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A COMPREHENSIVE EVALUATION OF 'ACTIVE SMART POLYMERS "A SYSTEMATIC REVIEW AND FUTURE PERSPECTIVE"

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ABSTRACT

Smart polymeric materials exhibit significant changes in their properties when subjected to minor changes in their surroundings. These environmental factors can include temperature, pH levels, chemicals, and light. These materials, which are sensitive to stimuli, can be either artificially created or naturally occurring. Over the past decade, the utilization of smart materials in various biological applications has gained significant importance. These applications encompass solving biological problems such as bio separation, drug delivery, biosensor design, tissue engineering, protein folding, and microfluidics. The objective of these endeavors is to imitate the intelligent behavior observed in biological systems and ultimately regulate complex systems like immune responses at desired levels. The remarkable versatility and untapped potential of smart polymeric materials position them as an exciting intersection between the fields of chemistry and biology.

Keywords: *Polymers, Smart devices, Biomaterial, Robots, Medicine.*

Introduction

Polymer materials were initially studied for their use as static structural components (Ling et al 2019) However, there is growing interest in advanced polymer materials that exhibit special functions in response to external conditions, similar to the intelligence observed in nature (Peponi et al 2017). These polymers are referred to as smart polymers or stimuli-responsive polymers. The motivation for exploring these active smart polymers came from scientists' attempts to mimic animal locomotion (Franinović and Franzke 2019). Early rigid robots attempted to emulate animal movement, starting with quadruped stair climbers. However, these robots were not able to accurately mimic animal behavior due to their legs being different from real legs. Researchers then aimed to develop robots that could move more like snakes (e.g., ACM-R5) or bipedal robots like M2. However, these robots relied on motor-based mechanisms rather than muscle-based locomotion, which is characteristic of animal-based systems. Consequently, the question arises: Can we create a muscle-based locomotion system (Chopra et al 2013)

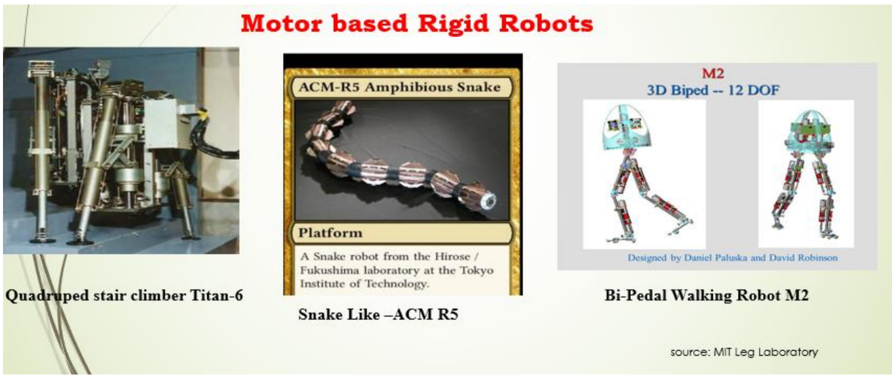

Fig.1. Motor based Rigid Robots.

Active smart polymers are capable of being developed to respond to external stimuli. These polymers can change their shape or size when exposed to specific triggers. There are two categories of active smart polymers:

1. Active polymers, which respond to non-electrical inputs such as pH, magnetic or electric fields, and light. An example of an active polymer is Azobenzene, which is photo-responsive.

2. Electro-active polymers (EAPs), which respond to changes in electrical input.

Let's take the example of Azobenzene, an active smart polymer that falls under the category of active polymers. Azobenzene is a chemical compound consisting of two phenyl rings connected by a N=N double bond. It exhibits a light-responsive behavior due to the presence of N=N double bonds. When visible light is applied, the N=N bonds adopt a cis-conformation, causing the polymer to bend. Under a UV light source, the polymer transitions to a trans conformation, resulting in the polymer becoming flat. This alternating flat-bent sequence can generate an inchworm-like motion. Consequently, the system achieves motion that is actuated by light.

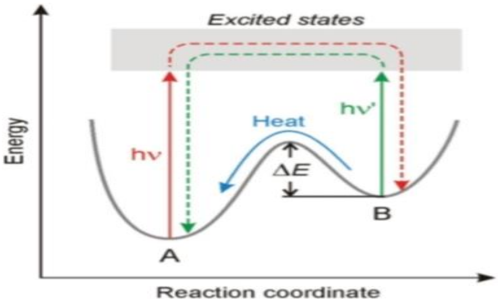

Fig. 2.A simplified energy diagram is used to represent the conversion between two isomers of a photochromic system.

