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Active Polymers: An Overview

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1.1 Introduction

In this time of technological advancements, conventional materials such as metals and alloys are being replaced by polymers in such fields as automobiles, aerospace, household goods, and electronics. Due to the tremendous advances in polymeric materials technology, various processing techniques have been developed that enable the production of polymers with tailor-made properties (mechanical, electrical, etc). Polymers enable new designs to be developed that are cost-effective with small size and weights [1].

Polymers have attractive properties compared to inorganic materials. They are lightweight, inexpensive, fracture tolerant, pliable, and easily processed and manufactured. They can be configured into complex shapes and their properties can be tailored according to demand [2]. With the rapid advances in materials used in science and technology, various materials with intelligence embedded at the molecular level are being developed at a fast pace. These intelligent materials can sense variations in the environment, process the information, and respond accordingly. Shape-memory alloys, piezoelectric materials, *etc.* fall in this category of intelligent materials [3]. Polymers that respond to external stimuli by changing shape or size have been known and studied for several decades. They respond to stimuli such as an electrical field, pH, a magnetic field, and light [2]. These intelligent polymers can collectively be called *active polymers*.

One of the significant applications of these active polymers is found in biomimetics—the practice of taking ideas and concepts from nature and implementing them in engineering and design. Various machines that imitate birds, fish, insects and even plants have been developed. With the increased emphasis on "green" technological solutions to contemporary problems, scientists started exploring the ultimate resource—nature—for solutions that have become highly optimized during the millions of years of evolution [4]. Throughout history, humans have attempted to mimic biological creatures in appearance, functionality, intelligence of operation, and their thinking process. Currently, various biomimetic fields are attempting to do the same thing, including artificial intelligence, artificial vision, artificial muscles, and many other avenues [5]. It has been the dream of robotic engineers to develop autonomous, legged robots with mission-handling capabilities. But the development of these robots has been limited by the complex actuation and control and power technology that are incomparable to simple systems in the natural world. As humans have developed in biomimetic fields, biology has provided efficient solutions for the design of locomotion and control systems [6]. Active polymers with characteristics similar to biological muscles hold tremendous promise for the development of biomimetics. These polymers have characteristics similar to biological muscles such as resilience, large actuation, and damage tolerance. They are more flexible than conventional motors and can act as vibration and shock dampers; the polymers are similar in aesthetic appeal too. The polymers' physical makeup enables the development of mechanical devices with no gears, bearings, or other complex mechanisms responsible for large costs and complexity [5].

Active materials can convert electrical or chemical energy directly to mechanical energy through the response of the material. This capability is of great use in rapidly shrinking mechanical components due to the miniaturization of robots [7]. Realistically looking and behaving robots are believed possible, using artificial intelligence, effective artificial muscles, and biomimetic technologies [8]. Autonomous, human-looking robots can be developed to inspect structures with configurations that are not predetermined. A multifunctional automated crawling system developed at NASA/JPL, operates in field conditions and scans large areas using a wide range of NDE instruments [9].

There are many types of active polymers with different controllable properties, due to a variety of stimuli. They can produce permanent or reversible responses; they can be passive or active by embedment in polymers, making smart structures. The resilience and toughness of the host polymer can be useful in the development of smart structures that have shape control and self-sensing capabilities [2].

Depending on the type of actuation, the materials used are broadly classified as nonelectrically deformable polymers (actuated by nonelectric stimuli such as pH, light, temperature, *etc.*) and electroactive polymers (EAPs) (actuated by electric inputs). Different types of nonelectrically deformable polymers are chemically activated polymers, shape-memory polymers, inflatable structures, light-activated polymers, magnetically activated polymers, and thermally activated gels [2].

Polymers that change shape or size in response to electrical stimulus are called electroactive polymers (EAP) and are classified depending on the mechanism responsible for actuation as electronic EAPs (which are driven by electric field or coulomb forces) or ionic EAPs (which change shape by mobility or diffusion of ions and their conjugated substances). A list of leading electroactive polymers is shown in Table 1.1.

Table 1.1. List of leading EAP materials

Electronic EAP	Ionic EAP
Dielectric EAP Electrostrictive graft elastomers Electrostrictive paper Electro-viscoelastic elastomers Ferroelectric polymers Liquid crystal elastomers (LCE)	Ionic polymer gels (IPG) Ionic polymer metal composite (IPMC) Conducting polymers (CP) Carbon nanotubes (CNT)

The electronic EAPs such as electrostrictive, electrostatic, piezoelectric, and ferroelectric generally require high activation fields (>150V/μm) which are close to the breakdown level of the material. The property of these materials to hold the induced displacement, when a DC voltage is applied, makes them potential materials in robotic applications, and these materials can be operated in air without major constraints. The electronic EAPs also have high energy density as well as a rapid response time in the range of milliseconds. In general, these materials have a glass transition temperature inadequate for low temperature actuation applications.

In contrast, ionic EAP materials such as gels, ionic polymer-metal composites, conducting polymers, and carbon nanotubes require low driving voltages, nearly equal to 1–5V. One of the constraints of these materials is that they must be operated in a wet state or in solid electrolytes. Ionic EAPs predominantly produce bending actuation that induces relatively lower actuation forces than electronic EAPs. Often, operation in aqueous systems is plagued by the hydrolysis of water. Moreover, ionic EAPs have slow response characteristics compared to electronic EAPs. The amount of deformation of these materials is usually much more than electronic EAP materials, and the deformation mechanism bears more resemblance to a biological muscle deformation. The induced strain of both the electronic and ionic EAPs can be designed geometrically to bend, stretch, or contract [2].

Another way to classify actuators is based on actuator mechanisms. The various mechanisms through which EAPs produce actuation are polarization, mass/ion transportation, molecular shape change, and phase change. Dielectric elastomers and piezoelectric polymers produce actuation through polarization. Conducting polymers and gel polymers produce actuation basically through ion/mass transportation. Liquid crystal elastomers and shape-memory polymers produce actuation by phase change.

As can be observed, various stimuli can be used to actuate active polymers. Development of polymers that can respond to a noncontact mode of stimuli such as electrical, magnetic, and light can lead to the diversification of the applications of active polymers. Electrical stimulation is considered the most promising, owing to its availability and advances in control systems. There has been a surge in the amount of research being done on the development of electro-active polymers (EAPs), but other kinds of stimulation have their own niche applications.

Initially, the electrical stimulation of polymers produced relatively small strains, restricting their practical use. But nowadays, polymers showing large strains have been developed and show great potential and capabilities for the development of practical applications. Active polymers which respond to electric stimuli, electroactive polymers (EAPs), exhibit two-to-three orders of magnitude deformation, more than the striction-limited, rigid and fragile electroactive ceramics (EACs). EAPs can have higher response speed, lower density, and greater resilience than shape-memory alloys (SMAs). However, the scope of practical applications of EAPs is limited by low actuation force, low mechanical energy density, and low robustness. Progress toward actuators being used in robotic applications with performance comparable to biological systems will lead to great benefits [2].

In the following paragraphs, all types of active polymers are briefly described and thoroughly reviewed in cited references. Also, some of the most recent developments for certain polymers are presented. Some of the applications of active polymers are given as well.

1.2 Nonelectroactive Polymers

1.2.1 Chemically Activated Polymers

A polymer can change in dimension by interacting with chemicals, but it is a relatively slow process. For example, when a piece of rubber is dropped into oil, it slowly swells by interacting with the solvent [2].

The first artificial muscle was a pH actuated polymeric gel developed in 1950. Since then, a wide variety of polymer gel materials have been developed that can respond to stimuli such as pH, temperature, light, and solvent composition. The interaction with surroundings causes a change in shape or size of these polymers. Some of these polymers are sensitive to pH in aqueous environments.

Most of the earlier work on the gel muscles was done on pH actuation. Cross-linked polyacrylic acid gel is the most widely studied polymer for chemical actuation. This gel increases dimensionally when moved from an acid solution to a base solution and shows weak mechanical properties. To find stronger polymers, different materials were developed during the last 20 years.

Yoshida *et al.* [10] developed an oscillating, swelling-deswelling, pH-sensitive polymer gel system. Rhythmic swelling-deswelling oscillations were achieved by coupling temperature and pH-sensitive poly (*N*-isopropylacrylamide-co-acrylic acid-co-butylmethacrylate) gels with nonlinear oscillating chemical reactions. A pH-oscillating reaction was generated in a continuous-flow-stirred tank reactor, in which the pH of the system changed after a specific time interval. When polymer gels are coupled with reactions in a reactor, an oscillating response is produced.

One of the interesting materials in the this family is the polyacrylonitrile (PAN) gel fiber [11], which when oxidized and saponified shows behavior similar to that of polyacrylic acid gels. The strength of the PAN fibers is higher, and the response time is minimal. A change in length of 70% was observed in a few seconds when the system was moved from an acid to a base, which is very fast compared to polyacrylic acid gels (which could take days or weeks). A volume change of more than 800% was observed for PAN fibers [12]. Moreover, among the available polymer based actuator materials, PAN fiber is already produced commercially in large volumes and used in the production of textiles and as a precursor for making carbon fibers. Coupled with a simple activation process, the easy availability of PAN fiber makes it one of the most suitable materials for use in the development of practical applications. It was found that when fibers transform into gels, they have stronger mechanical properties and larger volume change, more closely resembling biological muscle than any other polymer gel actuators [11]. The diameter of commercially available PAN fiber is on the order of microns in its swollen state, so the response time is rapid as the response depends on the dimension (diameter) of the fibers. The response characteristics of the PAN fibers were found superior to other chemically activated polymer materials, but still not comparable to the response characteristics of skeletal muscles. To improve the response characteristics, sub-micron diameter PAN fibers were produced using a process called “electrospinning.” Macroscopic observation of a PAN nanofiber mat made from electrospinning showed more than 600% deformation in a few seconds, but the mechanical properties of electrospun fiber-mat were found to be poorer than the commercial PAN fibers. Typically, the PAN fibers used in those of the textile industry are co-polymerized with a small amount of another polymer such as acrylamide, methyl acrylate, methyl methacrylate; therefore, there may be some differences in the mechanical properties of such modified PAN fibers. Efforts are underway to improve the mechanical properties and observe the deformational characteristics of the fibers on a microscale. The use of these PAN fibers has more potential in the development of the linear actuators and artificial muscles. For example, the force to weight ratio from experimentation in our lab showed that 0.2g of PAN fiber (5g in an activated state) can generate more than 150gm$_f$ (30–750 times of one weight) [13].

