Surface-Responsive Materials

T. P. Russell

Synthetic polymers offer a wealth of opportunities to design responsive materials triggered by external stimuli. Changing the length, chemical composition, architecture, and topology of the chains allows response mechanisms and rates to be easily manipulated; and devices based on the entropy of the chains, surface energies, and specific segmental interactions can readily be made. Although numerous applications exist, intriguing possibilities are emerging that have tremendous potential to further developments in surface-responsive materials.

A classic example of a responsive material is an elastic band. Within some finite limit, it can be stretched at a rapid rate of extension, and yet it is still able to respond to the applied deformation. The polymer chains are able to stretch and align, and this molecular mobility is typical of materials that we consider soft or responsive. In contrast, if I hammer a sheet of glass, it will shatter, which does not qualify it as a responsive material. The slow dynamics of the glass have impeded its ability to respond.

A beautiful, yet quite complex, example of a responsive material is seen in cell adhesion on a receptor-mediated surface. Whether a cell spreads on the surface depends on a delicate interplay between the cell and the surface involving attractive van der Waals interactions, electrostatic interactions, membrane elasticity, steric interactions, and receptor-ligand binding, to name a few. The restraints imposed by the surface require specific cellular responses, or spreading will not occur. To design and produce materials with a level of complexity comparable to that of a cell is only a dream at present. Yet materials can be produced that respond to an imposed force according to simple concepts. Several examples of synthetic polymers are discussed here that make use of the long-chain nature of the polymers to make them responsive in very unique ways.

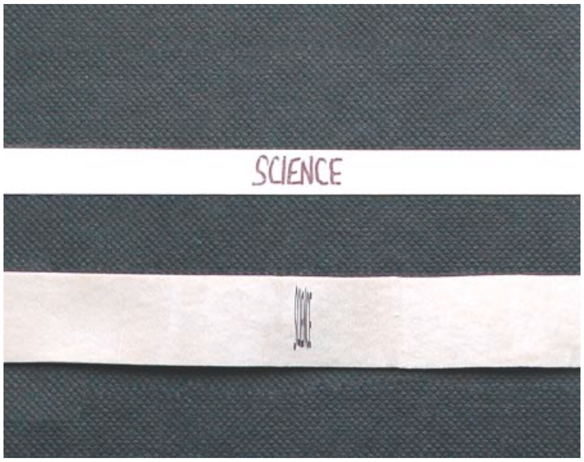

Fig. 1. (**Top**) "Science" was written on the surface of a stretched rubber band. (**Bottom**) The same rubber band after it was allowed to relax to its unperturbed state. The word "Science" is no longer legible.

Let's begin with a simple example that you may have used as a child to encode a secret message. Stretch a rubber band, as shown in Fig. 1A, and write a word on the band while it is stretched. Then allow the band to relax (Fig. 1B), and it is now impossible to discern what was originally written. Stretch the band again and the word magically reappears. This is a trivial example, to be sure, but let's consider what is happening. We assume that the deformation of the rubber occurs under constant volume. Because the deformation of the rubber is uniaxial, the length increases by $\lambda = L/L_0$, where L_0 is the initial length and L is the length after stretching, and the width and thickness decrease by $\lambda^{-1/2}$. The surface area on which the word was written also changes, increasing by $\lambda^{1/2}$ on stretching. So, after relaxing, the word is compressed in one direction and stretched in the other, making it illegible, but what happens to the ink? Assuming that the ink is affixed to the polymer, because the surface area has decreased, some of the ink must be dragged beneath the surface during the relaxation. Upon stretching, the ink is brought to the surface again.

If the ink is replaced with a reactive group, such as an amine, the stretching and relaxation of the rubber provide a simple means of controlling the number and areal density of reactive groups on the surface. Because stretching the rubber stores an elastic retractive force in the rubber, a responsive force has been implanted in the material. Once the network becomes mobile, as, for example, when exposed to heat or a solvent, the rubber will rapidly contract. A similar response can be achieved with stretched semicrystalline polymers, in which the crystals act as cross-linked points, or in glassy polymers with a frozen-in strain; and any polymer trapped in a nonequilibrium state can produce a similar response. Heat-shrink tubing, for example, is based on such a response.

