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Integrated bottom-up and top-down soft lithographies and microfabrication approaches to multifunctional polymers
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Luana Persano,*ab Andrea Camposeo*ab and Dario Pisignano*ac

Organic multifunctional materials are becoming increasingly relevant to many fields of technology. Bottom-up assembly processes to give well-defined supramolecular architectures are a powerful tool to control the size and organization of molecular and polymeric nano- and microstructures. The full exploitation of these molecular systems in devices, however, often requires a superior technological control which should span very different length scales, enabling nanoscale control as well as large-area patterning and interfacing of active molecules with electrodes, external optical excitation or collection, biotechnological and lab-on-chip platforms of practical use, and so on. This critically depends on the development of specific lithographic approaches which are inherently hybrid in their character, since they combine bottom-up and top-down nanofabrication strategies in a smart way. Here we review and discuss some of these relevant hybrid methods, with a focus on their ultimate applicability to device platforms. The invention of a successfully integrated bottom-up/top-down strategy for microfabrication of functional macromolecules relies on exploiting their peculiar physico-chemical properties, and on building genuinely cross-disciplinary know-how and technologies.

1 Introduction

In the last two decades, micro- and nanofabrication technologies have definitely moved away from simply being tools to pattern inorganic materials for optics or electronics. Instead, these technologies are becoming more and more powerful in...
generating and shaping layers, nano- or micro–nanostructures, made of polymers or of other molecular systems. Such a development has consequently greatly widened the range of applications enabled by lithographic techniques. In this framework, functional and so-called multifunctional polymers, namely organic macromolecules in which two or more favorable structural, optical, electronic, or biological properties are concomitantly present, are playing a pivotal role in motivating the development of advanced, specific lithographic techniques. Active polymeric patterns with feature resolution from the micro- to the nanoscale allow researchers to exploit both the enormous variety of chemical functionalities achievable by synthetic molecular design and biological routes, and the usefulness of structurally stable, patterned features embeddable in novel materials and devices. The resulting combination is extremely attractive for photovoltaic and light-emitting devices, chemical and biological sensors, energy harvesting systems based on piezoelectric organics, protective coatings and smart surfaces, hybrid biological and microfluidic chips, nanomedicine and tissue engineering applications. In addition, the possibility to blend these polymers with semiconducting or carbon-based nanostructures, including carbon nanotubes, nanofibers and graphene, further enhances existing structures and devices.

The realization of multifunctional polymer nanostructures, as well as their embedment into device platforms, can be carried out by either top-down or bottom-up methods. On one hand, the top-down concept has been driving miniaturization for decades. This approach is based on the realization of microstructures, nanostructures and devices following the reduction of the size of blocks of materials having larger dimensions. Therefore, the spatial resolution, namely the minimum feature size which can be obtained, depends mainly on the accuracy of the material removal. Such accuracy is in turn related to a large set of variables including especially temperature, used chemicals, and all the physical effects characterizing the interaction between soft matter and radiation. In addition, the capability to control and reduce diffraction in radiation beams used to expose materials often plays a key role, as recalled in the following. Instead, the bottom-up concept is inherently additive and involves the spontaneous or induced assembly of fundamental, nanoscale components into more complex architectures. In this framework, a special role is played by self-assembly processes, namely by the spontaneous organization of basic elements, including molecular components, into larger structures and systems. The assembly is driven by energy minimization and entropy maximization mechanisms, and requires some degree of adjustability of single building blocks. For these reasons, the assembly can be favored by thermal or external agitation. Furthermore, in many of these processes, fluids are important. They can favor the self-organization of assembling components through capillarity phenomena mediated by solid–liquid interfacial energies, solvent evaporation, etc. Involving directly molecular or even atomic constituents, the resolution achievable in principle by bottom-up lithographies is only limited by the granular nature of matter. However, reproducibility, throughput, and large-area processing are almost ubiquitously relevant issues.

When dealing with inorganic materials, the top-down and bottom-up concepts are generally well distinct, and different lithographic approaches can be effectively categorized into the two classes of methods. Basically, top-down techniques include exposure-based approaches, in which a polymeric resist is patterned by virtue of the variation of its solubility due to the interaction with specific radiation. Such radiation delivers a suitable amount of energy to the material. In turn, this energy allows the organic compound to either cross-link or decompose, depending on its specific formulation. The high resolution and the registration capability are important points of strength of these approaches, allowing overlay patterning. Exposure-based lithographies include single-photon optical lithography (schematized in Fig. 1a), multi-photon methods, holography, electron-beam lithography (EBL), X-ray lithography, etc. The radiation can be delivered either in parallel onto large areas or by serial writing, depending on individual technologies. In particular, the broad domain of photolithography includes many sub-techniques such as phase-shift, projection, and extreme-UV lithography. The achievable resolution is at the scale of, say, a few tens of nm and of a few nm for optical lithographies and for EBL, respectively. However, these figures can be obtained only with extremely controlled and optimized processes, and with highly expensive equipment. In most of the research laboratories, the minimum feature size which is routinely obtained is larger than the best performances reported above, by at least one order of magnitude. Following exposure, the development of the exposed resist in a suitable solvent removes selectively the polymer in the irradiated (for positive resists) or in the non-irradiated (for negative resists) areas. Then, wet or reactive ion etching or milling processes are used to transfer the pattern onto the underlying inorganic material. As an (costly) alternative, focused-ion beams can also be employed for direct milling on various materials. Another possibility of exposure-based techniques, enabled by careful chemical design, is to pattern directly active organic materials. This would allow one to define regions with specific functions, as demonstrated by photo-patterned, multicolor fluorene-based polymers exhibiting electroluminescence (Fig. 1b).
Bottom-up methods work at the nm- or even sub-nm scale and include the formation of colloidal nanocrystals and of epitaxially grown quantum dots and nanowires through self-assembly, which are important examples in nanochemistry and optoelectronics. Some approaches have been proposed, which rely on complementary lithographic strategies in order to realize devices with these nanostructures and nanoparticles. How the top-down and the bottom-up paradigms can be combined in a synergic way to fabricate field-effect transistors based on inorganic semiconductor nanowires has been recently the subject of a dedicated review.7

In general, the fabrication techniques suited to pattern functional polymers can lead to a more in-depth integration of different paradigms. These methods are often unconventional and largely hybrid in their character.8 They can show the capability to tightly control the formation of micro- and nanostructures by the choice of a well-defined set of process parameters (which is typical of top-down technologies), and to use molecular self-assembling processes and weak interactions (typical of soft matter and more in general of bottom-up approaches). Soft lithographies,9 nanoimprinting,10 patterning methods based on block copolymers (BCPs),11 and fabrication of polymer nanofibers by electrospinning,12 schematized in Fig. 1c–f, are naturally at the edge between top-down and bottom-up. Many of these techniques allow various molecular assemblies or eventual molecular recognition steps to be incorporated during nanofabrication. In all these techniques, resolution can be pushed below 10 nm. Many active organic materials benefit from being soluble in commonly used solvents, and their complex assembly behavior during drying can be driven by soft lithographic templates or by electrified jets leading to solid nano- or microstructures. Following solidification, the resulting features are structurally stable. This is due to the lack of transversal diffusion, which is related to the considerable size of macromolecules, and to the good mechanical properties, which are related to the favorable viscoelastic properties and glass transition behavior of many polymeric materials.