1.2.2 Shape-Memory Polymers

Shape-memory materials are stimuli-responsive materials that change shape through the application of external stimuli. The thermally-induced shape-memory effect is used widely. Thermally responsive shape-memory polymers change shape when heated above a certain temperature and can be processed into two shapes. One form, the permanent shape, is obtained through conventional processing techniques such as extrusion and injection molding. During this process, the material is heated above the highest thermal transition temperature (T_{perm}). The phase above T_{perm} forms physical cross-links which enable the polymers to form permanent shapes. The second phase fixes the temporary phase, acting as a molecular switch. The switching segments can be fixed above the transition temperature (T_{trans}), either the glass transition temperature (T_g) or the melting temperature (T_m). This transition temperature is usually less than T_{perm}. The material can be formed into a temporary shape by thermal processing or cold drawing and cooling below the transition temperature. When the material is heated above the T_{trans}, the physical cross-links in the switching phase are broken, forcing the material into a permanent shape known as recovery [14]. The operation of a shape-memory polymer is schematically depicted in Figure 1.1.

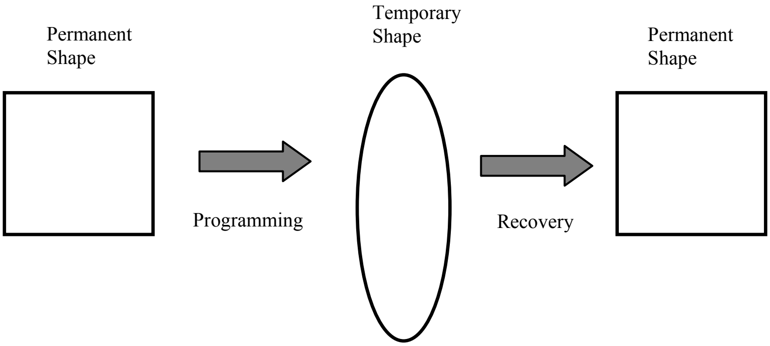

Figure 1.1. Cartoon showing one-way shape-memory effect produced by thermal activation. The permanent shape is transformed into a temporary shape through a programming process. The permanent shape is recovered when the sample is heated above the switching temperature.

As early as the 1930s, scientists discovered that certain metallic compounds exhibited the shape-memory effect when heated above a transition temperature. Since then, shape memory alloys (SMAs), such as the nickel-titanium alloy, have found uses in actuators and medical devices, such as orthodontic wires that self-adjust and stents for keeping blood vessels open. Despite their broad range of applications, SMAs are expensive and nondegradable, and in many cases, lack biocompatibility and compliance, allowing for a deformation of about 8% for Ni-Ti alloys [15].

Linear, phase-segregated multiblock copolymers, mostly polyurethanes, are the commonly used shape-memory polymers. Note that the shape-memory effect is not the property of one single polymer, but it is a combined effect of polymer structure and polymer morphology along with processing and programming technology. Programming refers to the process used to fix the temporary phase. The shape-memory effect can be observed in polymers with significantly different chemical compositions. A significant, new development in the design of shape-memory polymers is the discovery of families of polymers called *polymer systems*. The properties of these polymer systems can be tailored for specific applications by slightly varying their chemical composition [14]. The memory effect of shape-memory polymers is due to the stored mechanical energy obtained during reconfiguration and cooling of the material [16].

Shape-memory polymers (SMPs) are finding applications in varied fields from deploying objects in space to manufacturing dynamic tools [16]. The versatile characteristics of SMPs make them ideal for applications in dynamic configurable parts, deployable components, and inexpensive, reusable custom molds [16]. One type of SMP is the cold hibernated elastic memory (CHEM) structure that can be compressed into a small volume at a temperature higher than the glass transition temperature (T_g) and stored at temperatures below this T_g. When this material is heated again above $T_{g,}$ the original volume of the structure is restored. Volume ratios of up to forty times have been obtained [2]. Structures having different sizes and shapes can be erected by the self-deployable characteristics of these CHEM materials due to their elastic recovery and shape-memory properties. One of the advantages of these materials is that they are a fraction of their original size when compressed and stored below T_g and are lightweight. Commercial applications of these materials include building shelters, hangars, camping tents, rafts, and outdoor furniture. CHEM materials have good impact and radiation resistance as well as strong thermal and electrical insulation properties. One of the disadvantages of these materials is their packing needs: a pressure mechanism which may not be available readily in the outdoors, where they are most applicable [2].

Biodegradable and biocompatible SMPs are being developed which have tremendous potential in the development of minimal, invasive surgery technologies [14]. The permanent shapes of these fibers are programmed into a wound stitch, stretching to form thin fibers. This fiber is then heated above the transition temperature of the material inducing permanent deformation in the material sealing the wound. Biodegradable shape-memory polymers also show strong promise for implantable devices in biomedical applications [17].

1.2.3 Inflatable Structures

Pneumatic artificial muscles (PAMs, often called McKibben muscle) can be defined as contractile linear motion gas pressured engines. Their simple design is comprised of a core element that is a flexible reinforced closed membrane attached at both the ends to the fittings, acting as an inlet and an outlet. Mechanical power is transferred to the load through the fittings. When the membrane inflates due to gas pressure, it bulges outward radially, leading to axial contraction of the shell. This contraction exerts a pulling force on its load. The actuation provides unidirectional linear force and motion. PAMs can be operated underpressure or overpressure, but they are usually operated overpressure as more energy can be transferred. In PAMs, the force generated is related to the applied gas pressure, whereas the amount of actuation is related to the change in the volume. Therefore, the particular state of PAM is determined by the gas pressure and length [18]. The unique, physical configuration of these actuators gives them numerous variable-stiffness, spring like characteristics: nonlinear passive elasticity, physical flexibility, and light weight [19]. Like biological muscles, they are pull-only devices and should be used in antagonistic pairs to give better control of the actuation. Using an antagonistic pair provides control of the actuator stiffness allowing a continuum of positions and independent compliances. Like a human muscle, stiffness can be increased without change in the angle at the joint, giving an actuator control of both its stiffness and compliance [6].

PAMs, which are only one membrane, are extremely light compared to other actuators. Their power-to-weight ratio of 1 kW/kg was observed. They have easily adjustable compliance depending on the gas compressibility and varying force of displacement. PAMs can be directly mounted onto robot joints without any gears, eliminating inertia or backlash. They are easy to operate without such hazards as electric shock, fire, explosion and pollution.

The design of PAMs dates back as far as 1929, but, due to their complex design and poor reliability, they did not attract the attention of the research community. One of the most commonly used PAMs is the McKibben muscle (Figure 1.2, [20]) also called braided PAM (BPAM) due to its design and assembly. The muscle consists of a gas-tight bladder or tube with a double helically braided sleeve around it. The change in the braid angle varies the length, diameter, and volume of the sleeve. BPAMs have been widely used for orthotic applications because their length–load characteristics are similar to those biological muscles, but, due to the lack of availability of pneumatic power storage systems and poor valve technology, the interest in McKibben muscles has slowly faded in the scientific community. The Bridgestone Co. in Japan reintroduced the BPAMs for industrial robotic applications such as the soft arm, and Festo AG introduced an improved variant of PAM.

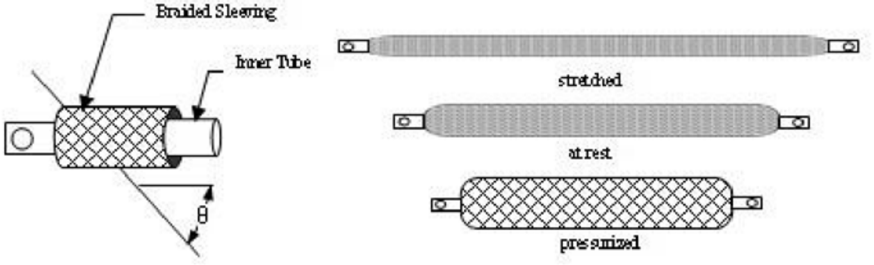

Figure 1.2. Braided muscle or McKibben muscle

Most of the PAMs used are in anthropomorphic robots, but various weak points exist in the design of braided muscle. They show considerable hysteresis due to the friction between the braid and shell, causing an adverse effect on the behavior of actuator, and a complex model is needed to determine the characteristics. PAMs generate low force and need an initial threshold pressure to generate actuation. They are plagued by low cycle life, but their generated force, threshold pressure and life cycle are dependent on material selection. The wires in the sleeve also snap from the ends during actuation, and they have limited actuation capacity (20 to 30%). A new design of PAM called netted Muscle (ROMAC) was designed to have better contraction and force characteristics with little friction and material deformation, but they have complex designs [18].

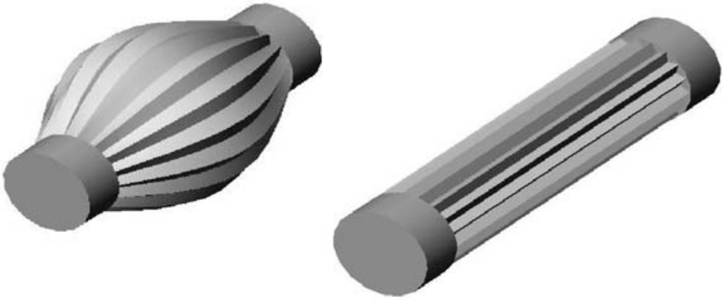

Figure 1.3. Schematic of a pleated, pneumatic artificial muscle in a stretched and inflated state

Another new PAM called pleated PAM (PPAM) (Figure 1.3) has a membrane rearrangement. The membrane is folded along its central axis to form an accordion bellows that unfurls during the inflation of the membrane. The membrane is made of a highly tensile, flexible material. Both ends of the membrane are tightly locked to the fittings. This design eliminates friction and hysteresis because the folded faces are laid out radially so the unfolding of the membrane needs no energy, giving a higher force output. PPAMs were found to be strong, operating with a large stroke and virtually no friction. They are very light in weight; a 60 g actuator pulls a 3500 N load and are easy to control when providing accurate positioning. PPAMs provide safe machine-man interaction. By using the right material, the material deformation can be eliminated while getting high tensile forces. Depending on the number of pleats, a uniform membrane loading can be obtained. As the number of pleats increases, a more uniform loading can be obtained. PPAMs need low threshold pressure to give high values of maximum pressure output. A maximum contraction of 45% was obtained that depended on the slenderness of the material [18].

