Intelligent Materials for Intelligent Textiles

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Abstract
Interest in intelligent materials has been growing rapidly since the late 1980s, and recently they have become an individual group of materials. A widely-accepted definition states that a material can be called intelligent when it simultaneously plays a role of a sensor, a processor and a transferring signal device. Intelligent polymers appeared much later than the metallic and ceramic materials. In this paper, a brief overview of selected intelligent polymeric materials and systems is given in order to attract the attention of the textile community and to suggest fields for their potential applications in intelligent textiles. The focus is put on piezoelectric, shape memory and electroactive polymers, as well as stimuli-responsive polymers. Theoretical and experimental evidence exists that such materials can also find applications as intelligent textiles, e.g. those which have the ability to change colour, generate and store heat, monitor health and many other functions.

Key words: *intelligent polymers, shape-memory polymers, piezoelectric polymers, electroactive polymers, stimuli-responsive polymers.*

Introduction

We have always been inspired to mimic nature in order to create our clothing materials with higher levels of functionality and intelligence. The development of microfibres is a very good example, starting from studying and mimicking silk, then creating finer and, in many ways, better fibres. However, up to now, most textiles and clothing have been lifeless. It would be wonderful to have clothing like our skin, which is a layer of smart material. The skin has sensors which can detect pressure, pain, temperature, etc. Together with our brain, it can function intelligently with environmental stimuli. It generates large quantities of sweat to cool our body when the surroundings are hot, and to stimulate blood circulation when cold. It changes its colour when exposed to a higher level of sunlight, to protect our bodies. It is permeable, allowing moisture to penetrate yet preventing unwanted species from getting in. The skin can shed, repair and regenerate itself. To study and then develop a smart material like our skin is itself a very challenging task.

Currently does not exist commonly accepted definition characterising intelligent materials, which leads to ambiguities in classifying different materials to this group. Moreover, the term "intelligent" is frequently used parallel to the other ones like "smart" or "adaptive". In this paper we consequently use the term intelligent materials. A widely accepted definition states that one can call the material as intelligent when it simultaneously plays a role of a sensor, processor and transferring signal device (actuator), accompanied by simultaneous feedback.

In the last decade, research and development in smart/intelligent materials and structures have led to the birth of a wide range of novel smart products in aerospace, transportation, telecommunications, homes, buildings and infrastructures. Although the technology as a whole is relatively new, some areas have reached the stage where industrial application is both feasible and viable for textiles and clothing [1].

Many exciting applications have been demonstrated worldwide. Extended from the space programme, heat generating/storing fibres/fabrics have now been used in skiwear, shoes, sports helmets and insulation devices. Textile fabrics and composites integrated with optical fibre sensors have been used to monitor the soundness of major bridges and buildings. The first generation of wearable motherboards has been developed, which have sensors integrated inside garments and can detect information regarding injury to and health of the wearer, and transmitting such information remotely to a hospital. Shape memory polymers have been applied to textiles in fibre, film and foam forms, resulting in a range of high-performance fabrics and garments, especially sea-going garments. Fibre sensors, which are capable of measuring temperature, strain/stress, sensing gas, biological species and smell, are typical smart fibres that can be directly applied to textiles. Conductive polymer-based actuators have achieved very high levels of energy density. Clothing with its own senses and brain, such as shoes and snow coats which are integrated with Global Positioning System (GPS) and mobile phone technology, can tell the location of the wearer and give him/her directions. Biological tissues and organs such as ears and noses can be grown from textile scaffolds made from biodegradable fibres. When integrated with nanomaterials, textiles can be imparted with very high-energy absorption capacity and other functions such as stain proofing, abrasion resistance, light emission, etc [1]. Incorporating of electronic devices into textiles leads to new branch of science called textronics [2].

Interest in exhibiting intelligent behaviour in polymers arose much later than was the case for metallic or ceramic intelligent materials. Within the last two decades, the role of intelligent polymers has grown rapidly due to promising research results proving that some polymers show properties useful for practical applications. The scientific data available indicates that the current level of knowledge on various intelligent polymers differs substantially. The basic reports have appeared in parallel with advanced developments which are ready for implementations. The most important of the intelligent polymers are piezoelectric, shape memory and electroactive polymers (conductive polymers, dielectric elastomers and polymer ionic gels) as well as stimuli-responsive polymers.