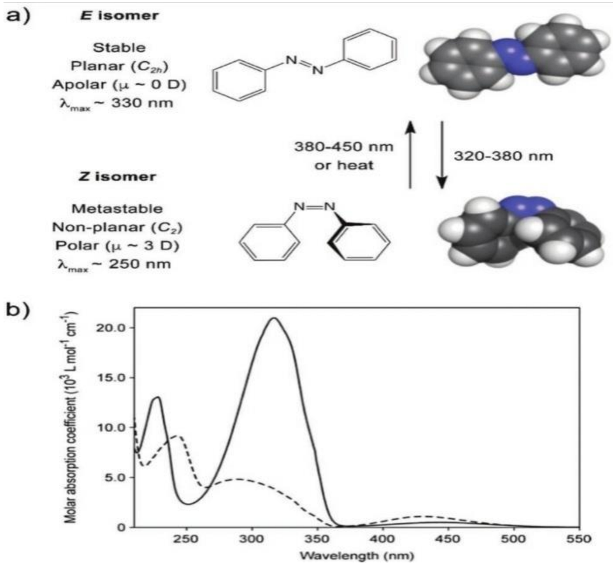

Fig 3. a) The photo- and thermally induced interconversion between the E and Z isomers of azobenzene is depicted. Additionally, b) the UV-visible absorption spectra of E-azobenzene (represented by a solid line) and Z-azobenzene (represented by a dashed line) in acetonitrile at room temperature are provided.

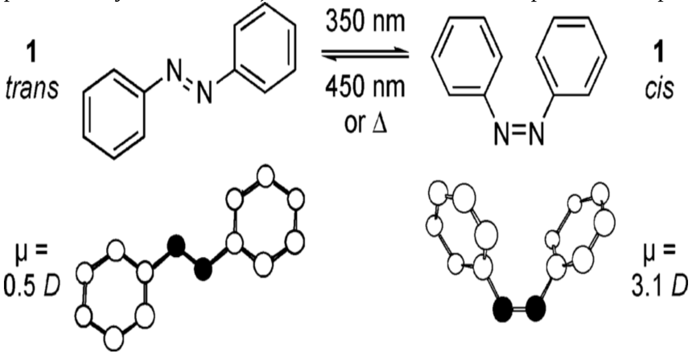

Fig.4. Inter-conversion of photo-switchable polymer azobenzene

Azobenzene and its derivatives exhibit reversible transformations upon exposure to UV or visible light. This transformation involves converting from the more stable trans-form to the less stable cis-form, which depends on the wavelength and temperature of the light. As a result of this process, the absorption characteristics of the molecule change. The strong absorption at 350 nm, associated with the trans isomer, decreases, while the absorption maximum at 450 nm, associated with the cis isomer, increases.The isomerization of azobenzene occurs with high quantum yields and without significant competing reactions. When azobenzene is irradiated with light, rotation around the N=N bond becomes restricted, leading to the breaking of the bond and the formation of a single bond that allows free rotation. This rotational or inversion motion leads to the conversion from trans-azobenzene to cis-azobenzene.The photoinduced isomerism of azobenzene results in significant structural changes, including a reduction in the distance between the para carbon atoms from approximately 9.0 Å in the trans form to 5.5 Å in the cis form. Moreover, the dipole moment of the molecule alters, with trans-azobenzene having an almost zero dipole moment, while the nonplanar cis compound possesses a dipole moment of 3.0 D.

The presence of electron-donating or electron-withdrawing substituents on the benzene rings of azobenzene affects the height of the inversion barrier in the ground state. This influences the ease or difficulty of the isomerization process. Consequently, azobenzene and its derivatives hold potential for applications in light-controlled chemical functions. They can serve as chemical condensers for light energy storage or mediators for chemical reactions. These findings open up the possibility of controlling chemical functions using an "on-off light switch" mechanism.

