CLASSIFICATION OF KEY ATTRIBUTES OF SOFT MATERIAL GRADIENTS

JAN GENZER
Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, USA

RAJENDRA R. BHAT
Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, USA; Becton Dickinson Technologies, Durham, North Carolina, USA

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2.1 INTRODUCTION

The Merriam–Webster dictionary identifies a gradient as (i) the rate of regular or graded ascent or descent; (ii) change in the value of a quantity (i.e., temperature, pressure, or concentration) with change in a given variable and especially per unit distance in a specified direction; (iii) a graded difference in physiological activity along an axis (as of the body or an embryonic field); and (iv) change in response with distance from the stimulus. While all these definitions fit the general description of gradients, we have to be more descriptive in order to introduce the general topic of this book. Specifically, by “soft matter gradient surfaces” we understand assemblies made of soft condensed matter, that is, liquids (including small molecules, molecular clusters, macromolecules), liquid crystals, colloids, gels, or foams, at interfaces and surfaces, where at least one of the attributes of such an assembly varies gradually as a function of the position on the substrate and/or in time between two extremes. The discussion that follows has been purposely broadened beyond the above definition; it also includes selected examples of structures that, although are not made of soft materials, facilitate the transport and partitioning of soft materials on surfaces. While the most obvious parameter to vary in a gradual manner is the concentration of species in question, we demonstrate below that other physicochemical characteristics of the material can also be altered gradually across the substrate. We discuss that one of the chief attributes of the gradient methods developed over the past four decades is that they can be combined to form complex gradient assemblies and geometries exhibiting gradual variation of two (or more) properties of the newly generated surface in two (or more) independent directions.

In our recent review, we discussed that soft matter gradient substrates can be fabricated by employing one of the two general class methods: (i) direct deposition and (ii) post-deposition modification. In the former category of techniques, gradients are built on a parent (typically flat) substrate by gradually putting down the gradient-building blocks (monomers, oligomers, polymers, etc.) via either naturally occurring processes (i.e., diffusion, propagating front, etc.) or man-made techniques (i.e., controlled sample dipping into a solution, position-dependent evaporation, or external field assisted deposition methods). In the post-deposition modification methodologies, a parent material, typically a flat substrate bearing a natural or predefined surface containing a functional “pre-coat,” is progressively modified either chemically or physically. All methods result in surface gradient assemblies comprising either a chemical (in most cases) or/and a physical (in selected cases) variation.

In order to facilitate the discussion, we classify gradient structures based on a few key attributes (Fig. 2.1). We note that any gradient substrate can belong to more than one category depending on its attributes. For instance, let us consider a case involving a gradient comprising assemblies of nanoparticles arranged in a gradual manner on a support. If deposited onto a flat substrate comprising a
gradient of adhesion precursors (i.e., chemical gradient), the particles, having an affinity for the precursor species, form two-dimensional (2D) gradient arrays. In contrast, when attached to substrates covered with a polymer layer having a continuously varying molecular weight (i.e., length), density, or chemical composition (i.e., chemical and physical gradients), the particles arrange into a 3D assembly. The directionality and dimensionality of the substrate gradient precursor set the direction and length scale of the particle arrays. To that end, the particle gradients can evolve in one or more directions and can be either continuous or discontinuous. The spatiotemporal gradient of the substrate causes a variation of at least one physicochemical property of the substrate. In the case of nanoparticle gradient, those can be light absorption, scattering, affinity toward some molecular moieties, conductivity, and many others.

Material gradients, both continuous and discrete, have facilitated major breakthroughs in combinatorial chemistry and materials science, including the design and discovery of catalysts and drugs, thereby enabling rapid technological developments with improved efficiency and lower research and production cost.\(^2,^3\) Gradient structures have also inspired the development of new analytical approaches and measurement tools\(^4^{–8}\) and have been proposed as structures that resist mechanical deformation and damage.\(^9\) Because several recent reviews have discussed the progress in generating and utilizing material gradient surfaces in detail,\(^1,^{10–27}\) we restrict ourselves to only outlining selected principal attributes of soft material gradient surfaces and pointing out limited case studies. We use the concept illustrated in Fig. 2.1 as a guiding template for such a discussion. The other chapters in this book provide additional details pertaining to many practical applications of such gradient structures.
2.2 GRADIENT ATTRIBUTES

Gradients can be classified into many categories depending on their physico-chemical nature. In most instances, the resultant structures exhibit typically more than just a single attribute identified, as in Fig. 2.1. Since a detailed discussion of the gradient attributes has been presented earlier,¹ we restrict ourselves to just a succinct summary.