As the use of intelligent materials grows, it has become increasingly important for scientists and engineers, working in fields ranging from material science to electronics and biomedicine, to understand the properties and potential of intelligent polymers.

Overview of intelligent polymers

Shape-memory polymers

Polymers showing a thermally induced shape-memory effect are the subject of growing interest, and have been studied intensively. Because it is relatively easy

to manufacture shape-memory polymers (SMP), these materials are a cheap and efficient alternative to well-established metallic alloys. SMP are distinguished by low density and have the capacity to recover from the large strain imposed by mechanical loading. The unconstrained recoverable strain limits in SMP are on the order of 100%, in sharp contrast to shape-memory metals. A very broad spectrum of possible application for shape-memory polymers covers the area from non-invasive surgery to technical devices.

The shape-memory effect results from the polymer structure that could be formed in the proper production techniques. Shape-memory behaviour can be observed for miscellaneous polymers that may differ significantly in their chemical composition. The shape-memory effect is observed in multiblock copolymers, mainly polyurethanes. The mechanism of the thermally induced shape-memory effect of linear block copolymers is based on the formation of a phase-separated morphology with one phase acting as a molecular switch [3]. As shown in Figure 1, if the temperature is higher than the transition temperature T_{trans} (e.g. glass transition T_g or melting point T_m) of the switching segments, these segments become flexible and the polymer can be easily deformed elastically. The temporary shape is fixed by cooling down below T_{trans}. If the polymer is heated up again, the permanent shape is recovered [4].

Piezoelectric polymers

Piezoelectric polymers have been known for more than 40 years, but in recent years they have gained a reputation as a valuable class of intelligent materials. The properties of those polymers are very different from those of ceramic materials, and they are uniquely qualified to fill niche areas where ceramics cannot perform as effectively. The piezoelectric strain constant (d_{31}) for polymers is lower than that of ceramic materials. However, piezoelectric polymers have a much higher piezoelectric stress constant (g_{31}), which indicates that they are much better sensors than ceramics. Piezoelectric polymeric sensors and actuators offer the advantage of processing flexibility because they are lightweight, tough, readily manufactured in large areas, and can be cut and formed into complex shapes. They also exhibit high strength and impact resistance. Other notable features of the piezoelectric polymers are low dielectric constant, low elastic stiffness, and low density, which results in high voltage sensitivity (excellent sensor characteristics) and low acoustic and mechanical impedance (crucial for the medical and underwater applications). Polymers also typically posses high dielectric breakdown and high operating field strength, which means that they can withstand much higher driving fields than ceramics. Based on these features, piezoelectric polymers posses their own established area for technical application and useful device configurations [5].

Among the existing piezoelectric/ferroelectric polymers, PVDF [poly(vinylidene fluoride)] and its copolymers P(VDF-TrFE) [poly(vinylidene fluoride-trifluoroethylene)] and P(VDF-TFE) – [poly (vinylidene fluoride-tetrafluoroethylene)] exhibit the best electromechanical performances. The copolymer P(VDF-TrFE) containing 50-80 mol% VDF has attracted much attention because the materials can easily be prepared to have a ferroelectric phase, which exhibits piezo- and pyroelectricity [6].

The PVDF becomes piezoelectric when stretched during fabrication. Thin sheets of the cast polymer are drawn and stretched in the plane of the sheet in at least one direction, and frequently also in the perpendicular direction, in order to convert the material into its microscopically polar phase. Crystallisation from a melt forms the non-polar α phase, which can be converted into another polar β phase by uniaxial or biaxial drawing; these dipoles are then reoriented by electric poling, as shown in Figure 2. An applied electric field of up to 100 kV/mm at an elevated temperature, typically 103 °C, causes a permanent polarisation that is maintained after the material cools to room temperature.

The electromechanical characteristics of the PVDF-based polymers originate from the crystalline regions in the material. The morphology of such polymers consists of crystallites dispersed within amorphous regions. The polarisation in PVDF depends on a number of factors, including polarising temperature and time, polarising process, electrode conditions, and the morphology of the material, but it can remain constant for many years if it is not degraded by moisture uptake or elevated temperatures. These semicrystalline fluoropolymers are currently the only commercial piezoelectric polymers [6, 7].