It is also clear that the integration of functional polymers into working devices for optoelectronics, nanoelectronics, microfluidics and biotechnology has to pass through one or more top-down fabrication steps. These are critical to couple organic micro- or nanostructures with further functional layers, metal electrodes, scaffolds for structural support, etc., or to give polymers new or enhanced functions. Interfacing patterned polymer structures to electrodes and other device features needs the combination of lithographic methods specialized for organic active materials and of more conventional, top-down fabrication strategies.

For all these reasons, research on integrated patterning approaches, applied to functional polymers and to device platforms based on them, is nowadays vibrant. This feature article comprises five sections. In the next section, we present an overview of some remarkable lithographic and nano-microfabrication techniques. When applied to active organic polymers, these methods have a clear added value with respect to conventional technologies. Then, we move to consider integrated bottom-up and top-down methods, and how these can open new directions in terms of device fabrication. Finally, we draw some conclusions together with an outlook of these hybrid and extraordinarily promising concepts.
2 Micro–nanofabrication techniques for organic materials

Approaches to pattern functional polymeric materials need to meet a few crucial requisites in order to not deteriorate the physico-chemical properties of organics:

(i) Patterning should be preferably carried out at room temperature and without the use of high-energy radiation or other factors promoting oxidation.

(ii) Flexibility is often important, meaning the capability of patterning and nanofabrication technologies to be used with as much polymers as possible, and, whenever possible, of producing flexible nanostructures and devices whose mechanical properties can be tailored for specific applications.

(iii) Last but not least, operational simplicity and cheapness, which are always desired in lithographic technologies, are especially sound for methods targeting molecular compounds. In fact, these are key factors determining how much each technique is actually accessible by low cost bio-organic laboratories.

2.1 Soft lithography

Soft lithography was invented by Whitesides and coworkers in the early 1990s. This set of techniques has been the most successful to pattern functional organic materials. Several outstanding reviews already exist in the literature, therefore we limit here to summarize the main aspects making soft lithographies so flexible and easy to integrate with complementary lithographic procedures. The fundamental characteristic of soft lithography is the use of elastomeric molds made of polydimethylsiloxane (PDMS), of its hard variant obtained from trimethylsiloxy-terminated vinylmethylsiloxane and methylhydrosiloxane–dimethylsiloxane copolymers, of photocurable perfluoropolyether, or of other polymers. These molds serve as basic elements to define and transfer patterns onto the ultimate target materials. The elastomeric molds are produced by replica molding, namely by in situ polymerization of the initially pre-polymeric, fluid elastomeric compound against the features of a master structure (Fig. 1c). In turn, the masters are to be generated by other, often conventional lithographic methods, hence soft lithography has to be considered as complementary to (and largely enhancing) standard patterning approaches more than a strategy to replace them. The replica molding is the key enabling technology at the base of the soft lithography approach, and how much soft lithographies can be applied to functional polymers and different solvents critically depends on the elastomer used to produce replicas. Afterwards, the molds carrying a negative copy of the master features are peeled off and are placed in conformal contact with a substrate. The pattern transfer is therefore performed by a mechanical contact without the need for radiation beams and potentially harsh chemicals as those used in most of the etching processes. Therefore soft here means gentle, chemically flexible, as well as suitable to be applied to soft matter, including functional polymers. The ultimate resolutions are not limited by beam diffraction as in optical lithography, but instead by the size and conformation of macromolecules at the nanoscale, and by pattern distortions potentially occurring during the process due to the soft character of both elastomeric elements and polymers to be patterned. With properly optimized conditions and parameters, features with transversal and vertical dimensions of a few nm, or even sub-nm, can be obtained, fully in line with values achievable with much more expensive, low-throughput high-resolution writing techniques such as EBL. In fact, while the serial, lithographic production of suitable masters presenting features at the nm- or sub-nm scale is very demanding, the enormous potentialities of replica molding in terms of achievable resolution have been better demonstrated by transferring into elastomers’ alternative master structures derived from biology or chemistry, such as ionic crystals showing vertical steps of 0.3–0.5 nm, single-walled carbon nanotubes of ~1 nm diameter, micelles of various shapes, viruses, etc. The spatial uniformity of the so-produced features is at the sub-nm level as well. Indeed, the other point of strength which deserves to be mentioned is the extreme cheapness of these approaches, making soft lithographies fully accessible to organic chemistry and biotechnology laboratories. At least in some cases, soft lithography is demonstrated to be compatible with overlay registration, thus enabling multilevel fabrication of complex devices with accuracy reaching a few hundreds of nm for sufficiently rigid elastomeric elements and exhibiting high potential integration with techniques using rigid photomasks.

Whether a specific soft lithographic technique has to be considered prevalently as a top-down or a bottom-up method largely depends on the details of the final pattern transfer step, which can be very diverse. Micromolding in capillaries (MIMIC), namely microfluidic lithography, and even nanofluidics can be implemented by using elastomeric elements as templates to define micro- or nanochannels, and applied to pattern many active polymers including conjugated compounds to realize organic waveguides, channels for field-effect transistors, light-emitting nanofibers and so on. In these approaches, polymeric solutions or prepolymers are let to flow into elastomeric channels due to spontaneous capillarity or external pumping, and solid features are obtained following solvent evaporation through the molds or from the open channel terminations, or upon curing. Micro- and nanofluidic lithographies are therefore inherently additive methods, generally performed entirely at room temperature, and very suitable to pattern active materials given that the used solvents are compatible with the elastomers constituting the molds. As an alternative, various solvent-assisted methods assisted by elastomeric molds have been developed in the last two decades, which may be of particular interest in combination with the use of conjugated polymers to realize active electronic or photonic components including distributed feedback lasers. Microcontact printing (µCP) is another well-established method, in which the patterned surface of the mold is inked by molecules and placed in conformal contact with the target substrate. In this way, molecules are transferred onto the target only when this is in contact with the protruding features of the mold, and when the substrate–ink interactions are stronger than the attractive
forces between the ink molecules and the elastomer. The classical working scheme of μCP is therefore based on a covalent substrate–ink interaction, assisted by non-covalent, van der Waals or electrostatic links organizing the transferred molecules in ordered monolayers. In many other cases, the ink transfer can be primed by electrostatic forces as well, and printed molecules are just physically adsorbed on the target substrate. While being much more easily applied to molecules with low molar mass rather than to polymers, μCP is quite relevant in terms of bottom-up and top-down integration. In particular, involving so closely molecular self-assembly, μCP is the soft lithographic method which more effectively builds on the bottom-up concept.