2.2.1 Gradient Type

Substrates can be made, which possess gradual variation of any physicochemical property. Here we concentrate on chemical, physical, and mechanical gradients because they are among the most widely studied and used structures. Figures 2.2–2.4 show a pictorial representation of selected methods that lead to the formation of such gradient patterns on substrates.

Chemical gradients have been formed by various techniques involving the direct deposition (see Fig. 2.2 and Fig. 2.3) and post-deposition modification methodologies (see Fig. 2.4). Various methods have been developed that utilize directed deposition of atomic (i.e., metals) or molecular clusters (i.e., small synthetic precursors, peptides, nanoparticles) to fabricate 2D material gradients (Fig. 2.2). In addition to depositing metals or small organic moieties, techniques have been introduced that enable the formation of 3D gradient layers (Fig. 2.3) by either (i) laying down larger organic clusters (i.e., proteins) or nanoparticles or (ii) preparing polymer layers. While the former class of methods leads to the formation of “quasi 3D” soft material structures with a gradual density variation across the substrate, thicker 3D gradients have almost exclusively been formed by coating flat substrates with a relatively thick (a few nanometers to micrometers) polymer layer. In some instances, gradient structures have also been prepared by using external fields or pH modulation during material deposition on the surface. We discuss the formation of 3D gradients in more detail in Section 2.2.2.

Earlier, we mentioned that gradient structures can also be formed by post-deposition modification methods (see Fig. 2.4) that encompass exposing homogeneous substrates to a gradual dose of either a chemical or a physical modifier. Other post-deposition modification techniques of preparing surface-bound chemical gradients involve preparing self-assembled monolayer (SAM) films and either (i) altering the chemical functional groups in the original molecules (typically photooxidation of end groups) to another group by an external beam or (ii) selectively removing certain sites on the substrate and filling the empty sites with another molecule.

Physical gradients possess a gradual variation of some physical property; the two most widely explored types of physical gradients involve structures that exhibit a gradual variation of substrate rigidity (i.e., Young’s modulus), roughness, or porosity. Biologists have long been interested in preparing and utilizing supports with gradients in modulus because it impacts cell motility (so-called durotaxis). Ingenious approaches leading to fabrication of such
FIGURE 2.2 Selected methods of creating 2D or quasi 2D gradients by deposition: (a) metal deposition via shadowing; (b) vapor deposition of organosilanes; (c) depositing self-assembled monolayer (SAM) on top of a mechanically pre-deformed substrate, so-called mechanically-assembled monolayer (MAM); (d) diffusion of alkanethiols in polysaccharide matrix; (e) liquid diffusion of organosilanes; (f) immersion technique applied to SAMs; (g) deposition of organosilanes by means of silicone elastomer stamps with different curvatures; (h) printing alkanethiols from stamps of variable thickness; (i) forming a concentration gradient of two charged molecules in a solution and imprinting them onto a stamp, which could then transfer the gradient pattern onto a substrate; (j) deposition of SAMs by means of reaction gradients in bipolar electrodes; (k) SAM gradients formed by microfluidic lithography (μFL); and (l) embossing topographical patterns in soft waxes.
FIGURE 2.3  Selected methods of creating 3D gradients by deposition: (a) gradients of proteins by means of heterobifunctional photolinkers; (b) knife-edge coating technology; (c) grafting onto method in conjunction with temperature gradient heating of the substrate; (d) immobilization of PEG by diffusion and grafting; (e) position-dependent UV dose to monomers in contact with activated surfaces; (f) gradual immersion of substrates into polymerization media; (g) solution draining method for preparing polymer brushes; (h) forming a molecular gradient of an initiator on a substrate followed by grafting from polymerization; (i) opposite grafting density counter-gradients of two polymers formed by sequential grafting from two different set of initiators; (j) preparing random copolymer brushes by steadily adding a new monomer (M2) into the polymerization mixture containing another monomer (M1); (k) preparing statistical copolymers by microfluidic mixing of two monomers followed by chamber filling method; and (l) solution and surface gradient using microfluidics.
FIGURE 2.4 Selected methods of creating gradients by post-deposition modification: (a) hydrolysis of poly(vinylene carbonate)
[98]; (b) radio frequency (RF) plasma discharge[99,100]; (c) corona discharge[101]; (d) UV/ozone modification of hydrophilic SAMs across prisms with variable UV transparency[102]; (e) UV coupled to an optical cable[103]; (f) beam of electrons[104–106]; (g) replacement lithography of alkanethiols[107]; (h) combination of corona treatment of the surface and surface-initiated polymerization[20,101,108–110]; (i) combination of electron beam bombardment of the surface and surface-initiated polymerization[104–106,111]; (j) position-dependent annealing of porous polyethylene sheets[112]; (k) position-dependent annealing of nanosphere sheets[113]; (l) chemical polishing of rough metal plates by immersing the sample vertically into a solution of an etchant[114].
unique structures have been developed by Wang et al.,123,124 Wong et al.,125–127 and others.128,129 The utilization of such structures in biological applications is discussed later in Section 2.3 of this chapter. Techniques facilitating the fabrication of surfaces with position-dependent variation of topography/roughness have also been developed that employed (i) selective removal of one chemical component from the multicomponent chemically modulated surfaces;130 (ii) sintering of the resultant porous substrates112 or close-packed sheets of nanospheres113,131–134 using position-dependent heating; or (iii) “chemical polishing” of rough metal plates by immersing the sample vertically into a solution of an etchant;114 (iv) phase separation of immiscible polymer films cast onto surface gradient substrates;135 (v) photolithography-assisted molding of pillars and holes;136 and other methods.137 Such substrates were then used to investigate the effect of substrate topography on cell adhesion.138