Copolymerisation of vinylidene fluoride with trifluoroethylene (TrFE) results in a random copolymer (PVDF–TrFE) that has a stable, polar β phase. This polymer does not need to be stretched; it can be poled directly as formed [7].
Typical applications of the piezoelectric polymers comprise sensing and actuating devices in medical instrumentation, robotics, optics, computers and also ultrasonic, underwater and electroacoustic transducers and microphones. Potential applications of piezoelectric polymers cover artificial muscles, bio-inspired robotics, active pump applications, sensors to monitor intracellular conditions, and actuators as valves for controlled drug delivery [5, 8].

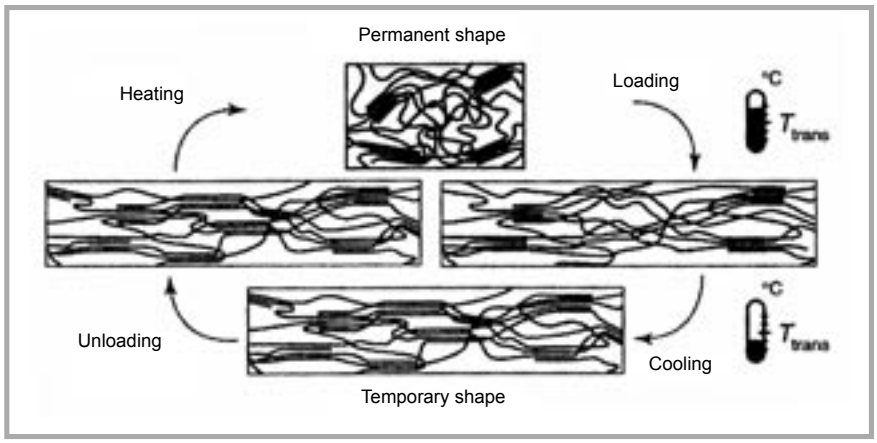

Figure 1. *Schematic illustration of the thermally induced shape-memory effect for a multiblock copolymer [4].*

Electroactive polymers

Electroactive polymers (EAP) are one the most important and promising group

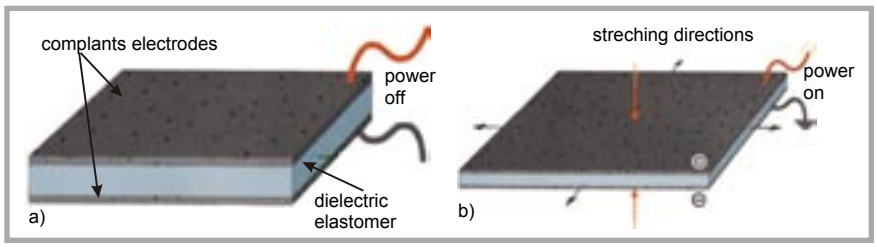

Figure 3. *Principle of dielectric elastomer actuators: a) initial state, b) activated state [14].*

of intelligent polymers. They respond to electrical stimulation with a significant change in shape or sizechange. They are lightweight and easy to control. EAP materials can easily be formed in various shapes, their properties can be engineered, and they can potentially be integrated with microsensors to produce actuators.

Available EAP materials can be divided into two distinct groups: electronic (driven by an electric field or Coulomb forces) and ionic (involving mobility or diffusion of ions) [9]. The first group includes such polymers as electrostrictive, dielectric, ferroelectric and liquid crystals; the second includes conductive polymers, ionic gels and polymer-carbon nanotube composites. Polymer-carbon nanotube-based nanoactuators and robotic systems are able to manipulate nanosize objects in a controlled, reproducible and reversible manner. The electronic EAPs are driven by an electrical field and they require high activation voltage. The ionic EAPs are involved with the mobility or diffusion of ions and require lower voltage [10].

The discovery of electrical conductivity in molecular charge transfer (CT) complexes in the 1950s promoted the development of conducting CT polymers. In 1980, superconductivity with molecular CT complexes was discovered. The conductivity in the CT complexes arises from the formation of appropriate segregated stacks of electron donor and acceptor molecules, as well as a certain degree of charge transfer between the stacks. Various conjugated polymers with excellent electrical properties have been synthesised over the past 25 years. The most common are polypyrolles, polyanilines and polythiophenes. Certain conjugated polymers also possess interesting optical and magnetic properties. These unusual optoelectronic properties allow them to be used for a large number of applications including sensing devices, actuators, non-linear optical devices and light emitting displays [11]. Various applications are being explored in such fields as medical, aerospace, entertainment and consumer products. The recent development of sensor arrays (conducting polymer electronic 'noses', DNA chips, etc.) is revolutionising the way in which many chemical and biomedical tests are performed in both research and clinical diagnostic laboratories. Sensor arrays consist of many different sensors on a single chip, and enable complex mixture systems to be identified, even without separation.