Genzer and Efimenko (*1*) used this change in surface area to great advantage by attaching perfluoroalkanes to the surface of a cross-linked poly(dimethylsiloxane) (PDMS) elastomer. Perfluoroalkanes have a low surface energy and are hydrophobic, with a water contact angle of ~100°. When the elastomer was relaxed, the contact angle with water increased by ~30°, making the surfaces "superhydrophobic." This results from an increase in the areal density of the perfluoroalkanes due to a decrease in the surface area of the elastomer. Unlike a self-assembled monolayer, the chemical attachment of the perfluoroalkanes to the elastomer means that the attachment will be long-lived, resistant to a surface reconstruction, and nonpermeable. Any external force or stimulus, such as heat, that causes the elastomer to deform will change the wetting characteristics of the surface and can be used to tailor its wetting properties.

This concept can be further extended. Rather than anchoring short-chain alkanes, functionalized long-chain polymers can be anchored to the surface, as shown in Fig. 2. The maximum number of polymer chains that can be anchored to an unstretched surface is limited, because at high coverage all the attached chains must stretch in order to accommodate the anchoring of yet one more chain to the surface. If, however, the underlying substrate is initially stretched, then by relaxing the elastomer, the areal density of chains can be increased by $\lambda^{1/2}$. Thus, simply by changing temperature, the surface functionality can readily be manipulated.

The retractive force stored in a stretched rubber band is entropic in origin. Thus, heating a stretched network will cause it to retract. Now consider a relaxed cross-linked, elastomer in contact with a solid surface, in which some of the elastomer chains contain functional groups that interact favorably with the solid as, for example, by chemisorption (Fig. 3). The partition function, defining the entropy of the chains in the network, is defined in terms of the total number of configurations of the chains and the energy associated with each configuration. The higher the energy of a configuration, the less probable

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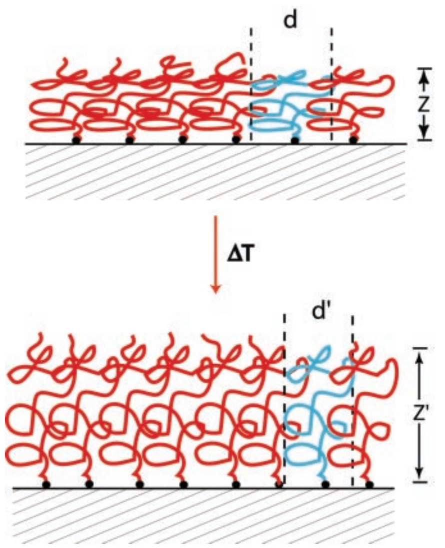

Fig. 2. Polymer chains anchored to a surface with a characteristic thickness *Z* and cross-sectional area *A*. Allowing the underlying substrate to relax causes the thickness to increase to *Z′* and the cross-sectional area to decrease to *A′*. The areal density of the chains has increased because of the relaxing of the underlying network. *d* and *d′* are the cross-sectional areas of the chains before and after contraction of the substrate by increasing the temperature by Δ*T*.

will be that configuration, but there is still a finite probability that it will occur. As the chains in the network sample configuration space, the favorable interactions of the functional groups on the chains with the surface will anchor the network chains to the surface. While increasing the adhesion, the network chain attachment reduces the entropy of the network. This loss in entropy translates into a stored energy tending to pull the chains from the surface. When the temperature is increased, the elastic restoring force of the network chains increases, and eventually this force exceeds the force binding the chains to the surface. Thus, the network chains are pulled away from the surface and the adhesion decreases. Khongtong and Ferguson (*2*) recently demonstrated this effect in polybutadiene elastomers, in which, in response to a temperature change, the force required to peel the elastomer from the surface decreased markedly. The loss in adhesion is reversible, because reducing temperature allows the network chains to reattach to the surface.