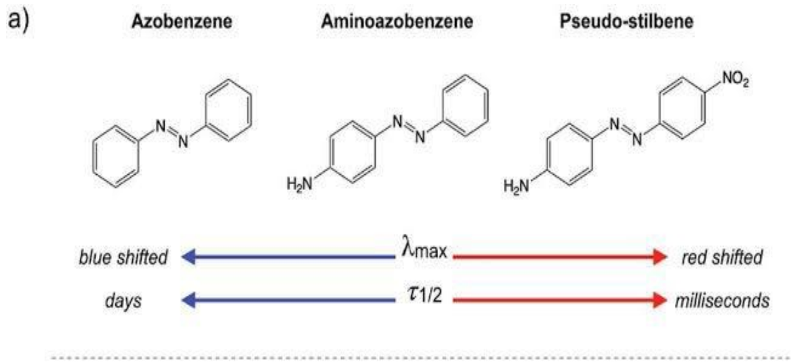

Fig.5.*Tuneable photo-switching of Azobenzene using different substituents*

Ionic Polymer metal Composites:

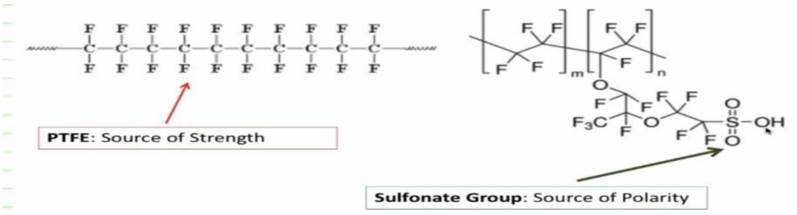

Fig.6. Structure of Nafion

Working mechanism of IPMC: Ionic polymer metal composites (IPMCs) are nanomaterials that mimic muscle-like behavior when exposed to an electric field or voltage. They consist of an ionic polymer, such as Nafion® or Flemion®, with chemically plated or physically coated surfaces using conductive materials like platinum or gold. IPMCs have gained attention as lightweight, flexible, and soft materials that efficiently convert electrical energy into mechanical energy. They exhibit significant bending strain response at low activation voltages.With the increasing demand for flexible and miniaturized actuators and sensors in the field of soft robotics, IPMCs have emerged as promising materials over the past two decades. As a type of electroactive polymer (EAP), IPMCs offer numerous advantages in soft robotics, including their lightweight, flexibility, softness, efficient conversion of electrical energy into mechanical energy, large bending strain response at low voltages (around 1-3V), low power consumption, rapid response, mechanical and chemical tolerance, stability, and ease of miniaturization. They can be used as soft actuators in applications such as microrobots and underwater robots. Additionally, IPMCs can convert mechanical energy into electrical energy and possess self-sensing capabilities, making them suitable for sensing applications.For example, Nafion is a perfluoro sulfonated proton conductor commonly employed as a proton conductor in fuel cells, water filtration, and caustic soda production. It allows the movement of cations while preventing the movement of anions or electrons.The structure of an IPMC typically consists of a thin electrolyte membrane sandwiched between two noble metal electrode layers. When an electric field is applied, cations and water molecules migrate towards the cathode, resulting in strain and bending of the IPMC towards the anode. Conversely, mechanical deformation or other stimuli applied to the IPMC can induce ion migration, resulting in potential differences on both sides of the IPMC.

IPMCs can have four components: a mid-layer, cations, solvents, and electrode layers. Researchers have focused on optimizing these components to enhance the performance of IPMCs. By arranging plated electrodes in a non-symmetric configuration, the applied voltage can induce various deformations such as twisting, rolling, torsion, turning, bending, and more. Conversely, applying physical deformations to IPMC strips can generate voltage signals, making them useful as sensors and energy harvesters. IPMCs, as electroactive polymers, work effectively in both liquid and air environments.