EAPs have also been used to make microelectrochemomechanical systems (MEMS) or electrochemomechanical actuators, used as 'artificial muscles'. Actuators based on conjugated conducting polymers are capable of producing at least 10 times more force per unit of cross-sectional area than a biological muscle, with a strain of typically between 1 and 10%. The high force-generation capabilities, high work densities per cycle and low operation voltages make conducting polymer actuators very attractive for use in robotics, prosthetics and MEMS, and many other applications, in place of conventional electrostatic and piezoelectric actuators.

Dielectric elastomers are of particular interest for the present application, due to their high actuation speed and very large strains [12]. The dielectric elastomer actuator is a three-component system consisting of a soft dielectric elastomer between two compliant electrodes, as shown in Figure 3.a. Application of an electric field polarises the elastomer, generating a 'state of stress' within the dielectric medium called the Maxwell stress. Coulomb forces arise between the oppositely charged electrodes; the actuator stretches in the directions perpendicular to the force, and thins in the direction parallel to the force (Figure 3.b) [13].

Dielectric elastomers can be used for intelligent assemblies and textiles which change their surface quality. As shown in Figure 4, compliant electrodes are uniformly spaced as dots over and under the dielectric elastomer. After application of an electric field, the elastomer changes

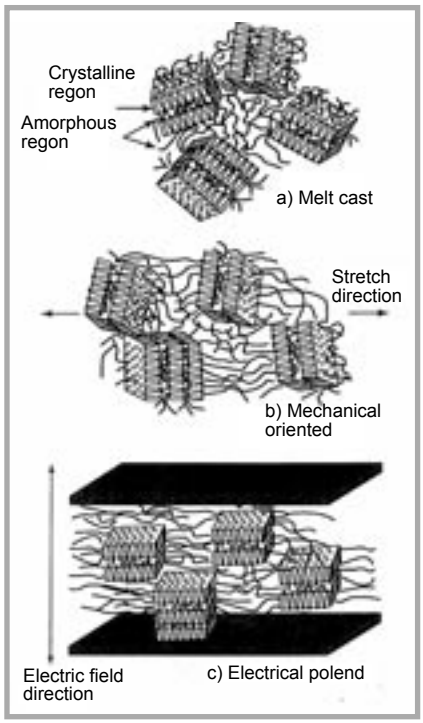

Figure 2. *Schematic illustration of random stacks of amorphous and crystal lamellae in a PVDF polymer [5, 6].*

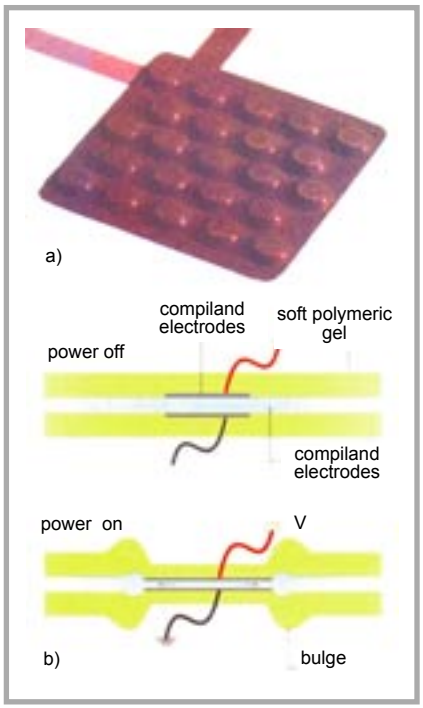

Figure 4. *Intelligent surface based on dielectric elastomer [15]; a) photo of the surface, b) schematical view of switching on power.*

its thickness between electrodes, which results in bulging on the material's surface. The effect of bulging is more visible when the surface is made from a soft polymeric gel. Such intelligent surfaces can be used as camouflage clothing in military contexts [14].