Surface energy affords a very powerful means of designing responsive materials. In general, for multicomponent systems or materials composed of heterogeneous polymers, the lower-surface-energy component is located at the surface. One sees applications of this in scratch-resistant surfaces, where a low-surface-energy additive fills a scratch that has exposed a high-energy surface, or in magnetic disks, where a low-surface-energy lubricant spreads over the underlying magnetic media if the read/write head contacts the disk. Now consider the reverse case, in which the desired functional component has a high surface energy. The functional groups would lie hidden beneath the surface, and in response to an external stimulus, the surface would need to rearrange. Falsafi, Tirrell, and Pocius (*3*) discuss precisely this type of behavior in pressure-sensitive adhesives, which are elastomers containing both low-surface-energy aliphatic acid side chains and high-surface-energy carboxylic acid side chains. At a free surface, the aliphatic portions of the chains segregate to the surface. However, when two such elastomers are pressed together, a rearrangement occurs at the interface, allowing hydrogen bonding of the acid side chains, which promotes adhesion.

The interplay between the surface energies of components in a heterogeneous polymer was beautifully demonstrated by Chaudhury and coworkers (*4*, *5*). An amide functional perfluorinated ether (PFE) was attached to a PDMS elastomer. As expected, x-ray photoelectron spectroscopy showed that the lower-surface-energy PFE preferentially segregated to the free surface, but the amide functionality was buried beneath the surface. The perfluorinated chain in PFE is hydrophobic, whereas the amine functionality is hydrophilic. When in contact with a drop of water, the advancing contact angle was high (~140°), as would be expected for a hydrophobic surface. However, the receding contact angle was only ~40°, showing that the surface was now hydrophilic. Consequently, a surface rearrangement occurred, in which the amide functional groups were drawn to the surface. Removal of the water allowed the system to return to its original state. A large hysteresis in the contact angle can be used to direct the flow of fluids on a surface and has even be used to cause the flow of fluids uphill (*6*).

Diblock copolymers are composed of two chemically distinct polymers joined together at one end. The immiscibility of the two blocks results in the microphase separation of the copolymer into ordered nanoscopic domains. The difference in the surface energies of the components forces the orientation of these domains parallel to the surface, with the lower-surface-energy block located at the surface (*7*–*9*). This is shown schematically in Fig. 3 for a symmetric diblock copolymer that microphase-separates into alternating lamellae of the two blocks. Nakahama and co-workers (*10*, *11*) used this property to design materials that reconstruct in response to a change in the environment. In particular, block copolymers were prepared in which one block was hydrophilic and the other was hydrophobic. At equilibrium, the lower-surface-energy hydrophobic block migrates to the air surface and the hydrophilic block is hidden beneath the surface. Upon exposure to water, a surface reconstruction occurs, opening channels to the underlying hydrophilic block, as shown schematically in Fig. 4. The longer the exposure to water, the greater is the reconstruction, until only the hydrophilic block is in contact with the water. The applications as a delivery mechanism enabled by such a morphological rearrangement are quite evident. Designing a specific functionality into the higher-surface-energy block allows it to be easily brought to the surface by a change in the environment.

Because the domains in these block copolymers are typically tens of nanometers in size, properties such as the glass transition temperature or the melting temperature are similar to those seen in the bulk. This provides yet another means of manipulating response, as shown by de Crevoisier *et al.* (*12*) in controlling the tack or stickiness of a polymer. A copolymer was designed containing low-surface-energy perfluoroalkyl side chains. These side chains phase-separated into liquid crystalline domains that were preferentially located at the surface. At low temperatures, the surface energy and the tack were low. With increasing temperature, the liquid crystalline domains disordered, and the surface energy and tack sharply increased over a narrow temperature interval as the perfluorinated side chains mixed with the aliphatic portions of the copolymer. The temperature of this transition was tuned by changing the composition of the copolymer. For the specific copolymer studied, this occurred near body temperature, making these materials suitable as responsive grips for sporting equipment such as baseball bats, tennis racquets, and golf clubs, or for garments with cling.

