $f = 50\%$ and a symmetric decaying for $f > 50\%$.

2.1.3 Block Copolymer Applications

Block copolymers have received much attention in the past two decades with increasing applications in nanotechnology. Nonetheless, their commercial interest has started over 50 years ago. Block copolymers can be found in products as shoe soles, tire treads, adhesive tape and asphalt additives that combine high-temperature resilience and low-temperature flexibility. The importance of block copolymers can be seen in their wide array of combined properties made possible by different conjoined polymers.

The applications in nanotechnology are related to the scale of the microphase separation and to the tunability of the microphases, regulated simply by the molecular weight and composition, and to the wide range of chemical and physical properties of the constituent polymer blocks.

Block copolymer films have been used principally in nanolithographic etching processes, where the polymer phases function as a mask with high density of features [20]. They have also been utilized to develop periodic photonic band gap materials.

The first example was a simple 1D photonic crystal made with high molecular weight lamellae [21].

Other block copolymer applications in nanotechnology include porous membranes based on the large surface/volume ratio, low density and pore size monodispersity [22].

The replication of one or more phases to use a block copolymer as sacrificial template has been widely demonstrated. Metals are typically deposited by electroless deposition, while oxides and other dielectrics are produced by atomic layer deposition (ALD) or sol-gel chemistry [23].

The replication of the gyroid morphology into metals was also achieved by electroless deposition of nickel for catalytic applications [24] and by sol-gel chemistry to create a highly porous SiO_2 structure with a reduced refractive index.

Gyroid block copolymers have found applications in supercapacitors [25], solar cells [26] and nanoporous membranes [27], and represent to date a versatile structure for an increasing number of applications.

However, the main limitation of the block copolymers applications in nanotechnology lies with the fact that, while the self assembled structure is locally very precise, it is difficult to control its order on larger scales. The domain size of the periodic ordering are typically of several tens of the lattice constants, limiting the long-range order to 2–3 μm .

In the next chapter I will discuss a fabrication process that enables the ordering of the gyroid block copolymer into domains of several hundreds of microns, an essential requirement for engineering applications and optical characterizations.

2.2 Metamaterials

Metamaterials are artificially structured materials which are engineered to gain their properties not only from their composition, but from their design. Their geometry, size and arrangement can affect the waves of light or sound in a unconventional manner, giving rise to properties which are not available in any other bulk material (the word ‘meta’ means ‘beyond’ in Greek, and in this sense the name metamaterial refers to ‘beyond conventional materials’). The structural units have dimensions much smaller than the wavelengths of interest, so that the metamaterial is perceived homogeneous by the incident waves and their electromagnetic response is expressed in terms of homogenized material parameters.

Sought-after properties in metamaterials are the simultaneous negative electric permittivity ϵ and magnetic permeability μ . This leads to a negative refraction as demonstrated by Veselago in 1968 [28]. Negative index metamaterials have the potential to form superlenses, overcoming the diffraction limit, or to enable novel optical effects, including cloaking [29, 30].

Although negative permittivity is quite common in metals at optical wavelengths, it is very unusual to find natural materials that exhibit a magnetic response at terahertz or higher frequencies [31].

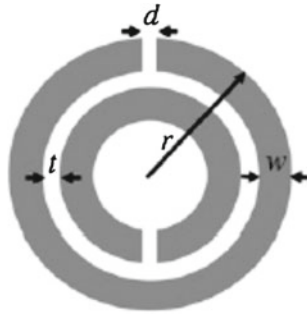


Fig. 2.9 Split-ring structure proposed by Pendry et al. [32]

However, a metamaterial made of a conductive but not-magnetic material designed as a split-ring resonator (SRR) can display a magnetic response and negative permeability at the resonance frequencies of this oscillator, as first predicted by John Pendry in 1999 [32]. A single cell SRR consists of a pair of enclosed loops with splits in opposite sides as shown in Fig. 2.9. They represent a paradigm example of a metamaterial system. A magnetic wave penetrating the metal rings produces an oscillating current flow that induces local magnetic dipole moments giving an effective magnetic response and thereby an engineered permeability.

When a SRR array is combined with an array of conducting wires it can create a medium with simultaneous negative permeability and permittivity.

Smith and coworkers showed evidence of negative index refraction with ring resonators in 2001 [33]. The first metamaterials were demonstrated at microwave frequencies and then scaled to the mid-infrared [34]. However, further down-scaling requires a different approach as a consequence of the strong deviation of metals from ideal conductors at high frequencies [35]. Moreover, to extend metamaterials to optical frequencies requires scaling the constituting features from the millimetre size down to the nanometre scale.