Stimuli-responsive polymers

Polymers that alter their characteristics in response to changes in their environment have been of great interest recently [7]. A responsive macromolecule is one that changes its conformation and/or properties in a controllable, reproducible, and reversible manner in response to an external stimulus (e.g. solvent, pH, or temperature). These changes in conformation (physicochemical) properties of the stimuli-responsive polymers can be used to create a large variety of smart devices, such as sensors, actuators and controlled release systems, for various practical applications [11, 16]. One of their most important applications is the controlled drug delivery system. The overall goals in developing controlled release devices are to maintain the drug in the therapeutic range and to target delivery to the specific tissues [7].

Several research groups have been developing drug delivery systems based on these responsive polymers which more closely resemble the normal physiological process. Drug delivery in these devices is regulated by an interaction with the surrounding environment (feedback information) without any external intervention. The most commonly studied polymers that have environmental sensitivity are either temperature- (Figure 5) or pH-sensitive (Figure 6) [7, 11].

Temperature-sensitive polymers (Figure 5) can be classified into two groups based on the origin of the thermosensitivity in aqueous media. The first is based on polymer-water interactions, particularly theirspecific hydrophobic/hydrophilic balancing effects and the configuration of side groups. The other is based on polymer-polymer interactions, in addition to polymer-water interactions [7].

It is also possible to apply stimuli-responsive polymers, especially environment-sensitive hydrogels, to temperature-sensitive textiles. Among the environment responsive polymers, used for this purpose, poly(N-isopropyl acrylamide) has attracted considerable attention due

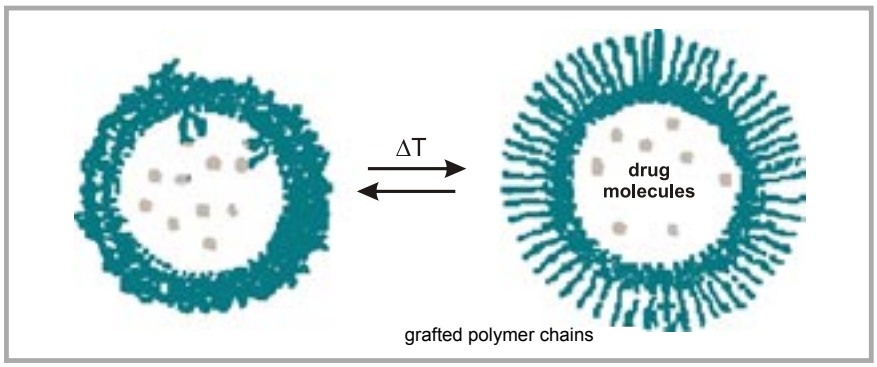

Figure 5. *Schematic illustration of the polymer-grafted capsule membrane for controlled release [18].*

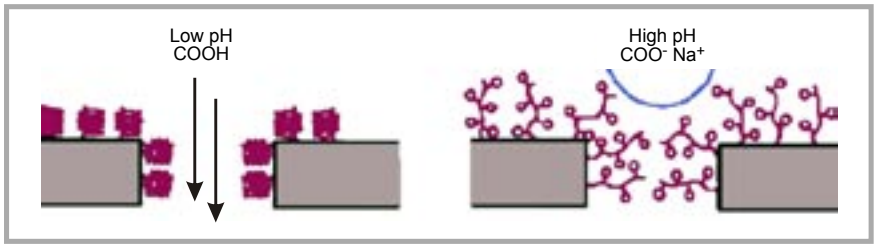

Figure 6. *Schematic illustration of pH-dependent water permeation through a porous membrane grafted with ionisable polypeptide [18].*

to its well defined lower critical solution temperature in an aqueous medium of temperature about 32 - 34 °C, which is close to body temperature [17].

The pH range of fluids in various segments of the gastrointestinal tract may provide environmental stimuli for responsive drug release. Polymer segments in such gels interact with each other through attractive or repulsive electrostatic interactions and through hydrogen bonding. The combination of these forces seems to result in the existence of several phases, each characterised by a distinct degree of swelling, and by the abrupt jumps occurring between them. The existence of these phases presumably reflects the ability of macromolecular systems to adopt different stable conformations in response to the changes in environmental conditions. A similar approach was proposed by Bell and Peppas; membranes (Figure 6) made from grafted copolymer showed pH sensitivity. By changing the pH of a solution, a drug may be rendered charged or uncharged.