2.2 Nanoimprint lithography

Nanoimprint lithography (NIL), proposed by Chou in 1996, is a powerful top-down technology. Similar to soft lithographies, it does not use radiation beams to expose resist materials, but it is based instead on the mechanical contact between a target organic material and a mold. The molds can be either inorganic (metallic, semiconductor, etc.) or organic (highly crosslinked or high-glass transition temperature polymers). Importantly, the initial pattern is not exploited as a master for realizing second-generation patterns in elastomers as in replica molding. In contrast, the mold is directly used to imprint the final target materials upon application of pressure and following heating (Fig. 1d). In conventional NIL, heating is needed to drive the target material, which is a thermoplastic polymer, above its glass transition temperature, \( T_{g} \). As known from the physics of the glassy state, this corresponds to lowering the polymer viscosity (or, in other words, its characteristic structural relaxation time) by many orders of magnitude, thus allowing the organic material to flow under the applied pressure and to fill the recessed feature of the imprinting mold.

From the physical viewpoint, NIL is described by the concomitant effect of at least two mechanisms. On one side, the pattern transfer is strictly related to the mechanical response of amorphous polymers to the external pressure. This response is influenced by the large conformational flexibility of individual polymer chains as well as by the presence of topological networks of entangled chains. A higher conformational flexibility is related to local molecular motions, whereas long-range, structural motions generally need the weakening of entanglements. Following the initial increase of temperature, the polymer film can reach its so-called rubber-elastic region, where the time-dependent shear compliance, \( J \), shows a plateau. At this stage the transferred deformation is still reversible, whereas at higher temperature or for longer heating times, irreversible patterning is obtained leading the polymer to its terminal flow region. Here \( J \) has a linear dependence on time. Another mechanism favouring imprinting involves pressure-induced volumetric contraction. A certain amount of free volume, \( \nu_f \), is always present at the nanoscale in deposited organic layers. \( \nu_f \) is roughly given by \( \nu - \nu_0 \), where \( \nu \) and \( \nu_0 \) indicate the specific molecular volume and the characteristic incompressible volume (hard core) of molecules, respectively. The reduction of \( \nu_f \) due to the application of an external stress helps the pressed film in taking the shape of the mold. The ultimate resolution achievable by NIL is of the order of a few nm, limited by the granular size of macromolecular chains and networks.

All these physical considerations apply to thermoplastic polymers, but some can hold for oligomers and conjugated polymers as well. These materials generally show a quite poor mechanical response due to the low molar mass and to the reduced amount of entanglements, therefore they are very difficult or impossible to pattern at high temperatures. In fact, NIL has been developed to work at room temperature (i.e., without leading polymers above \( T_g \)) and on a much larger variety of organic materials including conjugated polymers. Due to the slower response at room temperature, imprinting times are often longer than those used in conventional NIL. Notwithstanding the consequently reduced throughput, the peculiar advantage of room temperature NIL is the much higher chemical flexibility. In particular, the method is especially suitable for patterning functional polymers, since avoiding heating allows us to carry out the process in an uncontrolled atmosphere even with delicate materials which are easily susceptible to oxidation. Working at low temperature also means reduced deterioration of the pressing set-up together with a higher potentiality of use in conjunction with precision mechanics and optics for overlay alignment. For these reasons, room temperature NIL has been applied also in several experiments demonstrating a high degree of integration with other lithographic approaches. Finally, different physical and chemical mechanisms can be exploited to assist pattern formation during nanoimprinting processes besides viscoelasticity, including thermally driven or especially UV-driven cross-linking as in step-and-flash methods, and photothermal molding as demonstrated for the ultra-fast patterning of semiconductors and nanocomposites. Overall, similar to soft lithographies, the resolution achievable by NIL methods can be pushed at the nm scale, and three-dimensional patterns and architectures can be fabricated by various strategies, including the development of multilevel processes and of imprinting inclined with respect to the horizontal direction.

2.3 Block-copolymer lithography

A BCP is a macromolecule in which two or more chemically different homopolymer units (polyA, polyB, etc.), each made of many monomers (A, B, ...), are linked together. Each of these units is a block, and the simultaneous presence of different, covalently bound blocks in the molecule (polyA-b-polyB) leads to peculiar chemico-physical properties of the overall system. In particular, lithographic approaches based on BCPs are based on the capability of self-assembling of surface-deposited copolymer macromolecules, which can produce highly periodic and oriented, chemically anisotropic domains with extremely high feature resolution due to phase segregation (Fig. 1e). Indeed, the underlying physical mechanism at the base of these self-assembly processes is the aggregation of the chemically different blocks in spatially separated and dense domains, because of the poor relative affinity of the different monomer
species (i.e. because of the mutual immiscibility of the different components). Various topographies can be obtained in this way, including spheres, cylinders, lamellae, and gyroids, by controlling molecular parameters such as the length of the molecular chains and the volume fraction of each block component, and the thermodynamics at the base of the phase segregation process by which the system seeks to minimize its free energy has widely fascinated materials scientists.\textsuperscript{35} For example, the blocks can be described by the Flory–Huggins parameter (\(\chi\)) associated with the mutual interaction between the different constituent monomer species. \(\chi\) is directly related to the increase of energy due to a possible intimate mixing of the different species at the molecular scale. Hence, it is clear that blocks whose monomers show high \(\chi\) values will preferentially segregate into well-separated and chemically well-defined domains, due to the disfavored contact between the different monomer species.\textsuperscript{11,35} The resolution achievable in this self-organization is of the order of a few nm, which is much better than the resolution of features routinely obtained in optical lithography, the lateral uniformity of the features is in principle at the sub-nm scale, and BCP films, which can be deposited onto large areas by simple solution-based methods such as spin-coating, generally exhibit a remarkable mechanical stability. A lot of research has been focused on obtaining the highest possible degree of order (possibly in long ranges) in alternating the different domains in BCP films, on reducing the amount of defects at the separating interfaces, and on controlling the orientation of the resulting nanostructures. Indeed, as in other assembly processes, interfacial interactions with the substrate also play a crucial role, and the organization of copolymer blocks can be templated by previously realized geometries.

In particular, pre-existing chemical patterns with regions of different surface energies can strongly favor the preferential wetting of a specific region by a particular component of the BCP, thus enhancing and controlling the phase segregation in the deposited copolymer film. Another important issue is making the BCP self-assembly steps more and more compatible with other, well-established fabrication routes and with the geometries which are interesting for electronic and photonic devices. Fortunately, a proper process optimization allows features to be formed, which not only show highly controlled sizes and shapes but also differ substantially from those obtained under bulk conditions. For instance, the BCP lithography has been recently developed to produce nanoscale square patterns which are quite suitable for integrated circuit manufacturing.\textsuperscript{24} Arrays of lines with sharp bends, modeling patterns of interest for the production of microelectronic devices, can also be fabricated by using blends of BCPs on chemically patterned substrates.\textsuperscript{27} Pre-existing topographies used to direct self-assembly can also help in enhancing the registration capability of BCP lithographies, facilitating their application in multi-level processes for the realization of complex devices, and so on.