A wealth of different chain architectures

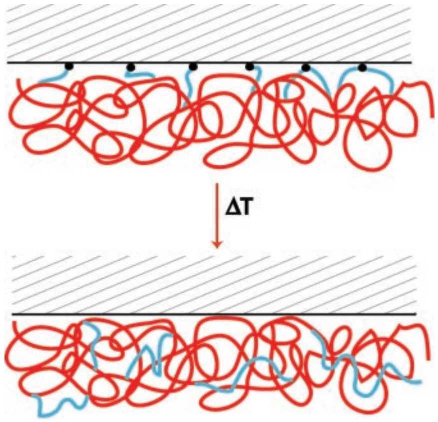

Fig. 3. A cross-linked elastomer with functional network chains is placed in contact with a solid surface. The functional chains interact favorably with the solid and are attached to the surface, locking them into a nonequilibrium configuration. When the temperature is increased, the retractive force on the anchored chains increases to a point where the bonding strength is exceeded and the chains are pulled away from the surface.

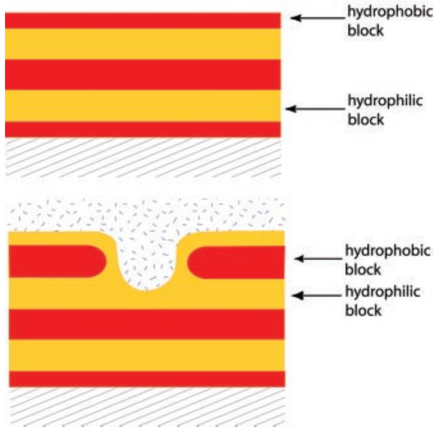

Fig. 4. Schematic of a symmetric diblock copolymer composed of a hydrophobic and hydrophilic block, with a lamellar microdomain morphology. In contact with air, the lower-surface-energy hydrophobic block is located at the surface. Changing the environment to water induces a surface reconstruction in which the hydrophilic block is located at the surface.

are also available in the design of polymers. These range from linear chains to highly branched architectures to dendrimers or starlike polymers. Chain ends will preferentially segregate toward the surface of a polymer melt because of the reflecting boundary condition (*13*). In mixtures of two polymers that are chemically identical and differ only in their architecture, the polymer with the larger number of chain ends per unit volume will segregate to the free surface. This has led to the development of polymers that can aid processing but are chemically similar to the bulk material. Mackay and co-workers (*14*, *15*) added less than 1% of a dendritic polymer to a linear polymer and were able to eliminate the surface instabilities that are observed during extrusion or blow-molding and that cause surface roughness, limit the throughput, or make the material unusable. Here the dendrimer rapidly diffused to the surface, eliminating a stick-slip behavior and stabilizing the flow.

Mayes and co-workers used chain architecture to design wettable membranes for water filtration (*16*), biodegradable tissue engineering scaffolds with cell-signaling surfaces (*17*), and cell-interactive coatings for biomedical applications (*18*). Consider a mixture of two linear polymers, hydrophilic poly(ethylene oxide) (PEO), and hydrophobic poly(methylmethacrylate) (PMMA). The PMMA is the lower-surface-energy block and segregates to the air surface. However, if comb-shaped polymers composed of a PMMA backbone with PEO side chains (polymers with a higher surface energy component but many chain ends) are mixed with PMMA, the amphiphilic comb polymers are driven by entropy to segregate to the surface (*19*). Thus, materials with highly desirable mechanical properties can be made to respond favorably to environmental changes. This is finding use in applications raging from antifouling water filtration systems to contact lenses.

Light is one of the simplest external stimuli that can be used to trigger a response. Ichimura *et al.* (*20*) used light to control the wetting characteristics of a surface by manipulating the photoisomerization of azobenze tethered to a surface. Exposure to ultraviolet (UV) light and then to blue light causes the azobenze to switch from the cis to the trans conformation. This isomerization causes a substantial change in the wetting characteristics of an oil droplet on the surface. By exposing the surface to a gradient in the light intensity, the areal density of the cis conformer can be altered and, therefore, a gradient in the wetting properties can be achieved. Thus, the droplet can be moved across a surface in response to light exposure.