A short actuation response time can be obtained to improve the flexibility of the actuator by employing high flow rate valves. This will occur through the development of a better closed-loop controller. These valves will be large and heavy and need high control energy which leads to a decrease in the energy efficiency of the whole system [19]. The diameter of the usable, transferable tubing is limited by the increase in gas viscosity, which increases the diameter. The flexibility is also compromised by large diameter tubing, and the efficiency of the system depends on the gas sources. Gas can be obtained from a reservoir or compressor motor or engine, or from a low-pressure reservoir with a heating chamber. The use of a compressor with a motor or engine will decrease the energy efficiency of the system and make it heavy and noisy. Using a heat chamber with a gas reservoir will enable higher efficiency as the heat energy is directly converted to mechanical energy [19].

It was found that the static characteristics of actuators are very similar to those of biological muscles, but actuators have a narrow, dynamic range. Actuators can be improved by employing lubricants to decrease the coulomb friction and viscous material is used to increase the viscous friction. One of the positive aspects of actuators is their high tension intensity compared to biological muscles. Their passive elastic characteristics can be improved using parallel and serial elastic elements. The pneumatic system used to drive the actuator needs more work to improve the efficiency of the whole system, and a lighter valve that can give a high flow rate needs to be designed. A light, quiet gas source with reasonable energy efficiency is needed, and to solve the tubing length and wrapping problem, better integration of tubing needs to be developed [19].

One of the main limitations of BPAMs for practical applications is short fatigue life (~10,000 cycles). Festo Corporation built a fluidic muscle to have a longer fatigue life by impregnating the fiber mesh into an expandable bladder [6]. The bladder, made from natural latex, was found to have 24 times more life than a synthetic silicone rubber bladder [2].

McKibben muscles have attractive properties for the development of mobile robots and prosthetic applications [21]. Most of the models used to predict the characteristics of McKibben muscles are concentrated on the effect of the braided sheath, but introducing the properties of the bladder into the design gave improved prediction of properties such as output force. A mathematical model is needed to understand the design parameters and improve desirable properties such as output force and input pressure, while minimizing undesirable properties such as fatigue properties. By coupling the effect of the properties of the braid and bladder, the performance prediction of the actuator was improved. Still, some discrepancies observed between the predictions of the model and the experimental results are believed to be due to mechanisms of elastic energy storage, the effects of friction between the bladder and braid, and friction between the fibers of the braid. The above effects are believed to be functions of the properties of braid and bladder, the actuation pressure, and the instantaneous actuator length [21].

A cockroach like robot with reasonable forward locomotion was built using only a feed-forward controller without any feedback circuit. The passive properties of BPAMs compensate for controller instabilities, acting as filters in response to perturbations, without the need for intervention of a controller. The speeds of BPAMs are higher when compared to biological muscles which are inherently slow because of neurological inputs [6].

1.2.4 Light Activated Polymers

The phenomenon of dimensional change in polyelectrolyte gels, due to chemically induced ionization, is explained by mechanochemistry. The deformation of polyelectrolyte gels produced by light-induced ionization was observed and labeled as the mechanophotochemicaleffect [22]. Observed irradiation with ultraviolet light caused the gel to swell by initiating an ionization reaction, developing an internal osmotic pressure. The gel collapsed when the light was removed and switched to its neutral state. The phase transition observed was slow due to the slow photochemical ionization and subsequent recombination of ions [23]. Phase transition due to visible light was observed later so harmful ultraviolet rays could then be eliminated when performing a phase transition.

Poly(p-*N,N*-dimethylamine)-*N*-gamma-*D*-glutamanilide) produces a dilation of 35% in each dimension, when exposed to light [22]. When irradiated for 10 minutes, poly(methylacrylate acid) gels buffered with *cis-trans* photoisomerizable (p-phenylazophenyl)trimethylammonium iodide dye produced a 10% elongation. The physical properties governing the deformation are (1) high polymeric amorphous or crystalline structures; (2) distinguishing features of porous, cross-linked gel matrices; and (3) suitable combinations of ionizeable groups. While (1) and (2) cannot be manipulated, the deformation properties of the gels can be controlled through (3). The deformation produced is independent of the stimuli used for ionization. The main demand on photoionization is that the charged species produced should have a sufficiently long life span to induce deformation; therefore, a suitable photoionization technique should be used.

A high-intensity light source is needed to produce meaningful concentrations of ions [22]. The observed transition was due to direct heating by the radiation, giving fast response. Gels were made from *N*-isopropylacrylamide with a light-sensitive chromophore and trisodium salt of copper chlorophyllin, and a 100-micrometer inner diameter capillary was used to form the gels. The phase transition experiments were carried out in a glass chamber where the temperature can be controlled within a $\pm 0.1^{o}$C range. Argon laser radiation with a 488 nm wavelength was used, and the light intensity varied from 0–150 mW. The incident beam had a Gaussian diameter of ~7 mm and focused diameter of ~20 μm, using a lens with a 19 cm focal length. At a temperature of ~35^{o}C, the gels gave a sharp, but continuous, volume change without any radiation. The transition temperature decreased as the intensity of light radiation increased. A more pronounced volume change was observed at a temperature of 33^{o}C when a 60 mW light was applied, and discontinuous volume transition was observed with 120 mW of radiation. The light-sensitive gels collapsed when radiation in the visible wavelength was used (Figure 1.4 [22]). Shrinkage was observed throughout the whole temperature range, but the largest effect was observed at a transition region. A discontinuous transition was observed at an appropriate “bulk” equilibrium temperature, when the intensity was varied from 0–150 mW [22]. The light intensity at the transition state varied from gel to gel, believed to be due to the variation in the ratios of gel and beam diameters or bleaching conditions [23].

The effect of irradiation was observed to transform continuous transition to discontinuous transition and decrease the transition temperature. The chromophores incorporated in the gel absorb light energy and dissipate heat locally by causing radiationless transitions, increasing the local temperature of the polymer. The temperature increase in the gel, due to radiation, is proportional to the light intensity and chromophore concentration [23]. The rate of observed deformation was dependent on the intensity of the light source and was found to be due to dilation instead of phase transition induced by photoionization. A 5% cross-linked polymer was too stiff to produce photo-deformation, but deformation was observed with 1.5% cross-linking. Potential applications envisaged include printing, photocopying and actinometry [22]. It was observed that the phase transitions were due to the radiation forces instead of local heating, as observed previously. A direct influence on the balance of forces was caused when a gel was irradiated with a laser beam and became shrinkage in the gel. The shear relaxation process induced gel shrinkage of several 10s of microns [24].

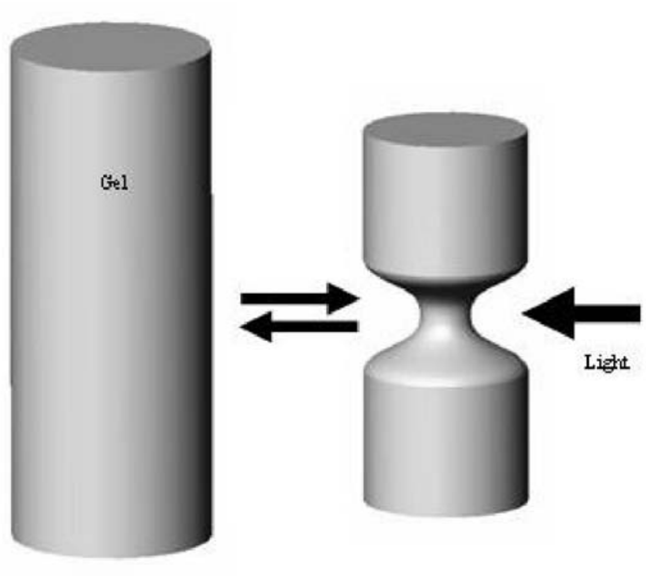

Figure 1.4. Cartoon showing the collapse of a light-activated gel under illumination

The combination of stimuli-responsive polymer gels and laser lights enables the development of a new gel-based system for actuation and sensing applications. It is known that radiation force immobilizes particles against Brownian motion and any convection [24]. These photoresponsive gels are used in such applications as artificial muscles, switches, and memory devices [23].

Azobenzene polymers and oligomers show surface relief features, when irradiated with polarized laser light. An atomic force microscope investigation of the amplitude mask irradiation of side-chain azobenzene polymers showed trenches and peaks, depending on the architecture of the polymer. Mass was transferred long distances, enabling the development of nanostructure replication technology. This technology, using polarized light, allows the storage of microscopic images as topographic features on produced polymer surfaces [25].

Extensive research is being conducted to discover other polymeric materials that change volume due to light exposure. These polymers are considered to be made of “jump molecules”—molecules that change in volume due to light exposure. Experiments have revealed that the volume change is not due to the heating of the water of hydration in the gel; instead, it is considered due to the contraction obtained by the attraction between the excited molecules in the illuminated region and surrounding molecules. Therefore, shrinkage is due to laser-induced phase transitions [2].

1.2.5 Magnetically Activated Polymers

Sensitive polymeric materials showing strain due to changes in the magnetic field are called magnetoelastic or magnetostrictive polymer materials, also often called ferrogels. The gradient of the magnetic field applied acts as the driving force [26]. A magnetic field induces forces on all kinds of materials; solid materials experience more forces than fluids. By combining fluidlike and solidlike properties in a material, the effect of magnetic force can be enhanced [3]. A magneto-controlled medium can be considered a specific type of filler-loaded swollen network. Ferrogels are a chemically cross-linked polymer network, swollen by a ferrofluid, which is a colloidal dispersion of monodomain, magnetic particles. In these gels, the magnetic particles are attached to the polymer chains by strong adhesive forces [26]. Under a uniform magnetic field, no net forces are observed on the gel, except the Einstein-de Haas effect which is caused by a change in the magnetic field vector. When these gels are subjected to a magnetic field gradient, the particles experience a net force toward the higher magnetic field. These particles carry the dispersing fluid and polymer network with them, producing a macroscopic deformation of the gel. Elongation, contraction, bending, and rotation can be obtained depending on the geometric arrangement of these materials. With their ability to create a wide range of smooth motions along with quick operation and precise controllability, these magnetic fields controlling soft and wet gels show good promise in the development of stimuli-responsive gels and actuators [26].