Several metamaterial architectures have been proposed in the past decade, some of which are summarized in Fig. 2.10. The operating frequency of optical metamaterials have already reached visible wavelengths, and negative refraction has been proved for light wavelengths between 720 and 760 nm [36].

However, some critical problems still remain unsolved. The main drawback for most potential applications of metamaterials are the high losses originated from the metal in the structure. These are a critical problem mainly at the infrared and optical frequencies where the metals differ from a perfect conductor. This results in high absorption and strong reduction of light transmission through the metamaterials.

Another problem in the fabrication of metamaterials is the development of truly 3D structures. The current metamaterials are generally limited to light coming from a narrow range of directions.

The proposed block copolymer based metamaterial is truly three dimensional and, as we will see in the following chapters, it displays strongly enhanced transmission,

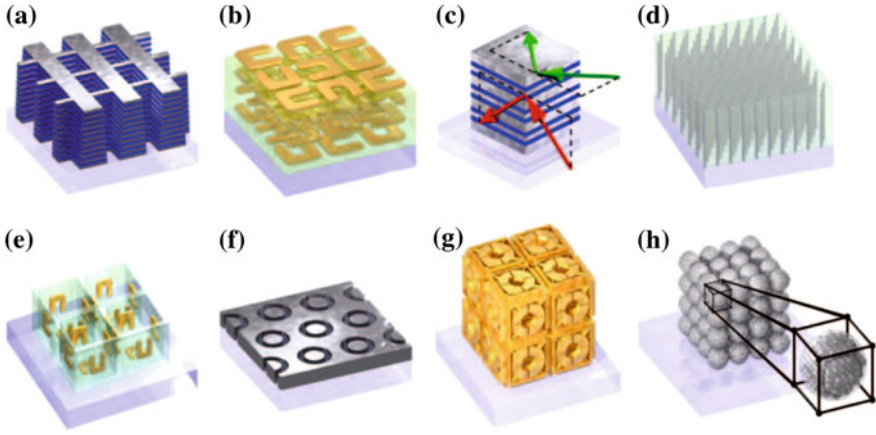


Fig. 2.10 Principal metamaterial designs proposed in the past decade. **a** Fishnet structure [37]. **b** Stereo metamaterial [38]. **c** Hyperbolic metamaterial [39]. **d** Metal-dielectric layered metamaterial [40]. **e** Three dimensionally oriented SRRs [41]. **f** Coaxial metamaterial [42]. **g** Connected cubic-symmetry metamaterial [43]. **h** Metal cluster-of-clusters array [44]. Adapted from [45]

i.e. it has low losses. Moreover, it is produced by self-assembly in contrast to the largely used top-down techniques of current metamaterials.

2.2.1 Chiral Metamaterial

It was recently proposed [46] that a chiral structure can offer a unique route to a negative refractive index for one circular polarization. A structure is defined as chiral if it lacks any planes of mirror symmetry.

The existence of chirality breaks the degeneracy of two oppositely circularly polarized waves. The two polarized beams experience different propagation speeds in a chiral media, i.e. the refractive index is increased for one circular polarization and reduced for the other. Therefore, if the chirality is strong enough, negative refraction may occur for one circularly polarized wave even when permittivity and permeability are both positive.

The first chiral metamaterial was proposed by Pendry in his pioneering work [46] as a “Swiss Roll” structure. Other theoretical works have also demonstrated negative refraction in the THz and microwave regimes [47]. The principal experimentally obtained chiral metamaterials are summarized in Fig. 2.11.

The complex structure of chiral metamaterials has been a significant challenge in the miniaturization to the nanometric scale. Standard top-down approaches such as lithography techniques are not ideal to fabricate complex three dimensional chiral structures whereas the self-assembly of gyroid block copolymer is an ideal candidate to produce a chiral metamaterial.