Once the BCP pattern is obtained, it can be used for a wide variety of further lithographic or micro-nanofabrication steps, such as the selective decoration of given domain species with nanoparticles, the fabrication of active polymer nanofibers and of nanoporous membranes, and the selective etching of the underlying substrate to transfer features to another organic or inorganic layer following the removal of a particular domain. Being so versatile, BCP lithographies are among the most suitable methods allowing top-down and bottom-up processing concepts to be mixed together, as reviewed in several examples in the next section. Finally, it is worth mentioning that, due to their flexibility, as well as to their cheapness and simplicity, these techniques are now moving from laboratories to industrial applications.

2.4 Electrospinning

\textit{Electrospinning} allows the formation of polymer nanofibers by an electrified jet of solution, in which molecular entanglements are sufficient to provide the spun body of fluid with viscoelastic behaviour.\textsuperscript{12,38,39} Being inherently based on weak intermolecular interactions and allowing formation of ultra-thin polymer filaments, thus shaping soft matter in an additive fashion through solution processing, electrospinning could be broadly categorized as bottom-up technology. The chemical flexibility of the method is quite high though not complete, because electrospinning is very suitable to process a wide range of plastic polymers and of their blends with other soluble molecules (dyes, soluble oligomers, proteins and enzymes) and with nanoparticles and micro-objects including living cells. In this process, a polymer solution is generally placed into a syringe, and an electric voltage bias (\(V\), in the range of 2–100 kV, most often around 10–30 kV) is applied between the syringe tip and a collecting surface by means of a high-voltage generator (Fig. 1f). Compared with other deposition methods from solution, the concentration of the polymer in the used solvent in electrospinning is generally high (5–30% in weight), thus favoring entanglements and consequently improving the viscoelastic properties of the jet. Firstly, a pendant droplet is found at the syringe tip, and an excess charge accumulates at the liquid–air interface due to the applied field. Such a droplet is progressively deformed following the increase of the voltage bias, thus forming a so-called Taylor cone, until electrostatic forces overcome the solution surface tension and a jet is extruded and moves from the Taylor cone to the collectors. The jet velocity is of the order of \(1 \, \text{m s}^{-1}\) and the jet accelerations are of hundreds of \(\text{m s}^{-2}\), corresponding to deformation rates which can reach \(10^6\) to \(10^7 \, \text{s}^{-1}\). During the flight of the polymer solution jet from the spinneret to the collecting surface, the stretching of macromolecules is therefore relevant, and the solvent evaporation rates concomitantly which leads to the very rapid narrowing of the fluid body from the order of 100 \(\mu\text{m}\) (corresponding to the internal diameter of the syringe tip) to potentially less than 10 nm. Most of the reduction of the jet transversal size seems to occur during a few instability stages, setting along the trajectory of the jet which is rectilinear only in the first part. The interplay of jet instabilities, solvent evaporation, and possibly phase-separation phenomena driving the assembly of macromolecules lead to a complex scenario and to the realization of...
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Continuous nanofibers which may have very different porosities and morphologies. As studied by Rutledge and coworkers, comparing the drying time \(t_d\), the so-called buckling time \(t_b\), and the characteristic phase separation time \(t_{ps}\) allows one to predict the resulting features of collected nanofibers. \(t_d\) and \(t_b\) are defined as:

\[
t_d = \frac{v_0}{A W_{cv}},
\]

\[
t_b = \frac{D(\phi_p - \phi_{p0})^2}{W_{BV}},
\]

where \(v_0\) is the initial liquid volume, \(A\) is the initial vapor-drop surface area, \(W_{cv}\) is the initial evaporation rate, \(D\) is the polymer–solvent mutual diffusion coefficient, and \(\phi_p\) and \(\phi_{p0}\) are the polymer fractions at the external skin which forms during the jet flight and at the fluid core, respectively. For instance, solid or porous fibers are obtained depending on whether the ratio, \(t_{ps}/t_d\), is greater than or less than 1, respectively. The buckling time affects instead the surface morphology. Indeed, solid fibers can be buckled (if \(t_{ps}/t_b > 1\)) or smooth (\(t_{ps}/t_b < 1\)). Analogously, porous fibers can be buckled (\(t_{ps}/t_b > 1\)) or smooth (\(t_{ps}/t_b < 1\)).

Overall, the complexity of the process is increased by the high number of experimental parameters, which include, beside the applied bias, the polymer solution concentration and the spinneret–collector distance (usually from several cm to a few tens of cm), a large set of other properties of the used solutions (polymer molecular weight, solution density, conductivity, viscosity, characteristic relaxation time and dielectric constant), of the specific used set-up such as the solution flow rate generally applied in the syringe by means of external pumps, and the environment in which fibers are realized, such as temperature, relative humidity, etc. Operationally, the process is instead simple and cheap, and easily scalable to the pre-industrial level, which explains in part its extraordinary success. What is more relevant in the present framework, however, is that electrospinning has been widely engineered in the last decade, in order to become, on one side, more and more compatible with conjugated and other functional polymers, which rarely show favorable viscoelastic properties and consequently are often difficult to electrospin directly, and, on the other side, integrated with other fabrication technologies and with a larger and larger variety of usable substrates, pre-patterned lithographic features, devices, and applications. For instance, varying the geometry of the collecting surfaces or their distance and movement relative to the spinneret is a direct way to control the position and assembly of nanostructures and enhance their integration in devices, or to achieve multifunctional polymer nanofibers. This is the case of near-field electrospinning invented at the Universities of California at Berkeley and of Xiamen. In this method the spinneret-collector distance is kept well below 1 cm, jet instabilities are avoided or greatly reduced, and motorized scanning tips or collectors are used to directly draw polymer nanofibers. Other advantages include the possibility to reach very high values of the electric fields (10^7 V m^-1), to use moderate bias (below 1 kV), and to enhance the stretching of polymer molecules and their orientation within the formed fibers. Near-field electrospinning has been applied to thermoplastic polymers such as polyethylene oxide, to conductive polymers such as polyaniline, and to piezoelectric polymers such as poly(vinylidene fluoride) (PVDF).