Electric and magnetic field-induced shape and movement was obtained in a polymer gel with a complex fluid as the swelling agent. Magnetic particles were incorporated into poly(*N*-isopropylacrylamide) and poly(vinyl alcohol) gel beads. The beads aligned as a chainlike structure in uniform magnetic field lines, and they aggregated in a nonuniform field due to magnetophoretic force. These magnetic gels give quick and controllable changes in shape, which can be exploited in applications mimicking muscular contraction [3]. The use of polymer gels as actuators creates a quick and reliable control system, and the use of electric or magnetic stimuli facilitates the development of these control systems.

A PVA gel, with magnetic nanoparticles, contracted in a nonuniform magnetic field (Figure 1.5 [26]), which is smaller than the field strength observed on the surface of common permanent magnets. By coordinating and controlling the magnetic field, muscle-like motion can be obtained, leading to the development of artificial muscles [3]. To better exploit these materials, the basic relationship between the magnetic and elastic properties of these materials should be investigated. The applied magnetic field on the gel can be better controlled using an electromagnet, where the current intensity gives the controllability. The relationship between deformation and current intensity needs to be determined for the efficient use of electromagnets [26].

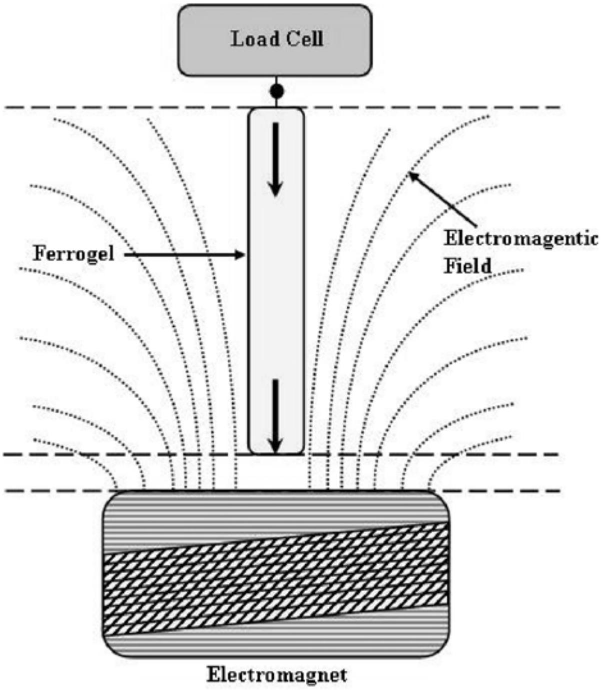

Figure 1.5. A schematic representation of the setup used to study the magnetoelastic properties of ferrogels

In a ferrogel, magnetic particles are under constant, random agitation when not under a magnetic field. Due to this random agitation, there is no net magnetic field in the material. It was observed that the magnetization of the ferrogel is directly proportional to the concentration of the magnetic particles and their saturation magnetization. In small fields, it was determined that the magnetization is linearly dependent on the field intensity, whereas in high fields, saturation magnetization was achieved [26].

For a ferrogel suspended along the axis of the electromagnet, the elongation induced by a nonuniform magnetic field depends on a steady current flow. A very small hysteresis was observed. It was determined that the modulus of the ferrogel is independent of the field strength and the field gradient. The relationship between elongation and current intensity found was a function of cross-linking densities as well. For small uni-axial strains, the elongation produced is directly proportional to the square of the current intensity [26]. The response time is only one-tenth of a second and observed to be independent of particle size. Ferrogels are generally incompressible and do not change in volume during activation [2]. Voltairas *et al.* [27] developed a theoretical model, in constitutive equations, to study large deformations in ferrogels when the hysteresis effect was not considered. This model can be used for quantitative interpretation of the magnetic field's dependent deformation of ferrogels for valve operations [27].

Through induction, magnetically heated, triggerable gels have been developed, where the heat generated from various loss mechanisms in the gel produces a thermal phase transition. The loss mechanisms include ohmic heating from eddy current losses, hysteresis losses, and mechanical (frictional) losses. Volume change was observed in these materials when a quasi-static (frequency of 240 kHz to 3 MHz) magnetic field was applied. When the field is removed, the gel returned to its initial shape, due to cooling of the material. Power electronic drives are being developed which will aid in the development of closed-loop servomechanisms for actuators. These materials show the potential in contact-less actuation and deformation wherever the magnetic field can reach, *e.g.* triggering gels under the skin [28, 29, 32].

MR rubber materials are being used in the development of adaptively tuned vibration absorbers, stiffness-tunable mounts and suspensions, and automotive bushings. These materials usually show continuously controllable and reversible rheological properties while under an applied magnetic field [30].

Magnetic polymers, with magnetic particles dispersed in a rubber matrix, have been used in magnetic tapes and magnetic gums for more than three decades [31].

1.2.6 Thermally Activated Gels

Thermally activated gels produce a volume change due to thermal phase transitions, usually within a temperature range of 20^{o}C to 40^{o}C. These polymers exhibit a contractile force of 100 kPa with a response time of 20–90 seconds [2]. Most of the studies on thermal phase transitions of gels were done on N-substituted polyacrylamide derivatives. Hirokawa and Tanaka (1984) first reported the volume phase transition of poly(*N*-isopropylacrylamide) (PNIPAAm) gel [69].

Poly(vinyl methyl ether) (PVME) is one of the most widely used thermo-responsive polymers. It undergoes phase transition at 38^{o}C; at a temperature below the phase-transition temperature, PVME is completely soluble in water. The polymer precipitates with an increase in the temperature, and the polymer network is transformed from a hydrophilic to a hydrophobic structure. When a gel was employed, the transition produced a volume change. PVME can be cross-linked into a hydrogel by gamma-ray radiation. High-energy radiation is the one of the most widely used methods to make cross-linked polymer hydrogels. With an increase in the temperature, water is expelled from the gel network, causing it to shrink. The volume phase transition, induced by temperature change, can be exploited in the development of thermoresponsive soft actuators, thermo-responsive separation, *etc*. [33].

The deformation characteristics of a thermoresponsive hydrogel can be controlled by incorporating surfactants, or ionic groups, into a polymer network. The deformation properties of the hydrogel vary depending on the type and concentration of the surfactant or ionic groups. Quick, responsive thermo-responsive hydrogels are being developed using porous PVME gels, which swell and shrink much faster than homogeneous gels. A 1 cm cube of PVME porous gel showed a response time of 20–90 seconds, with a change in temperature from 10–40^{o}C, where as a homogenous gel showed no response within the same time period. PVME porous gels show potential in the development of practical actuating devices due to this rapid temperature change [33].

Thermally sensitive polymer gels show great potential in the development of artificial muscles. Hot and cold water can be used for actuation, a favorable option compared to acid and base in chemically activated polymer gels. As the temperature increases, the swelling ratio of the PVME gel fiber decreases; this reaction increases as the temperature nears the transition point. A contractile force of 100 kPa was generated when the temperature was raised from 20 to 40ºC [33].

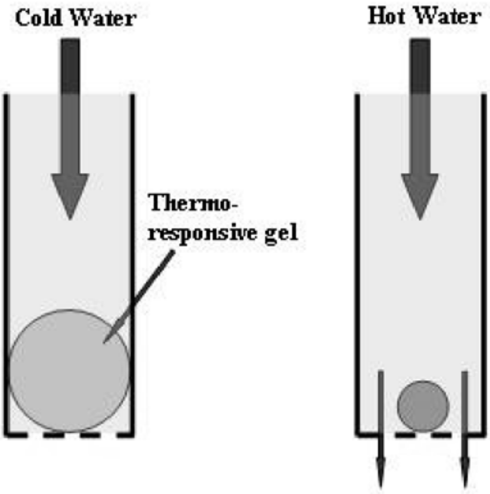

Figure 1.6. Automatic gel valve made of a thermoresponsive gel, which allows only hot water through the pipe

Thermoresponsive polymer gels are being studied for different applications. Modified NIPAAm gels are being developed for metered drug release by thermally controlling drug permeation. Gels can be used as a substrate for the immobilization of enzymes. In thermoresponsive gels, the activity of the immobilized enzyme was controlled by thermal cycling. Artificial finger and gel valve models were also developed using thermoresponsive polymer gels. The gel valve shrinks to allow only hot water while blocking the flow of cold water [33]. The solid-phase transition of a polymer was also used in the development of paraffin-based microactuators. Although large thermal expansion at the solid–liquid phase transition is a general property of long-chained polymers, the low transition temperature of paraffin was exploited in these actuators, using micromachining techniques which allow the production of many actuators on the same die. A deflection of 2.7 micrometers was obtained using a 200–400 micrometer radius device with a response time in the range from 30–50 milliseconds [34].

Thermally activated microscale valves are being developed for lab-in-a-chip applications. These valves will open and close due to a temperature-change induced phase transition (Figure 1.6). The valves also provide an advantage in production using lithographic techniques; noncontact actuation, which employs heating elements; or using heat from the fluid itself [35].

1.3 Electroactive Polymers

As stated earlier, since the last decade there has been a fast growing interest in electroactive polymers. The non-contact stimulation capability, coupled with the availability of better control systems that can use electrical energy, is driving the quest for the development of a wide range of active polymers. These polymers are popularly called electroactive polymers (EAPs), and an overview of various types of EAPs is given in the following sections.

1.3.1 Electronic EAPs

Based on the mechanism of actuation, EAPs are classified into electronic and ionic EAPs. Various characteristics of electronic EAPs have been discussed in previous paragraphs, but an overview of electronic EAPs is covered in this section.

1.3.1.1 Ferroelectric Polymers

Ferroelectric materials are analogous to ferromagnets, where the application of an electric field aligns polarized domains in the material. Permanent polarization exists even after the removal of the field, and the curie temperature in ferroelectric materials, similar to ferromagnetic materials, disrupts the permanent polarization through thermal energy [36].

Poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) is commonly used ferroelectric polymer. Local dipoles are created on the polymer backbone due to the high electronegativity of fluorine atoms. Polarized domains are generated by these local dipoles aligning in an electric field. The alignment is retained even after the removal of electric field, and the reversible, conformational changes produced by this realignment are used for actuation [36].