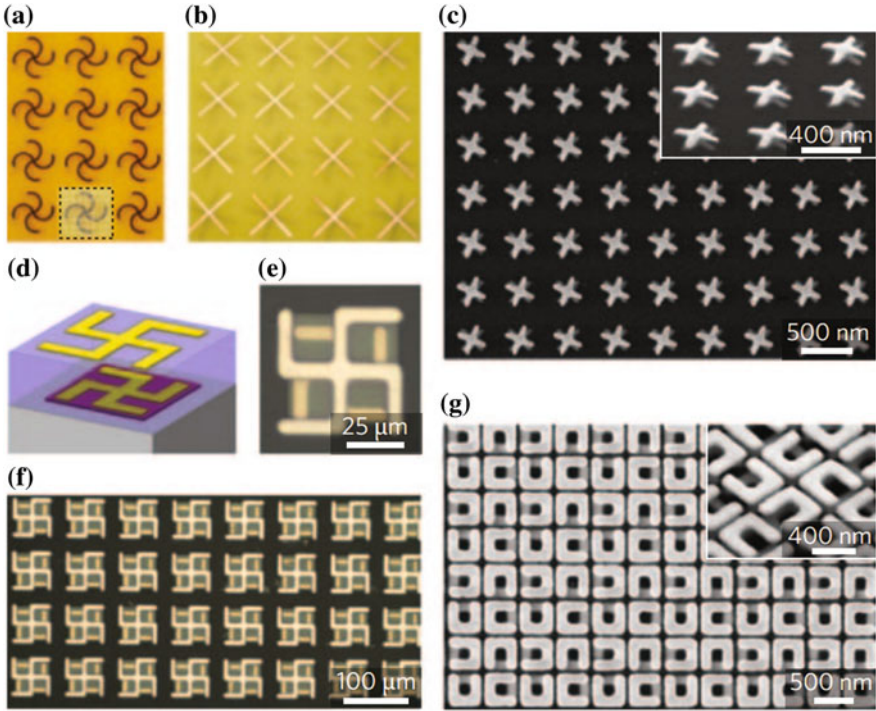


Fig. 2.11 Chiral metamaterial structures proposed in the past years. **a** Rosette chiral metamaterial with negative refraction at gigahertz frequencies [48]. **b** Cross-wire chiral metamaterials with negative refraction at GHz frequencies [49]. **c** Chiral structure composed of *right-handed* twisted gold crosses [50]. **d–f** Tunable chiral metamaterial [51]. **g** Twisted *U-shaped* split ring resonators [52]. Adapted from [45]

2.2.2 Surface Plasmons

Metamaterials with features on the nanometre scale derive their optical properties from surface plasmon waves. These are collective oscillations of free electrons on the surface of metallic interfaces with dielectrics. The free electrons dominate the interaction of light with metals. The optical electromagnetic field produces a force that displaces these weakly bound electrons. Since the electrons are negatively charged particles in a background of positive charges, the electron movement produces a restoring force. The free electrons can be considered as optically driven oscillators with a natural frequency of oscillation known as the plasma frequency. This is given by:

$$\omega_p = \sqrt{\frac{n_e e^2}{\epsilon_0 m^*}} \quad (2.2)$$

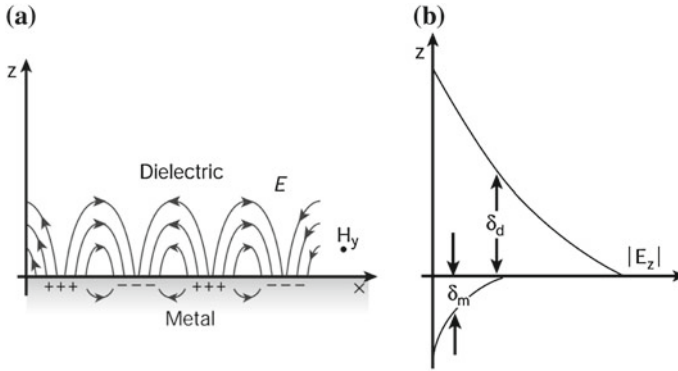


Fig. 2.12 **a** Electromagnetic wave and surface charges of surface plasmons at the interface between a metal and a dielectric material. **b** The field component perpendicular to the surface is enhanced near the surface and decays exponentially with distance. Adapted from [54]

where ϵ_0 is the dielectric constant of free space, e is the charge of the electrons, n_e is their number density, and m^* is their effective mass.

The interaction of the electromagnetic field and the surface free electrons produces surface plasmons that can propagate along the surface. In contrast to the propagating nature of the surface plasmons, the field perpendicular to the surface decays exponentially with distance from the surface. The field in this perpendicular direction is said to be evanescent. In the dielectric medium above the metal, typically air, the decay length of the field is on the order of one-half of the wavelength of light, whereas the decay length into the metal is determined by the skin depth, as represented in Fig. 2.12.