Stimuli-responsive polymers can also find application in intelligent textiles, as bulky protective and tough clothes for the winter. Some thermo-responsive macromolecules could be attached to the nanotube fibres that run along the fabric in the outer part of the cloth. The polymer would shrink when the fibres detect cold conditions from the surrounding environment, keeping the inside layers protected from moisture and cold air [1].

Summary

Among a variety of intelligent materials, polymers appear to be the most promising for applications in textile industry. They could help us to solve many problems of everyday life. The incorporation of intelligent polymers in textiles would allow several functions to be combined in one cloth. They could make them good-looking, light and thin, while at the same time being more protective and tougher. The polymers can change the surface property by altering the light scattering coefficient. Incorporating the fibre sensors in the cloth will enable the measurement of temperature, strain/stress, and the sensing of gases, biological species and smell.

The ideas proposed in this paper could become reality, as the technology of intelligent materials is developing so rapidly that it will soon affect many aspects of our everyday life. However, most of these developments will come from interdisciplinary efforts, combining knowledge from the fields of physics, chemistry, biochemistry, material science and electronic engineering.

References

1. *Intelligent fibres, fabrics and clothing, edited by Xiaoming Tao, CRC Press, Cambridge, (2001).*
2. *Gniotek K., Krucińska I.: „The Basic Problems of Textronics", Fibres & Textiles in Eastern Europe, vol. 12, 1(45)2004, pp. 13-16.*
3. *Gall K., Dunn M.L., Liu Y., Finch D., Lake M., Munshi N.A.: Shape memory polymer nanocomposites, Acta Materialia 50 (2002), p.5115.*
4. *Encyclopaedia of Polymer Science and Technology, vol. 4, Wiley & Sons, (2003).*
5. *Encyclopaedia of Smart Materials, vol. 2, edited by MEL SCHWARTZ, Wiley & Sons, (2002).*
6. *Li Z., Arbatti M.D., Cheng Z.Y.: Novel electroactive polymer system – PVDF based polymer blends, Proc. of SPIE, vol. 5385 (2004), pp. 99-107.*
7. *Encyclopaedia of Smart Materials, vol. 1, edited by MEL SCHWARTZ, Wiley & Sons, (2002).*
8. *Korde U.A., Wickersham M.A., Carr S, Jenkins C.H.M.: Active Control of Stiffness and Dumping of Piezoelectric Polymer Films, Proc. of SPIE, vol. 6168 (2006) 61681R, pp.1-10.*
9. *Bar-Cohen Y.: EAP as Artificial Muscles – Progress and Challenges, Proc. of SPIE, vol. 5385 (2004), pp.10-16.*
10. *Hanson D., Bergs R., Tadesse Y., White V., Priya S.: Enhancement of EAP Actuated Facial Expressions by Designed Chamber Geometry in Elastomers, Proc. of SPIE, vol. 6168 (2006), 616806, pp.1-9.*
11. *Dai L.: Intelligent Macromolecules for Smart Devices, Springer, London (2004).*
12. *Plante J-S, Dubowsky S.: On the Nature of Dielectric Elastomer Actuators and Its Implications for Their Design, Proc. of SPIE, vol. 6168 (2006), 61681J, pp. 1-11.*
13. *Goulbourne N., Frecker M., Mockenstrum E.: Electro-Elastic Modeling of a Dielectric Elastomer Diaphragm for a Prosthetic Blood Pump, Proc. of SPIE, vol. 5385 (2004), pp.122-133.*
14. *Bolzmacher C., Biggs J., Srinivasan M.: Flexible Dielectric Elastomer Actuators for Wearable Human-Machine Interfaces, Proc. of SPIE, vol. 6168, (2006), 616804, pp.1-12.*
15. *Ashley S.: Sztuczne mięśnie, Świat Nauki 11 (2003) 147, pp. 49-55.*
16. *Nanoengineering of Structural, Functional, and Smart Materials, edited by Schulz M.J., Kelkar A.D., Sundaresan M.J., CRC Press, Boca Raton (2006).*
17. *Baohua Liu, Jinlian Hu: The Application of Temperature - Sensitive Hydrogels to Textiles: A Review of Chinese and Japanese Investigations, Fibres & Textiles in Eastern Europe, vol. 13, 6(54)2005, pp. 45-49.*
18. *Ito Y., Ochiai Y., Park Y.S., Imanishi Y., J. Am. Chem. Soc. 119 (1997), p.1619.*

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