A special type of physicochemical gradient involves the generation of other gradients in liquids that can be transferred onto substrates,140,141 gradients of pH,142–144 and refractive index.145

2.2.2 Gradient Dimensionality

Section 2.2.1 discussed the methods that lead nearly exclusively to 2D gradients. True 3D soft matter gradient structures can be built by deposition techniques, whereby the 3D hierarchy is achieved either in a single step or by sequentially building layers on the substrate. Early work included the application of the “knife-edge coating” method,80,146–148 which enabled the formation of polymer layer with gradual variation of composition and thickness. Other efforts included plasma polymerization on surfaces,149–155 electrodeposition,156 and chemical vapor deposition.157 A very popular class of technologies involves chemical grafting of polymer chains to the substrate by employing either the so-called grafting onto or grafting from approaches.158

“Grafting onto” techniques, which are based on anchoring the chemically functionalized polymer chains onto reactive sites on the substrate, result in gradients in grafting density (i.e., number of polymer chains per unit area) of polymer chains, as demonstrated in a series of papers by Luzinov, Minko, and coworkers,81,159–162 and others.82,163 The “grafting from” methods involve building the polymer layer by carrying out polymerization directly from surface-bound polymerization initiator centers chemisorbed on the substrate. Numerous variants of this methodology have been reported.164 For instance, Liedberg and coworkers developed a versatile way of producing gradient assemblies of polymers by exposing activated surfaces to the solution of a monomer and carrying out free radical polymerization via exposure to ultraviolet (UV) light. They controlled the length of the grafted chain on the substrate by modulating the UV dosage by means of a movable shutter.83,165–167 Controlled radical polymerizations for instance, atom transfer radical polymerization (ATRP), have been employed widely for generating 3D gradient assemblies. For instance, Tomlinson and Genzer reported on gradients in molecular weight of the anchored polymer by either
gradually immersing a substrate decorated with surface-bound initiator SAMs into a polymerization solution or by gradually draining the polymerization solution from a chamber that had the initiator-covered substrate placed vertically in it. Wu and coworkers prepared polymer grafting density gradients on flat silica-based surfaces by first forming a gradient of organosilane-based initiator for ATRP by the vapor diffusion method followed by grafting from polymerization of various monomers. Wu later extended this design by forming “double” grafting density gradients of two chemically distinct counter-propagating polymer grafts. Polymer gradients have also been prepared by means of electric field gradients. Wang and Bohn reported on generating “double polymer gradients” by carrying out electrochemical deposition of ATRP initiator followed by grafting from polymerization, and electrochemically filling the “empty” spaces on the substrate with fresh initiator molecules from which another type of polymer was grown. Other methodologies for controlling the gradient nature of surface-anchored layers during ATRP have also been reported.