The polymers have a Young's modulus of nearly 1–10 GPa, which allows high mechanical energy density to be obtained. Up to 2% electrostatic strains were obtained with the application of a large electric field (~200 MV/m) which is nearly equal to the dielectric breakdown field of the material [2]. Up to a 10% strain was observed in ferroelectric polymers during the transition from the ferroelectric phase to the paraelectric phase, but the presence of hysteresis is a drawback. Hysteresis in ferroelectric materials is due to the energy barrier present when switching from one polarization direction to the other or when transforming from one phase to another [37]. A large field, in a direction opposite to the initial field, is required to reverse the polarization, dissipating substantial energy [36].

The energy barrier can be significantly reduced by decreasing the size of the coherent polarization regions to the nanoscale. This reduction is achieved by introducing defects in the polymer chains, which are created by electron radiation. Proper high electron irradiation eliminated the large hysteresis, and exceptionally large electrostatic strain was achieved. It is crucial to note that effective structures, induced by electron irradiation, cannot be recovered by applying a high electric field. For soft material, Maxwell stress can generate high strains. Ferroelectric polymers show better performance in strain and strain energy density compared to traditional piezoceramic and magnetostrictive materials [37]. Ferroelectric relaxors are practical, useful materials which show strong performance characteristics. When the Curie point in these materials is brought near to room temperature–the normal operating temperature–a nonpolar, paraelectric phase is present. This is achieved by introducing imperfections in the structure either by using radiation or incorporating a disruptive monomer along the chain [36]. These imperfections break the long-range correlation between the polar groups. Polarization is induced when an electric field is applied to these materials, but, due to the decrease in the energy barrier to the phase change, the hysteresis is reduced or eliminated [36]. The large molecular conformational changes (introduced) associated with the ferroelectric-to-paraelectric transition lead to macroscopic deformations that are used to generate actuation [36].

P(VDF-TrFE) contracts in a direction of the field and expands in the direction perpendicular to the field. The strain can be enlarged by prestraining, and moderate strains (up to 7%), with high stresses (reaching 45 MPa) have been achieved. High stiffness (70.4 GPa) was achieved but was dependent on the density of imperfections and a large work per cycle (approaching 1 MJ.m^{-3}) [36].

Ferroelectric polymers are easy to process, cheap, lightweight, and conform to complicated shapes and surfaces, but the low strain level and low strain energy limit the practical applications of these polymers [37]. Ferroelectric polymers can be easily patterned for integrated electronic applications. They adhere to wide variety of substrates, but they are vulnerable to chemical, thermal, and mechanical effects [38]. Ferroelectric EAPs can be operated in air, a vacuum, or water in a wide range of temperatures [2].

Limitations of ferroelectric polymers include fatigue of the electrodes, high electric fields, and high heat dissipation. Procurement of the fluorocarbons is also a problem due to environmental restrictions, and the *e*-beam irradiation process is expensive. The maximum strain of the polymers can be achieved only at an optimal loading condition that is dependent on the material used. This strain can decrease substantially above and below the optimal value [36].

The potential use of ferroelectric polymers can be extended by decreasing their operating potential. This can be achieved by using thin films (100 nm) or by increasing the dielectric constant. The film thickness is limited by the relative stiffness of the electrode material but can be overcome by using more compliant electrodes. The dielectric constant can be increased by adding high dielectric constant filler material. The operating temperature depends on the density of imperfections, which can be fine-tuned up or down to change the temperature range of operation. The typical range is between 20 and 80°C [36]. Instead of electrostatic energy, heat can also be used to activate ferroelectric polymers. Reversible actuation can be obtained when the materials are heated and cooled above and below their Curie points, which is just below room temperature [36].

1.3.1.2 Dielectric Elastomers

Dielectric elastomer actuators are made with an incompressible and highly deformable dielectric medium. When an electric field is applied across the parallel plates of a capacitor, the coulombic forces between the charges generate a stress, called the *Maxwell stress*, causing the electrodes to move closer. This movement squeezes the elastomer, causing an expansion in the lateral direction[39]. Dielectric elastomers are often called electrostatically stricted polymers (ESSP) actuators [2]. Figure 1.7 illustrates the operational mechanism of a dielectric elastomer with compliant electrodes. Dielectric elastomers show efficient coupling between electrical energy input and mechanical energy output [36]. Also, applying prestrain to dielectric elastomers can prevent the motion along an arbitrary direction and also introduce the motion to specific directions. It has also been observed that prestrain results in a higher breakdown potential of strains. These materials can be used as both actuators and sensors. With careful design, efficiencies as high as 30% can be obtained and be operated satisfactorily over large temperature ranges (e.g. silicone –100 to 250°C). Operation below the glass-transition temperature leads to the loss the of elastic characteristics of the material. Three commercially available materials are Dow Corning HS3 Silicone, Nusil CF 19-2186 Silicone, and 3M VHB 4910 acrylic. VHB is available in adhesive ribbons and silicones can be cast into thin films. The silicone surfaces are coated with conductive paint, grease, or powder to act as electrodes, and the typical voltages applied are in kilovolts (~10 kV) with currents in the range of less than several milliamperes [36]. Extensive theoretical and experimental studies have been done by de Rossi *et al.* [40] to characterize the effect of different electrodes and prestrain on the dielectric elastomers. The data presented help in the selection of the best electrode and prestrain values to obtain efficient response for different ranges of electric fields [40].

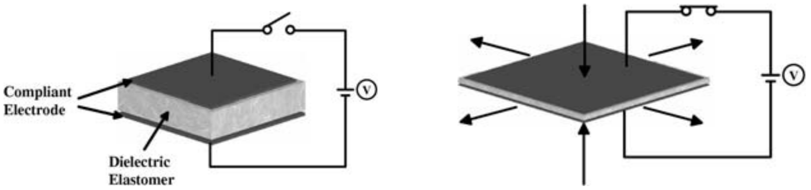

Figure 1.7. Operating principle of a dielectric elastomer

In general, the strain induced in a material is proportional to the square of the electric field and the dielectric constant. One of the ways to induce large strains is to increase the electric field, but the high electric fields involved in the actuation of dielectric elastomers can result in dielectric breakdown of the material. The strain can be increased using either a material with a high dielectric constant or films with low thicknesses. An electric breakdown field is defined as the maximum electric field that can be applied to dielectric elastomers without damaging them [41]. It was observed that the breakdown field increases with the prestrain of the elastomer. Dielectric elastomers require high electric fields for actuation (~100 V/μm), and it is a challenge to increase the breakdown strength of the elastomer at these fields. The small breakdown strength of air (2–3 V/μm) presents an additional challenge [36].

An actuator with three degrees of freedom (DOF) made of a dielectric elastomer, was developed recently. The structure has a wound helical spring with a dielectric elastomer sheet. The electrodes are patterned into four sections which can be connected to respective driving circuits. With this arrangement, the actuator can bend in two directions and also extend, giving it three degrees of freedom. Much larger deflections can be obtained from the above, and other envisaged applications include speakers (tweeters), pumps, and legged walking robots [36].

A newly designed lightweight, hyperredundant manipulator was developed which is driven by dielectric elastomers [41]; i.e. can produce precise and discrete motions without the need for sensing and feedback control. The manipulator showed great potential in the development of miniaturized actuators that have high DOFs; these binary robotic systems can have various applications from robotics to space applications. Dielectric elastomers are in the advanced stages of development for practical microrobots and musclelike applications, such as the biomimetic actuator developed by Choi *et al.* [42], which can provide compliance controllability [42].

The development of practical applications of dielectric elastomers requires the development of models for their design and control. The modeling of dielectric elastomers involves multiphysics, including electrostatic, mechanical, and material terms [43].

1.3.1.3 Electrostrictive Graft Elastomers

The electrostrictive graft elastomer is a new type of electroactive polymer developed in the NASA Langley Research Center in 1999 [44]. The graft elastomer consists of two components: flexible macromolecular backbone chains and crystallizable side chains attached to the backbone, called grafts (Figure 1.8(a)). The grafts on the backbone can crystallize to form physical cross-linking sites for a three-dimensional elastomer network and to generate electric field-responsive polar crystal domains (Figure 1.8(b)). The polar crystal domains are primary contributors to electrostromechanical functionality. When the materials is under an electrical field, the polar domains rotate to align in the field direction due to the driving force generated by the interaction between the net dipoles and the applied electric field. The rotation of grafts induces the reorientation of backbone chains, leading to deformational change and the polar domains randomize when the electric field is removed, leading to dimensional recovery. The dimensional change generated demonstrates quadradic dependence on the applied electric field as an electrostrictive material does [44].

From the experimental observations [44], it was noted that the negative strains were parallel to electric field and positive strains were perpendicular to the field. The same deformation was observed for a 180^{o} shift in the electric fields, and the direction of strains remained unchanged. The amount of strain is dictated by the electric field strength [44]. According to Wang *et al.* [45], the deformation of the graft elastomers can be described by considering two mechanisms: crystal unit rotation and reorientation of backbone chains. Crystal unit rotation draws the backbone chains toward themselves, causing an increase in the atomic density near the crystal units, that causes a negative strain. Local reorientation of backbone chains was considered to occur in three stages. In the first stage, a negative strain is generated in the direction parallel to the electric field and a positive strain perpendicular to the electric field. In the second stage, a positive strain is generated in both directions. In the third stage, negative strains will also be generated in both directions, due to the Maxwell stress effects [45].

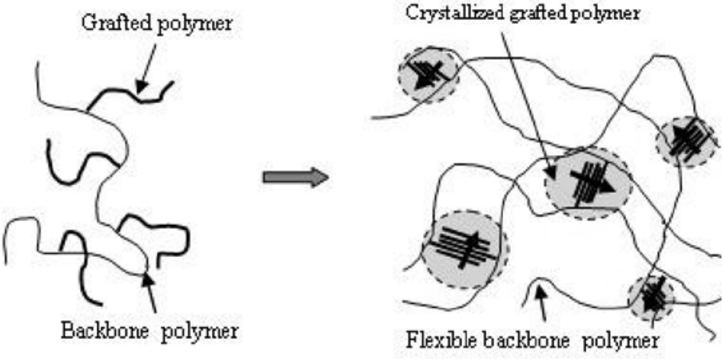

Figure 1.8. Schematic showing (a) molecular structure and (b) morphology of a grafted elastomer

One of the distinctive properties of graft polymers compared to other electrostrictive polymers is their high stiffness. Polyurethane has a modulus between 15 and 20 MPa, whereas modules of a graft elastomer are around 550 MPa, approximately thirty times more [44]. This property can be exploited in the development of an actuator that provides higher output power and mechanical energy density. Electrostrictive graft elastomers offer large electric-field-induced strains (4%) [44] and have several advantages such as good processability and electrical and mechanical toughness. Various bending actuators based on bilayers have been designed and fabricated. The sensitivity studies done by Wang *et al.* [45] showed that for a bilayer bending actuator, the curvature of the beam can be tailored by varying the thickness of the active layer. In this study, a 10% decrease in the thickness of active layer gave 30% more curvature in the beam.