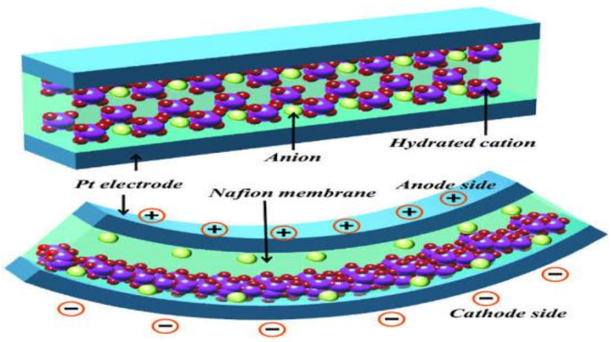

Fig.7. Mechanism of bending and sensing in Nafion

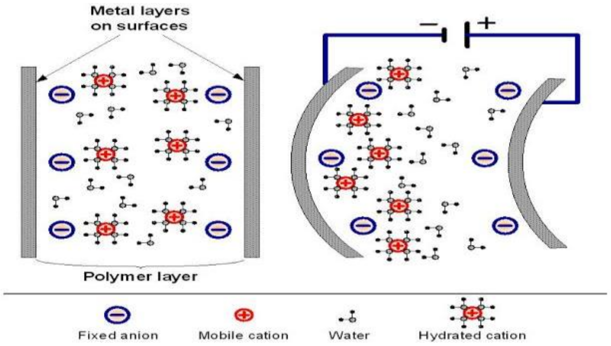

Fig.8.IPMCs exhibit actuation and sensing/energy harvesting through the migration of cations towards the cathode electrode when an electric field is applied or when mechanical deformation induces cation migration towards boundary surfaces. This migration leads to the generation of a voltage as a result of the Poisson-Nernst-Planck phenomena.

IPMC (Ionic Polymer-Metal Composite) exhibits a relaxation effect when a DC voltage is applied, causing a quick deformation followed by a slow reversal. This relaxation effect poses stability issues for IPMC actuators, hindering their application in soft robotics. Two methods are currently used to overcome this relaxation: adjusting water content and using ionic liquid as a solvent. Water content plays a crucial role in affecting the relaxation of IPMC. Dehydration affects the electromechanical parameters and morphology of IPMC, influencing its stiffness, surface resistance, and capacitance. Encapsulating IPMC at fixed water content can maximize its deformation without relaxation. Nafion, a copolymer of tetrafluoroethylene, is widely used as a membrane in proton exchange membrane fuel cells (PEMFCs) due to its high proton conductivity and low electron conductivity. Nafion's nanostructure and proton conductivity relationship are still being explored. IPMC has been proposed for various applications, including biomimetic robotics, underwater vehicles, optical systems, and biomedical devices. However, challenges like relaxation under DC voltage, poor output force, solvent evaporation, and non-standardized preparation steps need to be addressed for broader use in sensing and actuating fields. Recent research focuses on optimizing preparation steps, adjusting water content, and exploring alternative solvents. The bending capabilities of IPMC have significant implications for soft robotics, artificial muscles, and various medical and industrial applications.

IPMC finds vast application in industrial and medicinal sector including functioning as activators, transducers and artificial muscles.

- **Industries**

Mechanical holder: IPMCs can be utilized as holders at micro and macro scales, enabling the gripping of two membranes and inducing bending in opposite directions. To achieve this, two IPMC actuators are positioned parallel to each other, with their top surfaces facing each other. The terminals of the actuators are connected to the top and base surfaces of each actuator. Electrical wires connect the terminals to each other and to one terminal of the power supply. The length of the wires depends on the desired spacing between the two IPMC actuators, which is determined by the specific application requirements.

The key advantage of such an IPMC configuration is that it has three externally facing sides electrically. The actuators are connected to a generator box, and the terminals are located on the sides of the actuators. The terminals are linked to the electrodes within the generator box. These types of actuators find significant applications in power mixing, production line feeding, and other similar tasks. Linear actuators are specifically designed for the manipulation of robotics

Microelectromechanical systems (MEMS) Microelectromechanical systems (MEMS) and microrobots that incorporate electroactive polymers, specifically IPMCs, represent a promising technology for the fabrication of sensor and actuator microarrays. These microarrays find applications in various fields, including the development of photonic optical fiber switches based on micromirrors, disposable micro biosensors for real-time medical applications, and microfabrication processes requiring precise control of small materials. IPMC actuator microarrays offer immediate advantages due to their low-voltage activation, high speed, and the ability to be cut into arbitrarily small sizes from IPMC material sheets.A wide range of electroactive polymer materials, including IPMCs, are utilized in the construction of motors, translators, and controllers, such as ultrasonic motors and inchworms. In contrast to electro-ceramics, IPMCs are emerging as novel actuation materials with displacement capabilities that cannot be matched by rigid ceramics with limited flexibility. IPMC materials can be easily shaped into desired forms and used to fabricate MEMS-type components such as actuators and sensors. They can mimic the functionality of biological muscles and possess exceptional characteristics, including low density, high strength, large strain capabilities, and inherent vibration damping.