Further tailoring of 3D gradients can be accomplished by polymerizing two distinct monomers, thus forming copolymer gradients. Block copolymer gradients with a gradual variation of the length of each block and the overall polymer molecular weight were synthesized by sequential polymerization of two or three monomers combined with the methods of producing molecular weight gradient of surface-anchored macromolecules. Xu et al. reported on the formation of surface-anchored statistical copolymers on flat substrates with gradients in composition by means of microfluidic setups. The ability to create reactive sites on the surface by the post-deposition modification methods, such as corona treatment or electron beam bombardment, can also be coupled with grafting from polymerization methods, thereby creating 3D surface-anchored soft scaffolds.

Special cases of 3D chemical gradients are those prepared by the means of liquid mixing in microfluidic channels. What distinguishes this class of structures from the more conventional gradients is the fact that they are created inside a channel of a microfluidic device rather than by grafting on top of a solid substrate. Formation and characteristics of microfluidic gradients are discussed in Section 2.2.5.

### 2.2.3 Gradient Directionality

While all gradient structures are, by definition, directional, the most widely fabricated gradient assemblies are unidirectional, that is, they possess variation of a physicochemical property in one direction along the substrate. Structures enabling the variation of one or more properties in the same as well as counter-propagating directions have been fabricated. Simple unidirectional gradients constitute a subset of more general radial motifs, in which the gradual variation of a physicochemical character commences at a certain point on the substrate from which it propagates radially. Gradient directionality allows for more than a single property to be varied in a specimen, however.
A practical attribute of various gradient preparation methods is that they can be combined to form complex multigradient assemblies, allowing one to change two or more physicochemical properties across the substrate concurrently and independently of each other. These gradients can involve change of two different chemistries or can be made of two dissimilar characteristics, say, chemistry and roughness or chemistry and substrate rigidity (i.e., modulus) and many others. The simplest examples of such multigradient motifs are so-called orthogonal gradients, wherein two properties vary independently across the specimen in two perpendicular directions. Early examples involved the formation of orthogonal gradients exhibiting variation in (i) polymer film thickness/chemical composition,\(^{80}\) (ii) film chemical composition/process temperature,\(^{80}\) and (iii) film thickness/temperature.\(^{146}\) Later orthogonal motifs included polymer assemblies comprising gradual and independent variation in (i) molecular weight and grafting density (MW–\(\sigma\))\(^{17,18,188–190}\) and (ii) molecular weight of two blocks in a diblock copolymer (MW1–MW2).\(^{17,18,177,178,191,192}\)

One can extend the concept of multidirectional gradients even further. For instance, triangular gradients can be generated that allow for the variation of three independent material characteristics in three different directions. As an example, Tomlinson and coworkers recently reported on fabricating substrates decorated with triblock copolymers comprising independent variation of lengths (as well as composition) of three individual blocks.\(^{178}\)

### 2.2.4 Gradient Length Scale

Gradient substrates represent, in essence, a collection of many individual samples, each having a uniform discrete property. Consequently, any array of discrete sites on the surface, where the property (say, composition) of each element of the array changes gradually, can be considered to possess the attributes of a gradient. If the variation between neighboring properties is smooth, the gradient appears to be (nearly) continuous. In contrast, discontinuous gradients refer to designs involving gaps between neighboring homogeneous substrate characteristics. The dual nature of a continuous soft material gradient, that is, discrete on local scales (nano to micro) and continuous on mesoscale (micro to centimeter), makes it a powerful tool both for studying systematically various physicochemical phenomena and for driving certain phenomena. Further discussion on how the dual length scales exhibited by gradients facilitates their applications can be found in Section 2.3.