An electrostrictive-piezoelectric multifunctional polymer blend was developed [44] that exhibits high piezoelectric strain and large electric-field induced strain responses. A material with the above combination can function both as an electrostrictive actuator and a piezoelectric sensor [72]. Various electrical, mechanical, and electromechanical properties of these elastomer-piezoelectric blend systems can be optimized by adjusting the composition, molecular design, and processing techniques [73].

1.3.1.4 Electrostrictive Paper

Paper, as an electrostrictive EAP (EAPap) actuator, was first demonstrated at Inha University, Korea [2]. The EAPap was made by bonding two silver-laminated papers with silver electrodes placed on the outside surfaces (Figure 1.9). A bending displacement was produced when an electrical field was applied to the electrodes. The performance of the actuator depends on the host paper, excitation voltage, frequency and type of adhesive used to bond the papers. Fabrication of these lightweight actuators is quite simple [2].

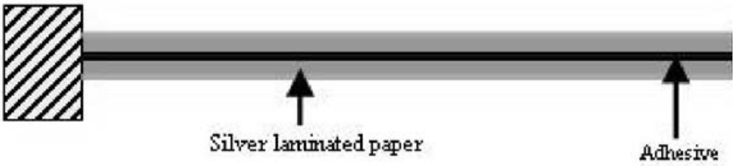

Figure 1.9. Schematic of the electrostrictive paper cantilever actuator

The successful development of a paper actuator for practical applications requires addressing various issues such as small displacement output, large excitation voltage, sensitivity to humidity, and performance degradation with time. In the initial studies, the electrostrictive effects were observed to be dependent on the adhesives used to make laminated layers. Different types of paper fibers such as softwood, hardwood, cellophane, and Korean traditional paper, all tested with various chemicals, were used to improve the bending performance of an EAPap actuator [46]. To eliminate the predominant effect of the electrodes, two different techniques were studied: the direct adhesion of aluminum foil and the gold-sputtering technique. It was determined, owing to the lower stiffness, that gold-sputtered electrodes gave better performance than aluminum foil electrodes. The paper with more cellulose, in an amorphous structure, gave a stronger response than the paper with crystalline cellulose. Cellophane gave a better response because of its amorphous cellulose with a low degree of polymerization. A combination of the piezoelectric effect and the ionic migration effect both associated with the dipole moment of the paper constituents is considered responsible for the strain observed in electrostrictive paper [46]. Although electrostriction may be an important mechanism of actuation, studies are needed to elucidate the fundamental physics of the actuation principle.

Various applications envisaged include active sound-absorbing materials, flexible speakers, and smart shape-control devices [2]. One of the unique applications being considered for the EAPap paper is an electronic acoustic tile, which broadcasts antinoise to cancel out sound or white noise in a room.

1.3.1.5 Electroviscoelastic Elastomers

Electroviscoelastic elastomers are the solid form of an electrorheological fluid (ER), which is a suspension of dielectric particles. When these ER fluids are subjected to an electric field, the induced dipole moments cause the particles to form chains in the directions of the field, forming complex anisotropic structures. During this process, the viscosity of the fluid increases greatly. An ER solid is obtained if the carrier in the ER fluid is polymerized. By careful selection, the carrier can be an elastomeric material and result in an electroviscoelastic elastomer. The ER elastomers have stable anisotropic arrangements of polarizable particles [2]. When an electric field is applied in the chain direction, these particles tend to move toward each other, creating stress, which causes deformation of the materials. Work can be obtained by opposing this deformation.

ER gels have unique advantages compared to ER fluids: no leakage, no sedimentation of particles, and ease of fabricating custom-made shapes and sizes. The key aspects of the structure of ER materials that are important for performance include the size and shape of particles, the dielectric properties, and the organization of the particles.

The numerical analysis of the ER response showed that it is strain dependent, and its response depends on the interparticle forces that increase as the particle spacing decreases [47]. It was observed that a polymer with low carrier density and mobility in an electric field would form an ideal matrix, and maximum ER responses can be observed when the particles align as a body-centered structure.

Metallic particles can be considered ideal due to their high polarizability, but their high density and conductivity precludes their use in ER fluids. This problem was eliminated in ER elastomers by maintaining enough gaps between particles in the elastomer to avoid a short circuit and by swelling the cured elastomer with curable silicone prepolymers [47]. The prepolymer acted as insulation between the particles to prevent shorts in the chain direction. The trapped particles in the swollen polymer act as isolated dipoles. The combined effect of these dipoles gives better performance.

Diluents were added to reduce viscosity and to increase swelling of the gel; the modulus of the gel doubled with an application of a 2 $kVmm^{-1}$ field, with only a 1% particle concentration. Potential applications include actuators, artificial muscles, smart skins and coating, displays, switches, valves, *etc*. [47].

1.3.1.6 Liquid Crystal Elastomers

Liquid crystal elastomers (LCE) can be activated by electrical energy applied through joule heating. LCEs are composite materials made of a monodomain nematic liquid crystal elastomer with conductive polymers distributed in the network structure [2]. In LCEs, actuation is produced through the stresses generated by the order change and alignment of liquid-crystalline side chains. These alignment changes are due to the phase changes induced by thermal or electrostatic energy [36]. Usually, flow induced in liquid crystals by stress fields prevents the build up of static forces. In liquid crystal elastomers, the liquid crystal molecules are bonded to cross-linked polymer backbones. This flexible polymer backbone allows the polymer chains to reorient themselves but prevents the flow of molecules leading to the build up of static forces that produce stresses and strains. These stresses are instead transferred, via the polymer backbone, to do mechanical work. This reorientation of the mesogens can be induced by temperature changes or by the application of an electric field [36]. The response times are typically less than a second, but the relaxation process is slower, in the range of 10 seconds. Cooling is needed to expand the material to its original dimensions [2].

In a thermally driven system, the rate-limiting factor is the heat transfer time constant that is governed by the thermal diffusivity of the base material. It is expected that the rate is proportional to the inverse of the square of thickness of the flat films. A time constant of 0.25 and 0.5 seconds was observed for a 100 µm thick flat film with heat transferred on one side, where as a time constant < 0.125

seconds was observed when heat was transferred from both sides. A time constant in microseconds may be obtained by using thin films (~1 μm) [36]. Efforts are underway to decrease the nematic isotropic transition temperature to below sub-ambient to obtain an effective elastic response [2].

The mesogen units in ferroelectric liquid crystals have intrinsic polarization or an anisotropic dielectric constant. These LCEs contract or expand in an electric field due to the reorientation of the mesogen units which induce bulk stresses and strains in the backbone. A better response can be obtained in electrostatically driven films because the electric field can be applied very quickly through the bulk of the material [36].

Factors influencing the response time include specific mesogens, the structure of the polymer backbone, and the degree of cross-linking. Faster responses can be obtained with smaller mesogens that have less cross-linked matrices [36]. Fast response time (~10ms) and large strains (~45%) were obtained from electrostatically driven and thermally driven LCEs, respectively. The applied electric fields are lower (1.5 to 25 MV/m) compared to those used in ferroelectrics and dielectric elastomers (approx 100 MV/m). Faster responses can also be obtained by irradiative heating of a thermally driven LCE film, but the cooling is still by conduction which is relatively slow in thick samples [36]. A reduction in response time was also demonstrated by employing a photoabsorption mechanism without the least effect on mechanical properties. The LCE films are coated with a thin layer of carbon on the surfaces to absorb more light energy and increase the absorption of heat by radiation [48]. Generally, the LCE samples consisted of 50–200 μm thick monodomain films, where the measured contraction stress, strain, and frequency gave values of 210 kPa, 45% and subsecond relaxation time, respectively. Optimization of the mechanical properties of these materials can be achieved through the effective selection of the liquid crystalline phase, the density of cross-linking, the flexibility of the polymer backbone, the coupling between the backbone and the liquid crystal group, and external stimuli [2].

LCEs are in the early stages of development, but it is known that due to the low stiffness and tensile strength of these materials, a relatively small change in load can induce large strains. Laser heating can be used to overcome the limitations caused by heat transfer during thermal actuation but at the cost of reduced efficiency [36]. LCEs are being studied to develop membranes that can separate right-handed and left-handed forms of drugs in the pharmaceutical industry [49]. Along with applications in artificial muscles and actuators, the elastomers can also be developed to be mechanically tunable optical elements. A swimming motion was obtained when a light was shone on a dye-doped LCE sample floating on water [50].

LCEs exhibit piezoelectric behavior: when the liquid crystals are in a smectic phase, the mesogens arrange themselves in a distinctive layered structure. The mesogens within a layer form a smectic C phase by tilting to one side at a constant tilt angle, and if the mesogen has a chiral center near the core, the chirality breaks symmetry in the unit cells, creating a degree of polarity without an external field. This material exhibits ferroelectric behavior in response to spontaneous polarization. The production of piezoelectric sensors and actuators from LCEs is easy because they do not require poling [2].

1.3.2 Ionic-EAPs

The following paragraphs give a brief overview of the various “ionic” electroactive polymers being developed.

1.3.2.1 Ionic Polymer Gels

As stated in the chemically activated polymer section, pH activated polymers such as PAN hold tremendous promise in actuator technology. However, pH changes using chemical solutions typically cause deformation of gels and are somewhat inconvenient. The formation of salts is inevitable due to the chemical reaction between the acid solution and the basic solution. The salts created may be attached to the polymer surface and block contact between the polymer chain and the protonated hydrogen ion environment, affecting the response time. The chemical actuation of synthetic gels is undesirable except in some underwater applications, and the development of the electrically driven system makes it a potential material in robotic applications. Control of the electrically driven system is easy, and the electrochemistry of the system comes into to play when electrical actuation is considered.