The integration of IPMC sensors and actuators with existing MEMS technology is straightforward since they can be easily processed and manufactured in large quantities, enabling them to be miniaturized and shaped into any desired geometry. The application of IPMC-MEMS technology extends to biotechnology as well. It can support advancements such as polymerase chain reaction (PCR), microsystems for DNA amplification and identification, micromachined scanning tunneling microscopes (STMs), biochips for detection of hazardous chemicals and biological agents, as well as microsystems for high-throughput drug screening and selection. IPMC-MEMS can also seamlessly integrate into high-performance active sensing systems, including accelerometers, dynamic motion sensors, and force sensors

Medicine

The unique characteristics of flexibility, stability, and softness make IPMCs suitable for various biomedical applications.

1) Artificial Cardiac muscles:

Artificial ventricular assist muscles can be developed using IPMCs to aid patients with heart deformities related to cardiovascular muscle functions. This potential IPMC device offers the advantage of avoiding complications such as thrombosis that are common with current artificial heart or heart-assist devices, which can occur when blood repeatedly contacts non-biological surfaces. The device needs to be gentle and electronically robust to avoid damaging the ventricle when exerting pressure. It should incorporate control mechanisms like pacing and cardioverting/defibrillating to operate in synchrony with the left ventricular contraction. Additionally, the device should be capable of transcutaneous charging of the embedded batteries. The device is primarily inserted in the patient's ribcage but is supported by a thin flexible stalk that extends to the abdomen, allowing the natural systolic and diastolic cycles of the heart to continue with minimal restriction. Alternatively, the supporting structure can be placed on the abdominal muscles. These details can be further refined during clinical testing and operation of such devices. In its current design, the device applies gentle or subtle compression to the left ventricle of a poorly functioning heart, increasing internal pressure and directing more blood from one or more sides in coordination with the ventricle's natural systolic contraction. Additionally, the system can provide arrhythmia control for the beating heart. The delicate fingers in the design incorporate strategically placed electrodes for monitoring the ventricular stroke, volume, and pressure.

2) Medicinal tools and pumps

IPMC actuators have the potential to be utilized in biomedical applications such as intra-cavity endoscopic surgery and diagnostics, serving as a guide wire or miniature catheter. These small strip or fiber-like IPMC actuators can be employed to navigate narrow internal cavities within the body. By utilizing tubular sections of IPMC material and strategically placing electrodes, peristaltic pumps can be created. The volume control of the fluid filled in the tube can be achieved by applying an appropriate input voltage at the desired frequency

Energy Reapers

The utilization of IPMCs as an energy-saving system has gained significant attention in recent years. This field is rapidly growing, focusing on harnessing energy from various types of fluid flows, including mobile, immobile, and oscillatory flows. The ability of IPMCs to convert mechanical energy into electrical energy is exploited in fluid environments. Different IPMC structures, such as fluttering flags and IPMC cantilevers, are employed for energy harvesting purposes. In one application, an IPMC strip cantilever is submerged in a liquid environment to extract energy. The modeling of the IPMC strip submerged in a fluid state considers the base excitation. Experimental work has also been conducted to analyze the submerged vibration of the IPMC and measure the corresponding electrical responses with different resistors. To achieve a few microwatts of power, it is necessary to use large IPMC samples. Advancements in the design process of these larger samples will undoubtedly enhance energy harvesting devices. The biocompatibility of IPMCs allows their use even in humid conditions. There is potential for utilizing IPMCs to harvest energy from microseismic or oceanic waves. It is essential to employ software modeling for the effective evaluation of IPMC-based systems in energy harvesting applications.

Active smart polymers find extensive applications in various fields, including robotics, self-healing materials, artificial muscles, actuators and sensors, separation and purification processes, shape-changing fibers, microfluidic devices, viscosity modifiers, and controlled release systems. In this discussion, we will focus on the detailed use of active smart polymers in robotics.

Robotics: One interesting application of muscle wire and a microcontroller circuit is seen in the development of a robotic hand. The robotic hand incorporates "stretched muscle wires" connected to the base of each finger. By applying current to the muscle wire, it contracts and returns to its original length, causing the ordinary wire to be pulled. Through programming the microcontroller, five outputs can be controlled to switch on and off, resulting in coordinated movement of the fingers. This movement is illustrated in figure 9 provided below.