While most gradient geometries reported span over a distance of a few millimeters to centimeters, certain fabrication methods allow for decreasing considerably the spatial dimension of the gradient patterns. These involve creation of molecular gradients on flexible substrates\(^{32}\); edge-spreading lithography\(^{46}\); deposition of organosilanes by means of silicone elastomer (SE) stamps with different curvatures\(^{48}\); UV laser irradiation of substrates via optical cable\(^{103}\); chemical conversion of alkenethiol-based SAM molecules with soft X-rays\(^{111,119}\) and electron beam,\(^{104–106}\) replacement lithography,\(^{107}\) or plasma polymerization.\(^{153}\) Novel gradient-forming techniques are constantly being developed that permit
the generation of chemical and/or physical gradients on nanometer-to-micrometer scale.\textsuperscript{193,194}

2.2.5 Gradient Temporal Dependency

Time dependency constitutes yet another important attribute of gradient substrates. Most gradient motifs are static so that their physicochemical properties correspond to the state present at the time of their creation. However, some soft material designs are capable of responding to a variation of external stimulus (i.e., solvent quality, pH, temperature, electric or magnetic field, ion concentration) or may be varied by adjusting the gradient attributes in real time.

The first category of gradient structures involves polymer assemblies that alter their properties as a function of solvent quality, pH, charge, or an external potential. Ionov and coworkers created responsive polymer surfaces\textsuperscript{195} comprising mixed brushes made of poly(acrylic acid) (PAA) and poly(2-vinyl pyridine) (P2VP),\textsuperscript{196} whose density changed gradually across the substrate in two opposite directions. These mixed brush gradients responded to the variation of pH by swelling the P2VP brushes at low pH and swelling the PAA brushes at high pH.

The second category of dynamic gradients includes structures that are produced by mixing liquids inside a microfluidic device. In these gradients, the time-dependent variation of the concentration of the various liquids is achieved in a flowing liquid.\textsuperscript{91} Here, multiple solutions are infused simultaneously into a network through various inlets. As the fluid streams travel down the network, they are repeatedly split, mixed, and recombined; and after several generations of branched systems, each branch contains different proportions of the infused solutions. As a result, a gradient is established—perpendicular to the flow—in a single large channel that combines all individual branches of fluids. Multiple studies demonstrated the versatility of this method in probing numerous biological phenomena,\textsuperscript{197–200} as well as in achieving spatial control of surfactants and micelles in solution.\textsuperscript{201}

A few nontraditional gradient types were created by varying external fields such as temperature,\textsuperscript{202–205} pH,\textsuperscript{206} and electrochemical potential. For instance, Isaksson and coworkers recently presented a method for producing a wettability gradient by an external voltage.\textsuperscript{207} Yamada and Tada reported on the formation of dynamic wettability gradients by first decorating substrates with ferrocenyl alkanethiols and then applying in-plane gradients in the electrochemical potential between the ends of the substrate. Reversibility in nitrobenzene and dichloromethane drop motion on wettability gradients has also been reported.\textsuperscript{199,208}

2.3 GRADIENT FUNCTIONALITY

The very nature of gradient surfaces makes them functional structures. Chemical and physical gradients are responsible for driving many important biological and physical processes, such as the directed movement of certain bacteria.
toward nutrients in response to the concentration gradients of molecules emanating from axon target or food source\textsuperscript{76,77,209} or locomotion of motor proteins, that is, kinesin, which can haul cargoes attached to them along microtubular “railroads.”\textsuperscript{210} Concentration gradients of molecules on surfaces also affect phenomena such as osmotic swelling, surface pressure, and surface wettability. Various fabrication methods leading to the formation gradients on surfaces can also be employed to record important physical phenomena. For instance, by immersing a flat substrate continuously into a polymer solution, one can study systematically the adsorption of polymers onto that substrate.\textsuperscript{211} Another example involves a study of polymerization kinetics: substrates decorated with polymerization initiators can be dipped slowly into the polymerization solution, thus producing a gradient in chain length of the surface-bound polymer. Measuring the chain length (by assessing the film thickness) of such polymers grown at various points along the gradient can reveal information about the kinetics of polymerization on surfaces in a very systematic and facile manner.\textsuperscript{84,85} Gradients are conveniently suited to screen important physico-chemico-biological phenomena, that is, protein adsorption on surfaces.\textsuperscript{1,20,23} The chief advantage of gradient structures in studying a complex phenomenon is that the monotonic variation of the physicochemical characteristics of the underlying gradient eliminates the requirement for interpolation to determine the surface response and enables unambiguous interpretation of adsorption experiments. We discussed gradient functionality in terms of four important sub-attributes, concerning the ability to tune, drive, record, and screen a phenomenon (Fig. 2.5). The ability of gradient surfaces to tune surface properties has been discussed in the preceding discussion; the latter three capabilities are outlined in the subsections below.