Light can also be used to induce a chemical reaction in a material. One example currently being studied is the photocleavage of a diblock copolymer (*21*), in which, as shown schematically in Fig. 5, the junction point of a diblock copolymer can be broken, producing two homopolymers from the block copolymer. Although the chemical constitution of the material has not changed, the characteristic morphology has. As mentioned, block copolymers microphase-separate into order domains that are tens of nanometers in size. Polymer mixtures, on the other hand, macroscopically phase-separate into domains that are many microns in size. Thus, in response to light exposure, the fundamental structure of the material has changed. The rate at which the change occurs can, of course, be controlled with temperature.

The microphase separation of block copolymers is usually dominated by the enthalpic interactions between the different segments of the block copolymer. When the temperature is increased (*22*), the interactions are weakened and the copolymer undergoes a transition from the ordered to the disordered state. However, block copolymers of polystyrene and poly(*n*-butyl methacrylate) were found to undergo a transition from the phase-mixed to the microphase-separated state with increasing temperature. This behavior was subsequently generalized to the homologous series of poly(*n*-alkyl methacrylates) (*23*) and was shown to be driven primarily by the entropy of the block copolymer. The flow properties of the copolymer are highly dependent on the morphology. In the phase-mixed state, the copolymer behaves like any polymer melt, whereas in the microphase-separated state it is resistant to flow. This ordering transition can be driven by pressure (*24*, *25*), an external force that is routinely used in the processing of polymer materials. This is precisely the behavior desired, in which the application of pressure causes the copolymer to mix and flow more easily and, upon the removal of pressure, the copolymer microphase separates and sets. These copolymers represent a new class of materials—"baroplastic" as opposed to thermoplastic—that open new avenues in the processing of polymeric materials.

Each of the examples discussed up to now relies on the uniform response of a surface to an external stimulus. However, it is also possible to design materials with a is built-in gradient. Using gradient fields or variable-rate dip-coating processes, for example, film thickness, composition, and morphology within a film can be gradually changed across a material in one or several directions. The size scale of the heterogeneities can be varied from the nanoscopic (as with block copolymers) to the macroscopic (as in polymer mixtures). Thin films of a photocleavable block copolymer exposed to a lateral variation in UV light produce a film in which the morphology uniformly changes from the nanoscopic to the macroscopic across the surface. It is not hard to envision a case in which a thin film of the copolymer is prepared and the exposure to UV radiation can be gradually varied across the surface, producing a template to functionalize the surface where the length scale of the interactions gradually changes across the surface. Such surfaces provide a route to simple sensors, in which an invading species will select the position on the surface with the optional interaction length scale.

Nanoparticles, which have large surface-

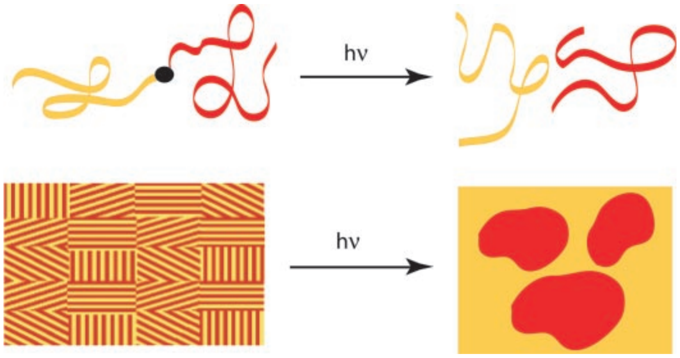

Fig. 5. A symmetric diblock copolymer with a photocleavable junction point. The diblock copolymer microphase-separates into lamellar microdomains with dimensions on the scale of tens of nanometers. Upon exposure to light with energy $h\nu$, where h is Planck's constant and ν is the frequency, the junction point is cleaved, producing two homopolymers. The two homopolymers macroscopically phase-separate into domains that are many microns in size.

to-volume ratios, afford further routes for the design of responsive materials. Functionalized ligands can be placed on the surface of gold or cadmium selenide nanoparticles. Such functional particles can be tethered to the base of the nanopores in thin-film arrays made from diblock copolymer templates. The conformation of the tethering chains will depend on the local solvent environment. Changing the pH, temperature, or solvent quality within the pores causes the chain to stretch or compress, allowing the nanoparticles to move up and down in the pores, exposing or hiding the interacting sites on the nanoparticles and trapping or repelling foreign materials approaching the surface.