Electrical actuation of polymeric gels was first studied by Tanaka *et al.* [51] on polyacrylic acid gels. The gel changed shape and size when placed between electrodes that were surrounded by an aqueous solution. The gel shrank near the anode when it touched the electrode, but when the gel was not touching an electrode, it swelled near the anode. The phenomenon can be reversed by reversing the polarity of the electric field. The electrolysis of water is considered to affects the pH of the solution near the electrodes and can be superimposed on the electrical response of the gel actuators. Due to electrolysis, the region near the cathode (a negative electrode) will become more basic, as OH^- is released. Similarly, the region near the anode will become more acidic. Due to this phenomenon, when the gel system is placed near the anode, it will contract. The bending of an acrylic acid-acrylamide copolymer gel was observed by Shiga and Kurauchi [52] when the gel was placed between the electric field in aqueous solution.

Note that the response of gels is not a material property but rather is dependent on the dynamics of the electrolytic reactions of the system, the geometry of the system, the composition of the electrolyte and electrodes, and the previous history of the gel. A detailed study of the relationship between the electric field and the volume change mechanism of polymer gels is needed to determine the possibility of building a practical mechanical system with an electrically induced polyelectrolyte actuator and to better control an electrochemically driven gel actuator that is free from undesired chemical reactions. Poor mechanical properties of ionic gels are a major constraint in the development of practical applications.

Electrical activation of PAN fiber bundles has been studied by Schreyer *et al.* [53]. When the PAN muscle is near the anode side, the muscle shrinks, and when in the cathode vicinity, the PAN fiber is elongated. The elongation and contraction is done simply by changing the polarity. Furthermore, using a high-conductivity material–such as graphite or platinum coating–the PAN fiber itself can be used as an electrode. The advantage of this method is that the control motion of the PAN actuator is quite simple; the disadvantage is that the conductive material on the

PAN surface is delaminated after three to four cycles. The actuation is completely stopped after the conductive material is wiped out [13].

For electrochemically driven PAN filaments, it was observed that the diameter changes in PAN filaments are quite similar to the pH activated ones, but with a longer response time (approximately ten minutes). Single strands of fibers produced an approximate force of 10 gm_f for both aforementioned activation methods and have similar standard deviation ranges. Force generation reached a steady state within a few seconds of the chemical activation system. On the other hand, it took approximately 10 minutes for the force generation to reach a steady state in the electrochemically-driven system [13]. Efforts are currently underway to improve the response characteristics utilizing submicron-diameter electrospun PAN fibers. Actuation of ionic polymer gels is slow due to the required diffusion of ions, and the large displacement produced by electrodes deposited on the gel surface causing damage. Better performance can be obtained by using thin layers and robust electroding techniques [2]. Figure 1.10 shows an electochemically driven PAN crane system [70].

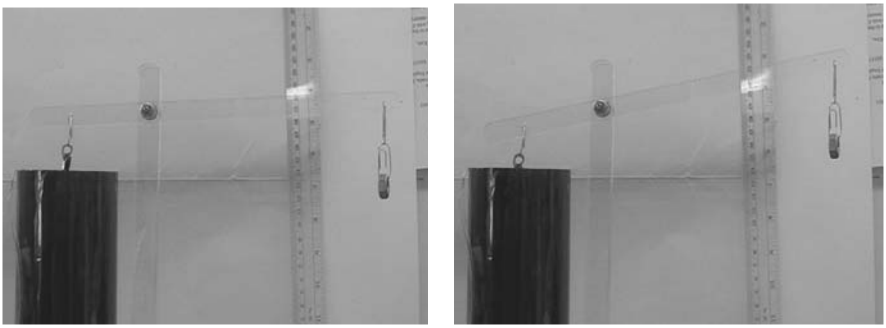

Figure 1.10. Working of PAN crane with electrochemically driven actuation system (left) before and (right) after 20minutes [70]

1.3.2.2 Ionic Polymer-Metal Composite (IPMC)

Ionic polymer-metal composites have been studied extensively in the past 15 years. Oguro *et al.* [54] initially determined that the composite of a polyelectrolyte membrane-electrode, which is a perfluorinated, sulfonate membrane (Nafion® 117) chemically coated with platinum electrodes on both sides of the membrane, deforms and bends when a low voltage (~1–5V) is applied across the electrodes in an aqueous solution [55]. A change in the ion concentration, induced by an electric field, attracts water and causes deflection toward one of the metal electrodes. Swelling occurs on one side and shrinkage on the other side due to the nonuniform distribution of water in the polymer electrolyte network [36].

An ion exchange membrane (IEM) forms the bulk of the material of the IPMC. IEMs are permeable to cations but impermeable to anions because of the unique ionic nature of the fixed perfluorinated polymer backbone. Different membranes can be used to make IPMCs, but the most commonly used are Nafion^{TM} from DuPont, USA and Flemion from Asahi, Japan. The primary applications of these polymers are in fuel cells used in hydrolysis. Nafion can exchange H^+ with other cations. The top and bottom electrode surfaces are formed when the metal ions are reduced by exchanging H^+ ions with metal ions. These two metallic surfaces have good conductivity and can be manipulated by the chemical process. IPMC's cross section resembles a sandwich with electrode layers outside and a polymer matrix in the center [55].

An ionic polymer consists of a fixed network with negative charges, balanced by mobile positive ions. The polymer network consists of pockets of solvents, and two, thin boundary layers are generated by the application of anelectric field. A cation-poor layer forms on the anode side while a cation-rich layer forms on the cathode side. Due to the accumulation of cations on the cathode side, water molecules move to this side and cause hydrophilic expansion. The stresses in the polymer matrix cause bending toward the anode. With time, the back diffusion of water molecules causes a slow relaxation toward the cathode. The degree of actuation obtained is a function of the type of polymer used, the type of counter-ion, the amount of water, the quality of metallization, and the thickness and surface area of the polymer membrane [36]. When a voltage higher than the electrolysis voltage of water is applied, blistering and damage to the electrodes was observed, causing degraded performance of the material [55].

The IPMC matrix is made of a hydrophobic polymer backbone and hydrophilic anionic sidechains and forms clusters of concentrated anions which neutralize cations and water within the polymer network. These ionic polymers, with a standard thickness, are commercially available. The solution-recasting technique developed by Kim *et al.* [56, 71] enabled control over the thickness of the films. Films with thickness in the range of 30 μm to 2 mm were produced. Ionic polymers were transformed into IPMCs by depositing metal on both sides. Metal particles (3–10 nm) were loaded on both sides penetrating the polymers up to 10–20 μm. These metal particles balance the charging at boundary layers. Metal particles are chemically loaded by soaking in $Pt(NH_3)_4HCl$ and then reducing through $LiBH_4$ or $NaBH_4$. Because this process is expensive, an inexpensive loading process was developed by Shahinpoor and Kim (2002) [56], where metal particles are physically loaded with electrode layer deposition. IPMCs produced in this way show properties comparable to chemically loaded IPMCs. This procedure also gives better flexibility in the selection of the electrode material: a wide variety of metals such as platinum, palladium, silver, gold, carbon, and graphite can be deposited by this procedure. Platinum is a widely used electrode material due to its high corrosion resistance and its higher deflection and work densities. The metal electrode decreases the surface resistance and increases current densities, giving faster actuation. IPMCs are being developed for wide range of applications and for hydrodynamic propulsion. Various swimming and flapping applications have been also been researched [36].

1.3.2.3 Conducting Polymers

Conducting polymers are electronically conducting organic materials. Actuation is produced in these materials when the electronically changing oxidation state–usually positive charges–leads to the flux of ions into or out of the polymer backbone, causing deformation. Solvent flux may also occur when there is a difference in ion composition. The insertion and removal of ions between polymer chains is considered the primary factor for dimensional change, whereas conformational change and solvent flux are considered secondary factors [36]. The basic structure of a conducting polymer actuator is a sandwich of two polymer strips with electrolyte between them (Figure 1.11). The polymer strips act as electrodes in electrochemical cells. When a potential is applied to the electrodes, oxidation occurs at the anode and reduction at the cathode. To balance the charges, ions are transferred into and out of the polymer and electrolyte. Swelling occurs when there is an addition of ions, and contraction is present when ions are removed. The sandwich bends when one electrode swells and the other shrinks, as shown in Figure 1.11 [2,57]. The chain orientation in the polymer network affects the rate of doping and redoping. The greater the orientation, the lower the rate of doping, which affects the response time of the actuators. But the higher orientation provides more achievable strength and modulus [57]. Linear actuators can easily be made by separating the electrodes from each other. Strains in this case are measured to be between 2 and 20 %.

The response of a conducting polymer actuator depends on the molecular diffusion when the electrodes are thick. When they are thin, the electrodes are limited by the RC time due to electric double-layer and electrolyte resistance effects. These issues can be addressed by using very thin electrodes with small interelectrode separation and filled with electrolytes that have high conductivity. By using this method, the conducting polymer actuator is a suitable material for the development of micromechanical actuator elements [57]. The most widely used conducting polymers include polypyrrole and polyaniline; thin films of these materials are usually produced by electrodeposition or chemical synthesis. The properties of these conducting polymers depend on the solvent and salt used during the electrodeposition synthesis. The cycle life of these polymers can be increased to hundreds of thousands using ionic liquid electrolytes. Forces up to tens of newtons are being obtained along with displacements of several millimeters. A displacement of 100 mm was obtained through mechanical amplification. Currents in the range of several hundreds of milliamperes have been used with voltages up to 10 V. In steady state, minimal current is needed to provide a catch state, where the deformation state can be held with minimal energy. This deformation can be exploited in robotic applications [36].

Compared to piezoelectric materials, conducting polymers are predicted to have higher work densities per cycle, slightly lower force generation, lower power densities, and require lower operational voltages. Conducting polymers suffer from disadvantages such as low cycle life and energy conversion efficiency, and they also need electrodes with large surface areas to achieve high actuation rates. Various applications for conducting polymer actuators being considered by researchers include actuators for micromachining and micromanipulation, microflaps for aircraft wings, micropumps, and valves for “labs on a chip”; actuators for adaptive optics and steer-able catheters; and artificial muscles for robotic and prosthetic devices [57]. Conducting polymer actuators need low actuation voltage, which is a special advantage for medical actuator applications such as catheters or for microactuators [57]. Conducting polymers are considered a suitable material as a matrix for enzymes in biosensors, which is believed to enhance speed, sensitivity, and versatility [58].