2.3.1 Driving a Phenomenon

If the gradient is to be utilized in driving a given phenomenon, for example, directing motion of some adsorbed objects, the gradient “steepness” has to be of the same order of magnitude as the length scale sampled by the moving object on the substrate. To that end, “shallow” gradients, whose steepness changes over a millimeter to centimeter range, are suitable for driving the motion of liquid drops.
while “sharp” gradients have to be employed for studying the mobility of much smaller objects. For example, cell locomotion can only be probed with gradients whose inherent length scale is on the order of a few tens to hundreds of microns.

Traditionally, soft material gradient surfaces have been employed in transporting liquids across surfaces by implementing the gradient in the interfacial tension at the front and back edge of the drop acting at the droplet/substrate/air interface. While relatively slow motion was observed in the initial studies, much higher drop speeds have been observed for small water droplets formed by condensation of steam onto a gradient surface, by vibrating the surface, by rolling the drop on a rough substrate decorated with a chemical gradient made of hydrophobic organosilane modifiers, or on wettability gradients prepared by embossing topographical patterns in soft waxes. A large body of work pertaining to probing the liquid motion due to “static gradients” as well as “dynamic gradients” has been presented recently. It is important to note that chemical reactions on gradient surfaces can also govern the movement of larger molecules, that is, dendrimers or nanoparticles.

Surface-bound gradients have been employed as “directional engines” capable of driving synthetic and biological macromolecules along surfaces. Over the past few decades, multiple experimental and theoretical studies have been published that reported on the response of living cells (orientation and migration) to the variation of chemistry (chemotaxis, haptotaxis), light intensity (phototaxis), electrostatic potential (galvanotaxis), gravitational field (geotaxis), mechanical properties (durotaxis), as well as substrate topography, or concurrent combination of several cues. Many of those studies employed either static or dynamic gradients in physicochemical properties or micropatterned arrays of asymmetric regions of sticky groups on the substrate that governed the locomotion of cells, kinesin or actin, and axon growth.

2.3.2 Recording a Phenomenon

Processes leading to the formation of soft material gradients on surfaces can be perceived as a convenient means of “recording” time-dependent physicochemical phenomena. The resultant gradient substrate then constitutes a convenient recoding medium, which further facilitates detailed and expedient “post-process” analytical platform.

Tomlinson and coworkers used the gradient geometry to study the kinetics of the surface-initiated controlled radical polymerization of poly(methyl methacrylate); they confirmed that the reaction obeyed the predicted dependence on the concentration of the activator and deactivator species in the polymerization mixture and established the “living” nature of the macroinitiator in surface-initiated ATRP. Shovsky and Schönherr employed gradient geometry to monitor reaction kinetics, rate constants, and activation energies and determined entropies associated with the surface reactions of alkaline hydrolysis of model SAMs on surfaces. The kinetics of post-polymerization reaction
of surface-grafted chains such as bromination of grafted polystyrene has been reported by Jhon and coworkers.\textsuperscript{268}

The gradient setup is conveniently suited for monitoring time-dependent adsorption of molecules from solution onto surfaces. Morgenthaler et al. reported on the adsorption of poly(l-lysine)-graft-poly(ethylene glycol) copolymers onto metal oxide substrates by gradually immersing the substrate into the copolymer solution.\textsuperscript{269} Jhon and coworkers employed a similar setup to study the effect of comonomer sequence distribution in random copolymers on adsorption on solid substrates.\textsuperscript{211} Adsorption studies of pluronics (PEO–PPO–PEO triblock copolymers) on wettability gradients helped establish that the PPO block was governing the partition of the pluronics on surfaces.\textsuperscript{270}