A wide range of external stimuli can be used to invoke a specific response from polymeric materials. This has given and will give rise to a broad spectrum of applications, ranging from melt-processing aids to biocompatible materials to chemical sensors. The unique characteristics of long-chain molecules offer a myriad of possibilities for playing with the chemistry, conformation, and dynamics of the chains to build in specific responses with well-defined response times and triggers, which are key elements in the fabrication of responsive materials.

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26. I would like to acknowledge enjoyable discussions with R. J. Farris at the University of Massachusetts, who knows an awful lot about rubber.

REVIEW

Polymer Vesicles

Dennis E. Discher[1]* **and Adi Eisenberg**[2]

Vesicles are microscopic sacs that enclose a volume with a molecularly thin membrane. The membranes are generally self-directed assemblies of amphiphilic molecules with a dual hydrophilic-hydrophobic character. Biological amphiphiles form vesicles central to cell function and are principally lipids of molecular weight less than 1 kilodalton. Block copolymers that mimic lipid amphiphilicity can also self-assemble into vesicles in dilute solution, but polymer molecular weights can be orders of magnitude greater than those of lipids. Structural features of vesicles, as well as properties including stability, fluidity, and intermembrane dynamics, are greatly influenced by characteristics of the polymers. Future applications of polymer vesicles will rely on exploiting unique property-performance relations, but results to date already underscore the fact that biologically derived vesicles are but a small subset of what is physically and chemically possible.

Vesicles and biomembranes have existed since the first cells and play critical roles in compartmentalization functions as varied as nutrient transport and DNA protection (*1*). Whereas phospholipids are the natural amphiphiles of cell membranes, vesicle-forming materials used in products ranging from cosmetics to anticancer agents can be synthetic as well as biological [e.g., (*2*)]. When suitably mixed in water or similar solvents, the oily parts of the amphiphiles tend to associate while the more hydrophilic parts face inner and outer solutions, helping to delimit the two interfaces of the membrane (Fig. 1A).

Despite the molecularly thin nature of these membranes, the vesicles that form by the relatively weak solvent-associated forces can effectively entrap dissolved compounds and can also accumulate, within the membrane cores, hydrophobic or fatty substances. Several skin-rejuvenating products, for example, not only encapsulate the water-soluble antioxidant vitamin C within lipid vesicles but also dissolve skin-healing vitamin E within the cores. Aggregation of more than 100,000 small amphiphiles such as lipids (with molecular weight $MW < 1$ kD) into the molecularly thin membranes also manifests itself in a dynamic, physical softness (*1*). As a consequence, many lipid vesicle properties such as encapsulant retention, membrane stability, and degradation are not particularly well controlled.

A polymer approach to vesicle formation—as summarized in this review—broadens the range of properties achievable through a widened choice of amphiphile MW and chemistry. To be clear, the systems reviewed are not polymerized vesicles in which amphiphiles are polymerized or cross-linked after vesicle formation; such an approach has generally started with lipid-size, reactive amphiphiles, and (if successful) generates membranes of the same basic architecture as lipid bilayers (*3, 4*). Instead, the focus here is on linear polymers with the intrinsic ability to self-direct their own assembly into membranes. Being lipid-like only in the latter sense, vesicle-forming polymers offer fundamental insight into natural design principles for biomembranes.

From archaebacteria to humans, cell membranes are self-assemblies of lipids (Fig. 1A, a) as well as integrated and peripheral membrane proteins (i.e., large and structured biopolymers). Since Bangham's 1960s description of lipid vesicles or "liposomes" (*5*), extraction and reconstitution of many such biomembrane systems has led to fundamental as well as technological advances. One example of note is the formation of HIV-like "virosomes" that have been made by integrating the cell-binding HIV protein gp160 into liposomes (*6*). A number of highly diverse synthetic systems have also been inspired, starting with 1970s "niosomes" (*7*) made from nonionic amphiphiles similar in size to lipids. From polyethylene glycol (PEG)–

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