The skin depth of noble metals in the visible spectrum is on the order of 20 nm [53]. As the strut thickness of the gold gyroid is only 10 nm, the entire gyroid network acts effectively as a ‘surface’ and all the material is permeated by surface plasmons.

As we will see in the next chapters the effect of surface plasmons in the gyroid metamaterial enables enhanced transmission through gold gyroid films of several hundred nanometers.

2.2.3 Gyroid Theoretical Models

The gyroid morphology has received increasing attention as metamaterial structure, leading to theoretical predictions of its optical properties. However, these results are still debated.

Hur et al. [55] have calculated the photonic band structures of single and double gyroids made of gold and silver. The double gyroid morphology was predicted to form a capacitor, leading to a different light propagation mechanism than in the single gyroid morphology. The light propagation was suggested to originate from

the coupled surface plasmons resonance on the closed loops formed in the double gyroid, supporting the surface plasmon propagation.

Negative refraction was predicted in silver and aluminium double gyroids, with n inversely proportional to the unit cell size and the frequency range controlled by the filling fraction. According to this study, the strong absorption deriving from the inter-band transitions impede the negative refraction in gold gyroids. Moreover, in the single gyroid, the lack of a counter electrode was predicted to inhibit light propagation through the metallic gyroid network.

Oh et al. [10] simulated the gyroid metamaterials by approximating the gyroid with three orthogonal helices. They identified one longitudinal and two degenerate transverse modes in the gold single gyroid. Their results suggest that the chirality may be smaller than expected as a direct consequence of the mixture of right- and left-handed helices shown in Fig. 2.4.

The only experimental work on gold gyroid metamaterials was presented by Vignolini et al. in 2011 [56]. It showed a strong reduction of the gold plasma frequency and circular dichroism. These results will be discussed more in detail in the next chapters.

References

1. Kratochvil P (1996) Glossary of basic terms in polymer science. *Pure Appl Chem* 68:2287–2311
2. Hamley IW et al (1998) The physics of block copolymers, volume 19. Oxford University Press, New York
3. Webster OW (1991) Living polymerization methods. *Science* 251(4996):887–893
4. Flory PJ (1942) Thermodynamics of high polymer solutions. *J Chem Phys* 10:51–61
5. Bates FS, Fredrickson GH (1999) Block copolymers—designer soft materials. *Phys Today* 52(2):32–38
6. Wu Y, Cheng G, Katsov K, Sides SW, Wang J, Tang J, Fredrickson GH, Moskovits M, Stucky GD (2004) Composite mesostructures by nano-confinement. *Nat Mater* 3(11):816–822
7. Nagpal U, Detcheverry FA, Nealey PF, de Pablo JJ (2011) Morphologies of linear triblock copolymers from monte carlo simulations. *Macromolecules* 44(13):5490–5497
8. Shefelbine TA, Vigild ME, Matsen MW, Hajduk DA, Hillmyer MA, Cussler EL, Bates FS (1999) Core-shell gyroid morphology in a poly (isoprene-block-styrene-block-dimethylsiloxane) triblock copolymer. *J Am Chem Soc* 121(37):8457–8465
9. Zheng W, Wang Z-G (1995) Morphology of abc triblock copolymers. *Macromolecules* 28(21):7215–7223
10. Oh SS, Demetriadou A, Wuestner S, Hess O (2012) On the origin of chirality in nanoplasmonic gyroid metamaterials. *Adv Mater* 25(4):612–617
11. Epps TH, Cochran EW, Bailey TS, Waletzko RS, Hardy CM, Bates FS (2004) Ordered network phases in linear poly(isoprene-b-styrene-b-ethylene oxide) triblock copolymers. *Macromolecules* 37(22):8325–8341
12. Schoen AH (1970) Infinite periodic minimal surfaces without self-intersections. Nasa technical note, D(5541)
13. Scherer MRJ (2013) Double-Gyroid-Structured functional materials: synthesis and applications. Springer Science & Business, New York
14. Große-Brauckmann K, Meinhard W (1996) The gyroid is embedded and has constant mean curvature companions. *Calc Var Partial Differ Equ* 4(6):499–523