Though generally ineffective to pattern large areas due to its serial character, this approach allows electrospinning to be used as an additive patterning technique of individual nanostructures, with extremely high positioning precision and sub-100 nm feature resolution, and with no need for masking or high-energy exposures. Different mechanisms such as pyro-electrodynamic shooting have also been demonstrated to be very effective for depositing individual nanodroplets, based on pyroelectric forces. Once deposited, individual polymer nanostructures can in turn enable other lithographic approaches, used as templates for shaping elastomeric elements for soft lithographies, as masking features for etching and lift off processes, or as functional elements per se, including light-emitting or piezoelectric filaments or droplets. Finally, the nanopottery approach is another example of how electrospinning can be developed, focusing the electrified jet on sharp electrode tips and forming free-standing, hollow coiled microstructures.

3 Bottom-up and top-down integration

The combination of soft lithographies based on molecular self-assembly with top-down nanofabrication methods has been proposed since the invention of µCP. µCP is an additive technique, which is an intrinsic merit since this allows the waste of material to be minimized. However microcontact-printed self-assembled layers can also be used as resists with nanoscale thickness in order to remove unprotected regions of the underlying substrate by means of selective chemical etching. This approach is nowadays well-established, and it has been used to realize many different devices both by inorganic and by organic functional materials. Furthermore, PDMS stamps can be accommodated by conformal contact on cylinders rolling over the target substrate, thus allowing the overall µCP throughput to be greatly improved. This concept of somehow making µCP dynamic also leads to using stamps moving or jumping during the process of fabricating polymer-brush microstructures. Some recent studies developed further the integration between soft lithographies and complementary patterning technologies, trying to go beyond the so-called “one template-one pattern” paradigm, which has been at the base of conventional methods based on replica molding. In fact, in standard soft lithography each particular pattern requires the dedicated design and fabrication of a specific master structure. This could be a bottleneck especially when working at relatively high resolutions, or when photolithography or EBL facilities are not promptly available. A possibility to tackle this issue is opened by PDMS-coated dip pen nanolithography stamp tips. The resulting approach is serial and has several advantages. It is a highly accurate and controlled variant of µCP in which molecular inks are delivered on surfaces by scanning probes, with sub-100 nm resolution and patterning speed up to the
order of 1 \( \mu m \) s\(^{-1}\). Another recently proposed method uses elastomeric polymeric microspheres, which can be fabricated with low cost and high throughput by means of microfluidic chips working with a continuous phase of water and surfactant and a dispersed phase of liquid PDMS. Each microsphere, once microsphere developed in the microfluidic device, is polymerized thermally, inked by molecular solutions, and then used for the continuous delivery of the ink to a substrate similar to a ball-point pen. In this way no master structure is needed (except for those allowing the original microfluidic devices to be fabricated), each kind of pattern can be transferred onto the target substrate with real-time control and speeds of many tens of \( \mu m \) s\(^{-1}\), and the transversal size of each feature can be varied to some extent through the mechanical compression of the rolling microparticle.

A different strategy involves the development of a photo-lithographic approach instead of replica molding to pattern PDMS elastomers. In principle these methods allow one to avoid realizing dedicated master structures, thus making the overall lithographic procedures easier, cheaper and more flexible. This can be done, for instance, by employing benzenophene as an additive to initiate the photo-polymerization of PDMS, or by exposing the already cured elastomer to UV-lithography and then transferring the features into PDMS by chemical development with a 1 : 1 (v/v) mixture of 1 M aqueous sodium hydroxide and ethanol. To define the optical pattern both conventional optical masks and organic features realized, for instance, by microfluidics, can be exploited, and the resulting, photolithographically patterned PDMS can in turn be then used for second-generation pattern transfer in various soft lithographies including replica molding and NIL-like soft embossing, thus demonstrating an intimate integration of optical and mechanical lithographies.

In addition, NIL can be combined with a variety of inherently bottom-up processes working at the nm- or sub-nm scale, particularly molecular imprinting (MIP) which can be exploited to generate specific sites for molecular recognition in polymeric patterns. In this approach, binding sites are obtained in cross-linked polymers by a molecular template such as \( (S) \)-propanol, \( (R) \)-propanol. Clearly, superimposing patterns (say, at the microscale or at higher resolution) to the molecular recognition sites working at the scale of \( \AA \), thus producing patterned films of molecularly imprinted polymers, would open interesting perspectives to realize surfaces with enhanced and specific binding properties. Applications may be in the fields of chemical separation and sensing. Reactive NIL is especially useful in this respect, since it allows patterns of such molecularly imprinted polymers to be obtained through UV or thermal polymerization with 100 nm spatial resolution (Fig. 2), which is much higher compared to previously explored methods. Together with such high spatial resolution, the advantages of the MIP-NIL combination over other approaches to prepare functional polymer patterns include the process cheapness and high throughput, as well as the high retained molecular selectivity. In this framework, innovative approaches involving soft lithographies have also been proposed. For instance, poly(methylmethacrylate) (PMMA) scaffolds realized from PDMS patterned molds have been imprinted with gelatin or even with whole cells in order to enhance subsequent cellular adhesion.

Similar combinations can be figured out which involve conjugated and multifunctional polymers as well, together with imprinted biomolecules.

BCP assembly is very well suited to be combined with etching of the underlying substrate material once one of the chemically anisotropic components has been selectively removed. This allows other functional organic materials to be processed, as well as inorganic semiconductors, metals etc. The so-called Airgap technology developed by IBM has been an important milestone for the integration of bottom-up and top-down methods, combining standard complementary metal–oxide–semiconductor fabrication with nanopatterning based on self-organization in polymeric layers, at the industrial scale. Here the metal wires of an electronic chip are mutually isolated by means of gaps, realized by using a nanoporous self-assembled polymer film. This promises a significant increase of the chip speed or equivalently a reduction of energy consumption. From the point of view of lithographic manufacturing, this approach capitalizes on the merits of polymer self-assembly, such as the operational simplicity, the low cost, and the possibility to pattern large areas with highly dense features. Three-dimensional nanostructures can also be produced by BCP thin films, starting from the cross-linking of cylinder-forming polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) with embedded reactive -N\(_3\) groups. This process passes through a complex assembly phenomenon, in which lamellar-forming BCPs on top of an underlying layer of cylinder-forming material leads to microdomains oriented normally with respect to the film surface, and through the removal of the PMMA component (Fig. 3a–d). These nanostructures are also able to enhance the photon extraction efficiency of devices typically produced by conventional growth and fabrication approaches, such as light-emitting diodes.