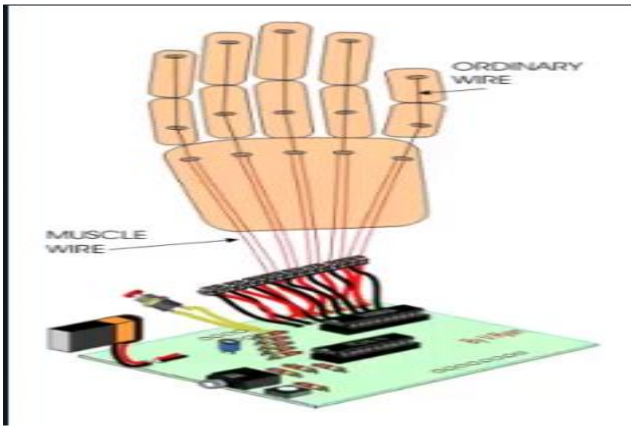

Fig.9. Working of Robotic hand

Now, we will look at the future perspective of these active smart polymers in the field of actuators and sensors. Look at the figure 10 given below taken from marketandmarkets research pvt. Ltd

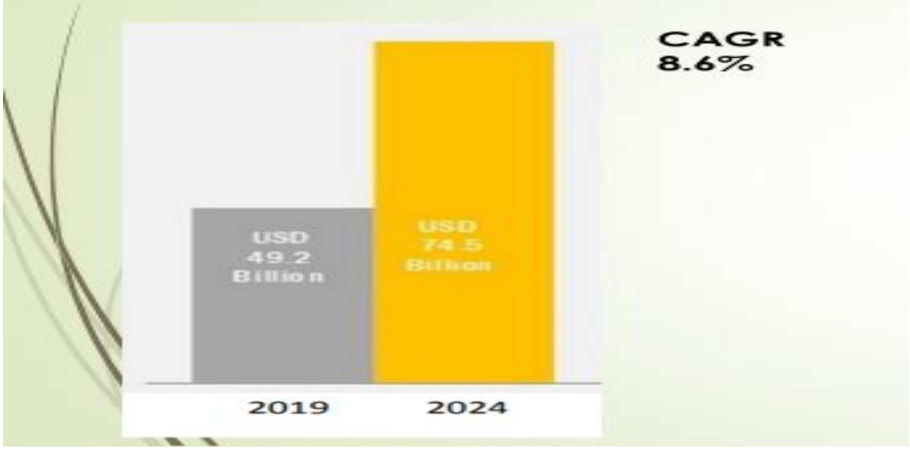

Fig.10. Future perspective of actuator market

The actuators market is projected to grow from USD 49.2 billion in 2019 to USD 74.5 billion by 2024, at a CAGR of 8.6% from 2019 to 2024.

Increasing investment in process automation across industry verticals, rising demand for robots, and technological advancements in actuators**.**

Now, we will see how much this actuator market has grown up to 2022 and is projected to grow in terms of region by how much Billion in terms of USD [11]. We can clearly get the idea of this by the figure 11 given below:

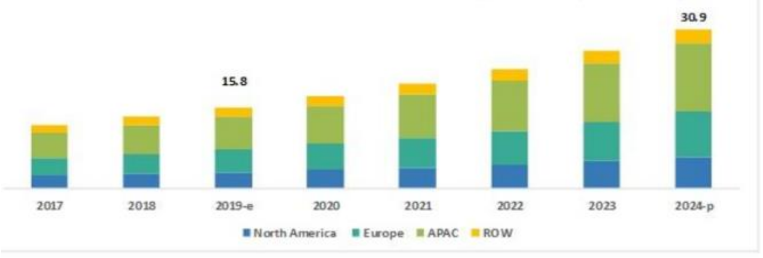

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Fig.11. Robotics and automation actuators, by region (USD Billion)

CONCLUSION:

This manuscript offers a brief glimpse into the intricacies and usefulness of smart polymeric biomaterials, aiming to showcase their versatility and potential. The concept of smart polymers is expansive and somewhat ambiguous, making it challenging to confine them to a single defined meaning, composition, or objective. In the context of human or artificial intelligence, this manuscript explores smart polymers as materials capable of processing environmental signals, enabling them to either initiate an action (responsive polymers) or emit a signal that serves as functional and analytical information (sensory polymers). These stimuli can be physical, chemical, or even biological in nature. Regardless of specific considerations, classifications, or analyses, the ultimate goal remains the development of smart devices, actuators, and sensors for advanced applications. Smart materials are on the cusp of significant progress and hold great promise in the intersection of chemistry and biology, paving the way for an exciting future.

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