15. Longley W, McIntosh TJ (1983) A bicontinuous tetrahedral structure in a liquid-crystalline lipid. *Nature* 303:612–614
16. Michielsen K, Stavenga DG (2008) Gyroid cuticular structures in butterfly wing scales: biological photonic crystals. *J R Soc Interface* 5(18):85–94
17. Saranathan V, Osuji CO, Mochrie SGJ, Noh H, Narayanan S, Sandy A, Dufresne E, Prun RO (2010) Structure, function, and self-assembly of single network gyroid (I4132) photonic crystals in butterfly wing scales. *PNAS* 107(26):11676–11681
18. Hyde S, Blum Z, Landh T, Lidin S, Ninham BW, Andersson S, Larsson K (1996) *The language of shape: the role of curvature in condensed matter: physics, chemistry and biology*. Elsevier, The Netherlands
19. Scherer MRJ, Li L, Cunha PMS, Scherman OA, Steiner U (2012) Enhanced electrochromism in Gyroid-Structured Vanadium Pentoxide. *Adv Mater Deerfield Beach Fla* 24(9):1217–1221
20. Segalman RA (2005) Patterning with block copolymer thin films. *Mater Sci Eng: R: Rep* 48(6):191–226
21. Edrington AC, Urbas AM, DeRege P, Chen CX, Swager TM, Hadjichristidis N, Xenidou M, Fetters LJ, Joannopoulos JD, Fink Y et al (2001) Polymer-based photonic crystals. *Adv Mater* 13(6):421–425
22. Hashimoto T, Tsutsumi K, Funaki Y (1997) Nanoprocessing based on bicontinuous microdomains of block copolymers: nanochannels coated with metals. *Langmuir* 13(26):6869–6872
23. Park C, Yoon J, Thomas EL (2003) Enabling nanotechnology with self assembled block copolymer patterns. *Polymer* 44(22):6725–6760
24. Hsueh H-Y, Huang Y-C, Ho R-M, Lai C-H, Makida T, Hasegawa H (2011) Nanoporous gyroid nickel from block copolymer templates via electroless plating. *Advanced Materials (Deerfield Beach, Fla.)* 23(27):3041–3046
25. Wei D, Scherer MRJ, Bower C, Andrew P, Ryhanen T, Steiner U (2012) A nanostructured electrochromic supercapacitor. *Nano Lett* 12(4):1857–1862
26. Crossland EJW, Kamperman M, Nedelcu M, Ducati C, Wiesner U, Smilgies D-M, Toombes GES, Hillmyer MA, Ludwigs S, Steiner U et al (2008) A bicontinuous double gyroid hybrid solar cell. *Nano Lett* 9(8):2807–2812
27. Li L, Schulte L, Clausen LD, Hansen KM, Jonsson GE, Ndoni S (2011) Gyroid nanoporous membranes with tunable permeability. *ACS Nano* 5(10):7754–7766
28. Veselago VG (1968) The electrodynamics of substances with simultaneously negative values of epsilon and mu. *Sov Phys Uspekhi* 10(4):509–514
29. Pendry JB (2000) Negative refraction makes a perfect lens. *Phys Rev Lett* 85(18):3966–3969
30. Pendry JB, Schurig D, Smith DR (2006) Controlling electromagnetic fields. *Science (New York, N.Y.)* 312(5781):1780–1782
31. Yen T-J, Padilla WJ, Fang N, Vier DC, Smith DR, Pendry JB, Basov DN, Zhang X (2004) Terahertz magnetic response from artificial materials. *Science* 303(5663):1494–1496
32. Pendry JB, Holden AJ, Robbins DJ, Stewart WJ (1999) Magnetism from conductors and enhanced nonlinear phenomena. *IEEE Trans Microw Theory Tech* 47(11):2075–2084
33. Smith DR, Padilla WJ, Vier DC, Nemat-Nasser SC, Schultz S (2000) Composite medium with simultaneously negative permeability and permittivity. *Phys Rev Lett* 84(18):4184–4187
34. Wu W, Yu Z, Wang S-Y, Williams RS, Liu Y, Sun C, Zhang X, Kim E, Shen YR, Fang NX (2007) Midinfrared metamaterials fabricated by nanoimprint lithography. *Appl Phys Lett* 90(6):063107–063107
35. Zhou J, Koschny T, Kafesaki M, Economou EN, Pendry JB, Soukoulis CM (2005) Saturation of the magnetic response of split-ring resonators at optical frequencies. *Phys Rev Lett* 95(22):223902
36. Xiao S, Drachev VP, Kildishev AV, Ni X, Chettiar UK, Yuan H-K, Shalaev VM (2010) Loss-free and active optical negative-index metamaterials. *Nature* 466(7307):735–738
37. Zhang S, Fan W, Panoiu NC, Malloy KJ, Osgood RM, Brueck SR (2006) Optical negative-index bulk metamaterials consisting of 2d perforated metal-dielectric stacks. *Opt Express* 14(15):6778–6787