Among other methods for so-called templated or directed self-assembly of BCPs, soft-graftcopolymerization uses BCPs and optical lithography together, being very promising in terms of low cost and ultralarge area patterning. The idea here is to fully exploit
the lateral confinement provided by pre-fabricated photolithographic micropatterns, to direct and orient the lamellar nanostructures made of different materials. Due to the integration of photolithography and BCP assembly, this method is especially versatile in terms of the possibly produced structures, and can be scaled up easily to pattern arbitrary areas with features having resolutions of few tens of nm. A similar strategy has been developed with 193 nm water immersion lithography which allows photosensitive features of 100 nm or even smaller to be easily obtained, to be then used as templates for guiding the BCP assembly. Other materials for generating effective sidewalls include metals and random copolymer brush layers as shown in Fig. 4a–d. Short chain PDMS brushes have been used as well onto posts made of hydrogen silsesquioxane resist with EBL, which allows the self-assembly of PS-\(b\)-PDMS to be controlled in two dimensional periodic patterns. In general, imposing lateral ordering and spatial confinement in BCPs can be easier than producing chemical pre-patterns with the aim of templating self-assembly and providing it with long-range periodicity, and notwithstanding its simplicity this approach can lead to an astonishing variety of possible functional structures. The general merits of this class of methods include the remarkable thermal and mechanical stabilities of the template structures, and the possibility of using commercially available compounds for realizing the templates. Molds for NIL or soft lithography, with various shapes and geometries, can also be a valuable option for producing BCP-templating topographies. The stability of the pre-fabricated pattern against solvent and against temperature variations is of course especially important to properly guide the self-assembly of the copolymers. In this respect, BCP self-organization can be even observed in more exotic systems, for instance within the confined region of an...
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electrospun jet and of core–shell nanofibers, resulting in the formation of internal patterns with well-defined phase-separated domains (Fig. 4e and f). More in general, the evaporative assembly of properly confined organic solutions can be exploited in a variety of hybrid lithographic methods which merge the top-down control of capillarity and evaporation geometries and phenomena at solid–liquid and liquid–vapor interfaces with the self-assembly properties of the deposited, non-volatile solutes. The latter include many conjugated and active polymers, on which this results in the easy and low-cost achievement of solid patterns with sub-micron feature resolution by so-called evaporative lithographies.

However, also chemical or other hybrid strategies can lead to an intimate integration of different lithographic methods. An excellent example is schematized in Fig. 5a, which shows how to realize lithographically defined, chemically patterned polymer brushes and mats or even features made of nanoparticles immobilized on the brushes. In this method, first photolithography is performed on a photosist deposited onto a cross-linked PS mat, and then etching is carried out by oxygen plasma (so-called breakthrough etch) and eventually by an additional step with a highly controllable lateral etch rate (so-called trim etch), to finely determining the feature size in polymers. This is the top-down part of the overall fabrication sequence. Afterwards, the remaining regions of the cross-linked PS mat with dimensions down to 10 nm leave exposed areas of the substrate underneath, which allow endgrafted polymer brushes [hydroxyl-terminated poly(2-vinylpyridine) or PS-PMMA random copolymer] to be grafted from spin-coated films, without affecting the polymer mat chemistry. Finally, the resulting chemical pattern can be employed to direct site-specific immobilization of metal nanoparticles or overlying PS-b-PMMA self-assembly, completing the ultimate, bottom-up part of the method. The main merit of this method is the very high precision in the definition of the chemical patterns at the 10 nm scale. Another recently proposed hybrid method exploits instead a smart combination of serial solvent annealing and EBL to induce the formation of coexisting sub-10 nm spherical and cylindrical domains in a PS-b-PDMS film, as schematized in Fig. 5b. Here, the exposure of a pre-deposited copolymer layer to either acetone or dimethylformamide (DMF) vapors leads to the formation of either cylindrical or spherical micro-domains, due to the differences in the swelling contrast of PS and PDMS in the two solvents. Interestingly, this assembly behavior is reversible, therefore successive exposures to different solvents lead to repeatedly switching morphologies. Then EBL is used to cross-link and stabilize the ultimately obtained morphology by spatially selective irradiation. Finally, a second exposure to solvent vapors can produce complementary patterns in the non-crosslinked regions as illustrated in Fig. 5b.

The transfer printing concept, schematized in Fig. 6, is inherently hybrid as well, and directly descends from original
μCP methods. This approach can be implemented in an either additive (as in μCP, Fig. 6a) or subtractive (Fig. 6b) way; it is extremely flexible in terms of usable materials and compounds (including organic semiconductors), and has many different variants each addressing the needs of specific device platforms.

It is especially useful for device fabrication in flexible electronics and optoelectronics, and for realizing lithographically defined features of sensors or chips implantable in the body. In all cases, the contact of a stamp with a substrate leads to the delivery of a material from a source surface to a target surface. In additive printing, the source is the elastic surface, and the ink material is delivered onto the substrate following contact. The roles of the stamp and the substrate are of course inverted in subtractive methods. It is clear that interfacial energies play a pivotal role in determining the release of the ink material from one surface to another. Deterministic assembly processes are also possible (Fig. 6c), in which the elastic mold is placed in contact first with a pre-patterned substrate from which it selectively retrieves some ink features, and then with a target substrate onto which the nanostructures or microstructures are finally delivered. This last variant combines subtractive and additive operations and has the merit of greatly reducing the overall amount of used material during transferring.

A very beautiful, recent example of lithographic integration merging together transfer printing and BCP lithography is based on using PDMS molds for directing the self-assembly of copolymers (Fig. 7a).

![Fig. 5](image)

(a) Schemes showing the formation of a chemical pattern, followed by nanoparticle immobilization or directed assembly. A film of cross-linked PS is patterned and etched, and a hydroxyl-terminated random copolymer of styrene and methacrylate is grafted onto the exposed spaces of the substrate. Nanoparticle immobilization and BCP directed assembly are also enabled in this way. Adapted with permission from ref. 66, Macromolecules, 2011, 44, 1876, DOI: 10.1021/ma102856t. Copyright © 2011, American Chemical Society. (b) Schematics of the formation of dual morphologies in PS-b-PDMS thin films through solvent annealing, electron-beam irradiation, and a subsequent solvent annealing. Cylindrical and spherical morphologies are formed by exposing the film to vapors of acetone and DMF, respectively. Adapted with permission from ref. 67, Nano Lett., 2011, 11, 5079, DOI: 10.1021/nl203445h. Copyright © 2011, American Chemical Society.

![Fig. 6](image)

Fig. 6. Schemes showing different transfer printing modalities: additive (a), subtractive (b), and deterministic assembly (c). Reproduced with permission from ref. 68, Adv. Mater., 2012, 24, 5284, DOI: 10.1002/adma.201201386. Copyright © 2012, WILEY-VCH Verlag GmbH & Co. KGaA.
components as in standard BCP lithography leads to very high-resolution topographic features (sub-10 nm).

A different strategy is based on the photoplasticization of azo-compounds, occurring by repeated photoisomerization of azobenzene molecules, which can be used for patterning purposes as in directional photofluidization lithography. This approach is directly built on the multifunctional properties of exposed organics, which have to show photomechanical effects leading to molecular alignment and mass transport and diffusion, following irradiation under given wavelength and polarization conditions. A nice example of the achievable pattern is provided by the complex evolution of the surface topography of azo-compounds, occurring by repeated photoisomerization, following irradiation under given wavelength and polarization conditions. An important feature of this approach for controlling surface features is of being basically additive, not requiring chemical development or etching to remove undesired polymer regions. In particular, the initial features can be obtained by many assembly methods including soft lithographies and especially MIMIC, which is additive, as shown in Fig. 8. Hence, the overall process minimizes the waste of functional material, and is flexible and cheap.