Substrates bearing gradient assemblies of surface-grafted polymer brushes have been used to monitor swelling/collapse of copolymer blocks with selective solvents.\textsuperscript{88,177,271} Several studies have demonstrated the suitability of combinatorial approaches to study the coalescence of droplets on chemically heterogeneous gradient substrates,\textsuperscript{272} order–disorder transition in grafted oligoalkanes on surfaces,\textsuperscript{36} and phase separation in immiscible homopolymer blends.\textsuperscript{273} Using gradient setup, Douglas and coworkers uncovered that the mechanism involved in forming molecular gradients of organosilane SAMs on silica flat substrates by vapor diffusion technique depends on the geometry of the diffusing system; in confined systems, the molecules did not order themselves in a classical diffusion-like manner but grew in a wavelike fashion that spread out from a source point.\textsuperscript{274}

In chapter 4 in this book, we report on studies using counter-propagating fronts employing two different organosilane molecules; in particular, we examine the collision between fronts made of two different chemical species and explore which type is thermodynamically “fittest/robust” (i.e., it displaces the other and thus “survives”).

\subsection{Screening a Phenomenon}

When employing gradients in materials property screening, that is, using the gradient structures as a library of individual homogeneous specimens, it is important to assure that the change in the characteristics of the individual library elements is small enough for one to unequivocally ascribe the measured property to the characteristics of underlying library elements. The actual size of the discrete spots on the sample, into which the overall gradient structure can be subdivided, has to be large enough and the gradient steepness has to be small enough so that each individual element of the library possesses a uniform property and is larger than the lateral resolution of a given analytical method used to probe such properties.\textsuperscript{148}

Since their first creation, gradient substrates have played a pivotal role in screening various characteristics of soft structures comprising oligomeric/polymeric components. Gradient geometries have enabled systematic investigation of the structure and surface morphologies in thin block copolymer films over a wide range of film thicknesses,\textsuperscript{147,275–279} phase behavior in polymer
blends, crystallization in thin polymer films, and thin polymer films, order–disorder transition in short alkane- and oligo(ethylene glycol)-based molecules on surfaces, and the structure of organic light-emitting diodes. Substrates decorated with wettability gradients have also been employed to probe the orientation of several liquid crystalline materials. Gradient geometries were utilized to probe the adsorption and absorption of inorganic or organic nanoobjects, that is, nanoparticles or nanowires, into SAM or polymer-based matrices, thus providing a convenient platform for testing the partitioning of nanoadsorbates inside organic grafts. Gradient geometries have also proved important in assessing mechanical characteristics of soft materials, including gradual transition from hard to soft tissues by self-assembling diblock copolymers displaying a “noncollagenic” block and a “stiffness tunable” block made up of elastin-like (soft), amorphous polyglycine (intermediate), or a silklike (hard) material, or establishing novel methods for systematic assessment of the elastic modulus of polymeric and nonpolymeric material thin films.

No other field of science and engineering has utilized soft material gradients for screening properties more frequently than biosciences because of the need to screen systematically many parameters that affect the partitioning of biomolecules at surfaces and interfaces. To this end, soft matter gradients have been employed in methodological studies of adsorption of surfactants, bacteria, and proteins. Surface-bound gradients have also been used successfully in studies pertaining to platelet adhesion; enzyme immobilization; cell adhesion, motility, and encapsulation; hybridization on biochips; biosensor design; tissue engineering; and other phenomena involving interfacial biomaterial interaction with man-made surfaces. A more detailed account of the application of soft material gradients in biomaterial and biological sciences can be found in recent reviews.

2.4 CONCLUSIONS

The purpose of this chapter was to classify soft material gradients in terms of their chief attributes and summarize briefly the progress achieved in the field over the past four decades. Owing to space limitations, we could not provide the necessary details about all the stimulating developments in the field; interested readers should consult recent comprehensive reviews on this topic as well as other reviews and research articles cited in this chapter. As we discussed, gradient surfaces have not only enabled generation of “appealing” material motifs on surfaces but more importantly have facilitated systematic studies of physicochemical phenomena, enabled generation of smart/responsive materials, and provided means of dynamically adjusting physicochemical aspects of surfaces. The field of material science involving the preparation and utilization
of soft material gradient surfaces has now evolved from its infancy into a mature scientific discipline, thanks primarily to the numerous researchers from various scientific disciplines, many of whom are contributors to this exciting book.

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