38. Katsarakis N, Konstantinidis G, Kostopoulos A, Penciu RS, Gundogdu TF, Kafesaki M, Economou EN, Koschny T, Soukoulis CM (2005) Magnetic response of split-ring resonators in the far-infrared frequency regime. *Opt Lett* 30(11):1348–1350
39. Fang A, Koschny T, Soukoulis CM (2009) Optical anisotropic metamaterials negative refraction and focusing. *Phys Rev B* 79(24):245127
40. Hoffman AJ, Alekseyev L, Howard SS, Franz KJ, Wasserman D, Podolskiy VA, Narimanov EE, Sivco DL, Gmachl C (2007) Negative refraction in semiconductor metamaterials. *Nat Mater* 6(12):946–950
41. Burckel DB, Wendt JR, Eyck GAT, Ginn JC, Ellis AR, Brener I, Sinclair MB (2010) Micrometer-scale cubic unit cell 3d metamaterial layers. *Adv Mater* 22(44):5053–5057
42. Burgos SP, de Waele R, Polman A, Atwater HA (2010) A single-layer wide-angle negative-index metamaterial at visible frequencies. *Nat Mater* 9(5):407–412
43. Güneş DO, Koschny T, Soukoulis CM (2010) Intra-connected three-dimensionally isotropic bulk negative index photonic metamaterial. *Opt Express* 18(12):12348–12353
44. Rockstuhl C, Lederer F, Etrich C, Pertsch T, Scharf T (2007) Design of an artificial three-dimensional composite metamaterial with magnetic resonances in the visible range of the electromagnetic spectrum. *Phys Rev Lett* 99(017401):1–4
45. Soukoulis CM, Wegener M (2011) Past achievements and future challenges in the development of three-dimensional photonic metamaterials. *Nat Photonics* 5:523–530
46. Pendry JB (2004) A chiral route to negative refraction. *Science* (New York, N.Y.) 306(5700):1353–1355
47. Zhao R, Koschny T, Soukoulis CM (2010) Chiral metamaterials: retrieval of the effective parameters with and without substrate. *Opt Express* 18(14):14553–14567
48. Plum E, Zhou J, Dong J, Fedotov VA, Koschny T, Soukoulis CM, Zheludev NI (2009) Metamaterial with negative index due to chirality. *Phys Rev B* 79(035407):1–6
49. Zhou J, Dong J, Koschny T, Kafesaki M, Soukoulis CM (2009) Negative refractive index due to chirality. *arXiv preprint [arXiv:0907.1121](https://arxiv.org/abs/0907.1121)*
50. Decker M, Ruther M, Krieglner CE, Zhou J, Soukoulis CM, Linden S, Wegener M (2009) Strong optical activity from twisted-cross photonic metamaterials. *Opt Lett* 34(16):2501–2503
51. Zhou J, Taylor A, O'Hara J, Chowdhury R, Zhao R, Soukoulis CM (2010) Chiral thz metamaterial with tunable optical activity. Technical report, Los Alamos National Laboratory (LANL), Los Alamos
52. Decker M, Zhao R, Soukoulis CM, Linden S, Wegener M (2010) Twisted split-ring-resonator photonic metamaterial with huge optical activity. *Opt Lett* 35(10):1593–1595
53. Hajiaboli A, Kahrizi M, Truong V-V (2012) Optical behaviour of thick gold and silver films with periodic circular nanohole arrays. *J Phys D: Appl Phys* 45(48):485105
54. Barnes WL, Dereux A, Ebbesen TW (2003) Surface plasmon subwavelength optics. *Nature* 424(6950):824–830
55. Hur K, Francescato Y, Giannini V, Maier SA, Hennig RG, Wiesner U (2011) Three-dimensionally isotropic negative refractive index materials from block copolymer self-assembled chiral gyroid networks. *Angew Chem(International ed. in English)* 50(50):11985–11989
56. Vignolini S, Yufa NA, Cunha PS, Guldin S, Rushkin I, Stefik M, Hur K, Wiesner U, Baumberg JJ, Steiner U (2012) A 3D optical metamaterial made by self-assembly. *Adv Mater* (Deerfield Beach, Fla.) 24(10):OP23-7

Optical Metamaterials by Block Copolymer Self-Assembly

Salvatore, S.

2015, X, 83 p. 65 illus., 26 illus. in color., Hardcover

ISBN: 978-3-319-05331-8