Conducting polymers have several properties–high tensile strength (>100MPa), large stresses (34 MPa), stiffness (~1 GPa modulus), and low actuation voltage (~2V)–that make them attractive actuator materials. However, in general, like other ionic EAPs, these materials have low electromechanical coupling (<1%), leading to low efficiency. Their efficiency can be improved by recovering a significant amount of energy. The low electromechanical coupling and voltages may require high currents for operation, a major constraint in the development of large autonomous applications. Practical applicability should also address encapsulation issues. Moderate strains (typically ~2–9%) can be obtained by mechanical amplification, and a maximum strain rate of 12%/s was observed. The strain rate is limited by the internal resistance of polymers and the electrolytes and ionic diffusion rate in the polymer backbone [36].

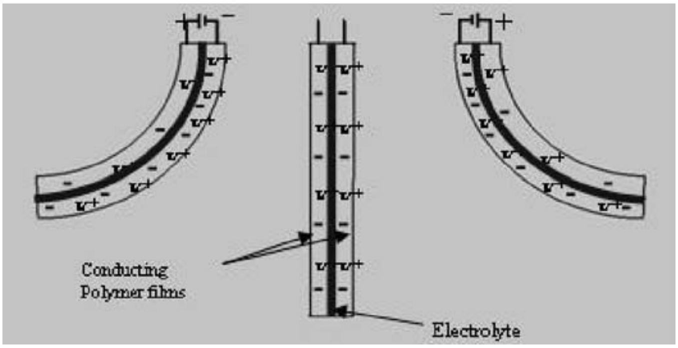

Figure 1.11. Schematic representation of three states during the electromechanical cycle of a rocking-chair type of bimorph-conducting polymer actuator. Both electrodes have the same concentration of dopant (K^+) when the cantilever is undistorted, and electrochemical transfer of dopants between electrodes causes bending either to the right or to the left.

The response rate of a polypyrrole (PPy) conducting polymer is being improved by using polymers doped with bis(trifluoromethanesulfonyl)imide (TFSI) and lithium bis(trifluoromethanesulfonyl)imide/propylene carbonate (LiTFSI/PC) as an electrolyte instead of water or propylene carbonate (PC). A response of 10.8% s^{-1} was observed, where the conventional PPy polymers gave a peak response rate of 0.1% s^{-1}, and a maximum strain of 23.6% was observed [59]. A linear actuator was developed using a PPy-metal coil composite which gave a strain of 11.6%. The composites provide tremendous flexibility in the design of actuators with a wide range of displacement and force capabilities, as they can be connected and bundled to suit the requirement. The composites can also be encapsulated and used in air [60].

Encapsulated polypyrrole actuators have been developed using a gel, doped with salt, as the electrolyte. The gel electrolyte was made of agar or polymethylmethacrylate (PMMA) and gave good actuation responses [61]. Composite conducting polymers, reinforced with textile fibers such as polyester-PPy or nylon-PPy, have good electrical properties and good structural properties, similar to textile fibers. These composites are believed to have great potential, with stealth and camouflage capabilities, in the design of aircraft fuselages. The composites can also be used in the design of continuous transport belts in coal mines, where static dissipation is of great importance. They are also being studied in the design of solar cells and displays [62].

1.3.2.4 Carbon Nanotube Actuators

Carbon nanotubes (CNTs) emerged as a formal EAP in 1999, bringing their exceptional mechanical and electrical properties to the realm of actuator technology [2]. Typically, single-walled carbon nanotubes (SWCNTs) have a minimum diameter of 1.2 nm but can be larger. Carbon nanotubes form bundles, due to van der Waal forces, are used in actuator studies, and have a typical diameter of 10 nm. The actuation of carbon nanotubes depends on charging the surface; therefore, multiwalled carbon nanotubes (MWCNTs) are considered inefficient because of their less accessible surface area [36]. Actuation was observed in nanotubes that were suspended in an electrolyte. The change in bond length, due to the injection of large charges into nanotubes, is considered responsible for the observed deformation. In a carbon nanotube, the electron flow path is provided by a network of conjugated bonds connecting the carbon atoms. The electrolytes form an electric double layer around nanotubes, creating an ionic imbalance between nanotubes and electrolytes (Figure 1.12 [63]). The C-C bond length also increases because of the repulsion between positively charged carbon atoms formed by electron removal. These dimensional changes are translated into a macroscopic deformation in a network of entangled nanotubes. When this network is used, the bond length changes translate into macroscopic deformation [2]. Coulombic forces dominate from low to moderate levels of charging, giving a parabolic relationship between the strain and the applied potential. At higher potentials, the relationship is lost because ions and solvent in the solution start exchanging electrons with nanotubes, discharging the double layer. The loss of the double layer limits the amount of maximum strain that can be obtained from CNT actuators; approximately 0.1% to 1% strains were observed. The problem of low strain is overshadowed by the huge work densities (~200 MJ/m^3) that can be obtained owing to the high elastic modulus (640 GPa) and enormous tensile strength (>>1 GPa) of these materials [36].

Present studies are being done on nanotube sheets or papers that are composed of bundle of nanotubes joined by mechanical entanglement and van der Walls forces. Actuators are fabricated by attaching strips of a CNT sheet on both sides of double-sided scotch tape (a mechanism similar to the one shown in Figure 10). Voltage applied in electrolyte bending was observed; the direction of the bending reversed with a change in the direction of potential applied [63]. Due to the random orientation and weak van der Walls forces between the nanotubes in CNT paper, the properties of these fibers and sheets were many orders in magnitude less than a single nanotube. Advances in carbon nanotube spinning techniques are providing ways to make a variety of macroscopic objects for different applications. It is believed that the unique mechanical and electrical properties of CNT strands will extend to larger scales. E-textiles are being developed composed of distributed layers of actuator and sensor segments, each segment consisting of woven CNT-based filament yarn sandwiched between two electrodes. These nanotube-based fabrics are believed to provide technology for a variety of macroscopic textile applications such as lightweight sensor systems, membrane structures with actuation and shape-changing capabilities, and power generation [64].

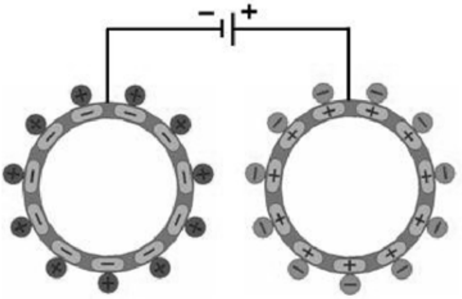

Figure 1.12. Schematic illustration of a charge injection in a nanotube-based electromechanical actuator [63]. Redrawn with pwermission from *Science* 284:1340. Copyright 1999 AAAS.

Nanotube actuators need significantly fewer volts compared to 100s of volts needed for piezoelectric actuators. Nanotube actuators have been operated at 350°C. If the mechanical properties of single nanotube can be translated to nanotube sheets, a strain of 1% will provide order-of-magnitude advantages compared to commercial actuators in work per cycle and stress generation capabilities. A maximum isometric actuator stress of 26 MPa was reported to work for a SWCNT actuator. The achievable strain is independent of an applied load, so the work done during constant load contraction increases linearly until the failure of the material occurs. High-stress applications are limited because of the creep effect. The potential applications of these nanotube actuators depend on the ability to improve the properties of nanotube sheets. These sheets are created by increasing the alignment and binding of the nanotubes. The strain rate of nanotube actuators is low compared to piezoelectrics, *etc*., and depends on ion diffusion [65]. The actuation strain rate and amount of strain for carbon nanotube sheet actuators have been improved by employing the resistance compensation technique. In the resistance compensation technique, a higher input voltage is applied to compensate for the ohmic drop that occurs across the electrolyte [66]. The strain rate of a CNT actuator depends on the rate of charge injection. Due to the availability of a huge internal surface area, enormous capacitance exists in carbon nanotubes. To obtain high strain rates, one of the critical requirements is to decrease the internal resistance of the cell. Another factor to be considered is the speed of ion transport in carbon nanotube fibers and papers [36]. It appears that the rate drops rapidly in large devices after several seconds. The rate drops further in composite carbon nanotube fibers due to the slow rate of ion transport in a polymeric binder. To develop large nanotube actuators, electrode spacing, diffusion distances, and conduction paths should be minimized by microstructuring. Due to the limited strains obtained, mechanical amplification is needed for practical applications, but their limitations include the high cost of materials, low efficiency, and poor bulk mechanical properties compared to single nanotubes [36]. At high positive potentials, a pneumatic mechanism was observed to provide giant actuation up to 300% of the thickness in the direction of carbon nanotube sheets [67].

Carbon nanotube-electroactive polymer composites are also exploited for their superior mechanical and electrical properties. They exhibit a deformation mechanism similar to polyaniline but with improved mechanical properties, allowing higher strains with higher stresses and mechanical energy densities [68]. A large electromechanical response was also reported for a carbon nanotube-nematic liquid crystal elastomer. Carbon nanotubes were aligned along the nematic director during preparation, creating a very large dielectric anisotropy. A uniaxial stress of ~1kPa at a constant field of ~1MV/m was reported showing a potential in the development of electrically driven actuators [7].

1.4. Concluding Remarks

It can be seen from the above reported research and the scale of the academic interest in active polymer materials, that they have the potential to become an indispensable part of future technological developments. With each polymer having its own niche applications, they are bound to be the materials of future. With growing emphasis on interdisciplinary research, different active materials can be combined to develop tailor-made, multifunctional properties, where single materials can act as sensors, actuators, structural elements, *etc*.

To date, the robotics community has adopted only two major active polymer technologies: dielectric elastomers and ionic polymer-metal composites because the maturity of these two technologies is inevitable. However, other technologies are also quite promising and leaves one the great potentials to use them in robotic applications. Two other technologies that the robotics community is currently considering are conducting polymers and electrostrictive graft elastomers. In later chapters, we will focus on four major active polymer technologies: dielectric elastomers (Chapters 2 and 3), electrostrictive graft elastomers (Chapter 4), conducting polymers (Chapter 5), and ionic polymer-metal composites (Chapters 6–10). We all expect that the robotics community will adopt other promising active polymer materials as their maturity and availability improve.

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