Indeed, as pointed out by Whitesides, microfluidic technologies used for lithographic purposes are inherently additive and greatly reduce material waste. The achieved resolution is related to the used, elastomeric channels which in turn depends on the previously fabricated master structures. In this respect, new possibilities have been opened to enhance resolution and fabricate functional polymer particles by integrating exposure-based curing methods with microfluidics. This is at the base of the continuous flow lithography (CFL) proposed by the Doyle group. In this technique, projection photolithography is carried out on negative resists which flow in microfluidic channels. This leads to the rapid photo-polymerization of solid particles having controlled shapes, which can be finally separated from the liquid resist, collected and used as self-standing functional micro-objects. Chemical anisotropy and multifunctionality can also be obtained in individual particles, performing photo-polymerization across sharp, heterosolution interfaces present in microchannels due to laminar flow (Fig. 9a–c). Recently, this approach has been combined with two-photon polymerization, which allows microfabricated polymer helices and other three-dimensional, complex active particles to be realized (Fig. 9d).

A different method to obtain three-dimensional, hierarchically ordered microparticles is based on the combination of holographic lithography (HL) on a photosensitive resist and surfactant templating as schematized in Fig. 8. Here, the polymer is exposed in 0.15 s with a controlled distribution of an electromagnetic field, given by constructive and destructive interference of multiple coherent beams. Such an optical pattern is in turn generated by means of an array of light-refracting microprisms produced in PDMS by replica molding from a master with an inverted pyramid-shaped groove array. Then, the patterned polymer serves as a template for infiltrating a silica precursor with a lyotropic surfactant phase such as tetraethylorthosilicate and a triblock copolymer. The final calcination and polymer removal lead to free-floating particles exhibiting a mesoporous structure which is the inverse replica of the original holographic pattern. The main advantage of this approach is the simple generation of the hierarchical structures with high degree of control.
The integration of electrospinning with exposure-based lithographies such as optical lithography, two-photon, or EBL, allows researchers to develop interesting hybrid technologies and to even obtain new organic–inorganic nanomaterials. Many different dopants can be mixed in electrospin solutions in order to obtain nanofibers made of blends or composites. Possible dopants include low-molar mass molecules such as biological compounds, fluorescent compounds, laser dyes, dispersed carbon nanotubes, graphenes, or semiconductor, metallic or oxide nanocrystals. When nanoparticles are used, however, their aggregation in solution, the possible clogging of the electrospinning die, and the eventual non-uniform distribution of the nanocrystals in the ultimately resulting nanofibers can constitute major problems preventing to fabricate reliable nanocomposite materials. Analogous issues, basically related to the unfavourable rheological properties of fluids with a significant solid component provided by nanoparticles, are often encountered in embossing methods and other lithographic approaches based on material flow. A largely applied strategy to overcome unfavourable flow conditions consists of in situ synthesis of nanoparticles inside solid samples. In this way, solid nanoparticles are obtained in the matrix of polymer nanofibers after electrospinning, or in polymeric patterns after molding processes, and this allows researchers to perform the lithographic fabrication steps under low-viscosity conditions, which helps to increase resolution and disfavors the formation of defects. This approach passes through the synthesis of suitable molecular precursors, which can be added to solutions or prepolymer without altering remarkably the pristine rheology, and which allows nanoparticles to be obtained following decomposition processes. A class of composite nanofibers realized in this way is made by PMMA and embedded CdS nanocrystals synthesized by in situ thermal treatments or EBL on cadmium thiolate precursors. Other examples include in situ approaches based on exposing electrospun fibers to a suitable gas or solution, thus inducing the formation of nanoparticles. In this way, for example, nanofibers spun from polymer/lead acetate ethanol/water solutions and then exposed to H$_2$S result in nanocomposites with PbS nanoparticles. Making the exposures spatially selective by suitable masking or templating elements would lead to the integration of bottom-up and in situ nanocrystal growth with top-down patterning control.

4 New directions in hybrid device fabrication

The intrinsic difficulty of bottom-up routes is the lack of order or patterning effectiveness at sufficiently long ranges, which generally makes these techniques hardly applicable to the production of real devices. This has motivated the development of various templating and imprinting approaches to drive and enhance self-assembly phenomena as described above. Another generally followed route, allowing realization of microelectronic devices based on conjugated materials, consists of coupling top-down deposited metal electrodes with active organic materials, which may include single crystals organized in two-dimensional arrays due to pre-patterned, microcontact-printed domains of octadecyltrihexysilane, light-emitting or conductive polymer nanofibers generated by electrospinning or by solvent-resistant soft lithography, and vacuum-sublimated molecular layers. In all these processes, bottom-up self-assembly of conjugated molecules is either exploited directly or it can be induced or even templated by proper soft lithographic steps carried out during device fabrication. Similar architectures of electrodes contacting individual or even dense arrays of electrospin piezoelectric nanofibers made of PVDF or of its
thermally stable copolymer, poly(vinylidene fluoride–trifluoroethylene), allow multifunctional devices to be obtained. These can be used as nanogenerators for mechanical energy harvesting, as accelerometers or as ultra-sensitive strain or pressure/force sensors.

NIL can be applied to make easier the fabrication of polymer thin-film transistors as shown in Fig. 11a–f. Here, the first part of the process consists of depositing a buffer resist (poly-methylglutarimide) and a top PS layer, imprinting by a three-dimensional silicon mold, and carrying out sequential dry and wet etching steps to transfer part of the pattern to the other layers underneath. This leaves exposed metal regions, which will serve as source and drain electrodes, and lateral features of inert polymers, which will serve as banks for the subsequent ink-jetting of semiconductor materials. The second part of the process relies on surface treatments allowing a wettability contrast to be obtained, and finally ink-jet printing of a conjugated polymer. The spin-coating of a dielectric layer and printing of the gate electrode complete the transistor fabrication that critically benefits from the self-alignment of different features as provided by the initial three-dimensional mold (which has to exhibit significantly protruding edges or features and allows one to avoid overlay registration steps in multilayer device production), and by a close integration of NIL, use of surface modifiers, and ink-jet printing of active polymers. Other devices based on active polymers are based on multilayer patterning through different and combined methods. A recently proposed demonstrator is a polymer distributed feedback laser whose emission can be tuned by means of applied electric fields and embedded layers made of non-linear optical (NLO) chromophores (Fig. 11g–i). These devices are produced by multilayer patterning steps including room-temperature NIL and photolithography.

Device applications of BCP lithographic methods are intriguing as well and include metal–oxide–semiconductor capacitors exhibiting capacity significantly increased (30%) compared to planar reference structures, field effect transistors based on multiple nanowires, memories, and so on. Furthermore, free-standing masks for etching and porous membranes can be realized by spin-coating PS-b-PDMS forming cylinders whose longitudinal axis is oriented perpendicularly to the film surface, detaching such a film from the underlying substrate by HF, and carrying out domain-selective treatments which include the oxidation of the PDMS blocks and the removal of the PS component by oxygen plasma. Other important applications are given by organic solar cells, where BCPs can be utilized as active materials given that suitable semiconductor or conjugated components are incorporated in the copolymers, and by hybrid organic–inorganic photovoltaic devices where BCP lithography can be a powerful tool to realize ordered patterns and improved bulk heterojunctions. Similar considerations hold for organic light-emitting devices.

Fig. 11  (a–f) Scheme of the realization of a polymer field-effect transistor by self-aligned, one-step, multilayered patterning. Adapted with permission from ref. 85, Adv. Mater., 2011, 23, 4107, DOI: 10.1002/adma.201101291. Copyright © 2011, WILEY-VCH Verlag GmbH & Co. KGaA. (g–i) Different cross-sectional view and scheme of an electrically tunable, organic distributed feedback laser device produced by multilayer patterning through photolithography and room temperature NIL. The scale bars are 500 nm (g) and 3 μm (h), respectively. Adapted with permission from ref. 88, Adv. Mater., 2012, 24, OP221, DOI: 10.1002/adma.201201453. Copyright © 2012, WILEY-VCH Verlag GmbH & Co. KGaA.
In device fabrication, an often critical parameter is the roughness of all the surfaces involved (metal, polymer, semiconductor, etc.). Too high roughness values can determine undesired lithographic pattern transfer, disconnected metal pads, bad organic–inorganic contacts, light-scattering and increased optical losses in microfabricated waveguides, and so on. In this respect, lithographic methods based on directed self-assembly of BCPs have been recently demonstrated to enable a tight control of the ultimate surface roughness. This approach works by means of positively charged polymersomes made of poly(2-(N,N-dimethylamino)ethyl methacrylate)-b-poly(tert-butyl methacrylate) (PDMAEMA-block-PtBMA) through reversible addition–fragmentation chain-transfer polymerization (Fig. 12a), solution self-assembly (Fig. 12b) and finally directed self-assembly on a target surface (Fig. 12c,d). While the initial assembly of the polymersomes on surfaces can even lead to an increase of the surface roughness at the nanoscale, calibrated annealing steps allow one to achieve a significantly reduced roughness, with root mean square values down to the scale of 0.1 nm.

A different procedure sharing some of these ideas is at the base of so-called self-perfection by liquefaction (SPEL, Fig. 12c). Here, polymer features undergo melting for a very short time interval (hundreds of ns), and the resulting decrease of viscosity (basically analogous to that of NIL in terms of the underlying glass-transition physics) is exploited to reassemble the nanostructures and to obtain a significantly reduced line-edge roughness (down to the scale of 1 nm). The process can be performed with one or more plates placed in contact or with a gap above the polymer feature, thus guiding the reassembly step as schematized in Fig. 12f.

Finally, various methods have been proposed to enhance the patterning capacity on or by functional polymer nanofibers, which may be of great utility for realizing a wide range of photonic and electronic devices. Interestingly, different approaches exploit different physical properties of the nanofibers, which may open further ways for lithographic integration in the near future. For instance, flash welding is an interesting processing method, in which conductive polymer nanofibers made of polyaniline and with quite low (bulk-like) thermal conductivity and simultaneously efficient photothermal conversion are rapidly exposed to flash light (with ms exposure times) and form welded regions and ultimately continuous films. Irradiating through optical masks or grids can thus lead to nanofiber-mediated polymer patterning with obvious potential device applications. A completely different method is based on performing room temperature-NIL on conjugated polymer, light-emitting electrospun nanofibers (Fig. 13). Demonstrated resolutions are of the order of 100 nm. Devices potentially realizable in this way include plasmonic resonators, organic nanofiber light-emitting devices with enhanced photon extraction efficiency or highly controlled emission directionality, polymer nanofiber distributed feedback lasers and photonic crystals. In addition, nanopatterning leads to tailoring the polarization of light emitted from the nanofibers. A reduction or an enhancement of the polarization ratio of emitted light is found upon imprinting wavelength-scale periodic gratings with features perpendicular or parallel to the fiber length, respectively.

5 Conclusions

In this feature article, we have limited our description to the main techniques which allow the hybrid character of the overall lithographic processes to be clearly appreciated. Many other processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly processes, however, are possible and would deserve to be mentioned in the broader framework of multifunctional polymer nanostructures, including, for instance, self-assembly
technologies to fabricate active polymer nanofibers and nanowires such as those using polycarbonate or alumina porous membranes and soft templates.

In general, a significant number of studies have already yielded an interesting degree of integration between complementary lithographic strategies on or through multifunctional polymers. It is clear, however, that a lot of challenges still remain open in order to lead the resulting devices to a more advanced development stage and then to the market. In particular, the embedment of patterned active polymers, or low-dimensional, functional organic structures with device architectures of actual practical use will need much more effort to improve the reliability and reproducibility of the obtained systems and interfaces, and better established lithographic interfaces to couple bottom-up organized macromolecules at the nanoscale with top-down defined systems of electrodes, flexible microscale components, addressable matrices and large optical circuits to be handled macroscopically. Materials increasing the reproducibility and accuracy of soft lithographies, such as elastomers with improved mechanical stability, can be an important strategy to further improve the reliability of lithographic results on active and multi-functional polymers. The increasing availability of specifically designed equipment and lithographic tools, enabling multi-level soft lithographies and NIL, will improve throughput and make easier the realization of multi-layer devices based on functional organics. Electrospinning is still performed on a largely empirical basis for many active compounds. For this and other processes, a more in-depth comparison of results from extensive experimental campaigns and findings from modelling and simulations will allow researchers to improve their knowledge of the many operational variables, and finally the overall nanofabrication reliability. Once optimized, electrospinning could be fruitfully combined with a complementary lithographic platform, including BCP-based and transfer printing methods, to control the position of individual nanofibers on devices, and to assemble complex photonic circuits. Indeed, applications may be the driving force for bringing hybrid patterning approaches on functional polymers closer to volume device manufacturing and to commercialization, particularly in the fields of flexible electronics, optoelectronics, and nanophotonics. The outlook for the related classes of devices is certainly good in the medium term, given the fact that active polymers can bring a significant added value to many of these applications. To be accomplished, these exciting objectives will certainly require the strengthening of a truly transversal way of thinking in terms of soft matter processing, as may be guaranteed only by genuinely cross-disciplinary teams of researchers, materials scientists and engineers.

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Notes and references
