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Self-Healing Polymers Coupling Shape Memory Effect

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ABSTRACT: In recent years, shape memory polymers (SMPs) and self-healing polymers (SHPs) have been research hotspots in the field of smart polymers owing to their unique stimulus response mechanisms. Previous research on SHPs has primarily focused on contact repair. However, in instances where substantial cracks occur during practical use, autonomous closure becomes challenging, impeding effective repair. By integration of the shape memory effect (SME) with SHPs, physical wound closure can be achieved via the SME, facilitating subsequent chemical/physical repair processes and enhancing self-healing effectiveness. This article reviews key findings from previous research on shape memory-assisted self-healing (SMASH) materials and addresses the challenges and opportunities for future investigation.
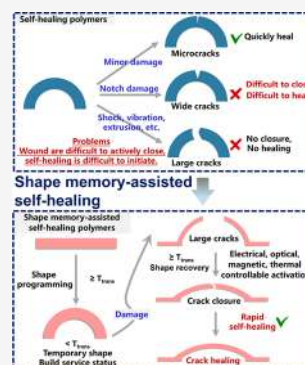
1. INTRODUCTION

Over the past decades, self-healing polymers (SHPs) have been synthesized successfully, drawing inspiration from and studying the autonomous healing abilities observed in natural organisms. Functioning as intelligent materials capable of autonomously repairing damage and restoring original properties upon injury, SHPs exhibit the capacity to detect and address cracks, thereby mitigating potential damage stemming from microcracks. Consequently, they enhance product durability and extend the lifespan of products, which is particularly important for applications that are susceptible to damage or located in poorly accessible areas.[1,2]

Through the investigation of the repair mechanisms and the dynamics of the self-healing process, various effective repair methods have emerged. Typically, these methods encompass physical self-healing, chemical self-healing, or a combination of physical and chemical processes. Based on the composition of repair materials, they are commonly categorized into two groups: extrinsic self-healing[3] and intrinsic self-healing.[4] The self-healing capability of extrinsic SHPs relies on embedding microcapsules or microvascular networks containing healing agents within a polymer matrix. However, this method is plagued by manufacturing complexity and the eventual depletion of mending agents after multiple injuries. In contrast, intrinsic SHPs derive their self-healing ability from the breakage and reorganization of the dynamic bonds within the polymer network. This approach enables repeatable self-healing without the need for pre-embedded repair agents.

The process of inducing intrinsic SHPs chemical bond reconstruction through external stimuli to repair damage has been extensively studied. However, a significant challenge arises when materials inevitably suffer destructive damage in harsh environments, leading to slow diffusion or even failure of molecular chains between the wound interfaces. At this point, the lack of interface contact between cracks becomes the primary obstacle hindering wound healing. External force-assisted interface contact is a common choice to initiate self-healing behavior. However, this reliance on external forces hinders the practical application of SHPs. An effective strategy to overcome this obstacle is to exploit the shape memory effect (SME) to promote repair.[5,6]

The SME enables a material to deform in response to a specific stimulus, reverting from a temporary shape to a predefined or programmed shape (permanent shape).[7,8] By integration of the SME into SHPs, the closure of physical wounds can be facilitated through the shape recovery process. This, in turn, enables the subsequent chemical and physical repair processes to proceed smoothly, resulting in effective self-healing. In this Perspective, we provide a brief overview of the fundamental concepts of shape memory polymers (SMPs) and SHPs, with a focus on the latest advancements in SMASH polymers. We also discuss the challenges and opportunities of SMASH polymers based on existing research findings.
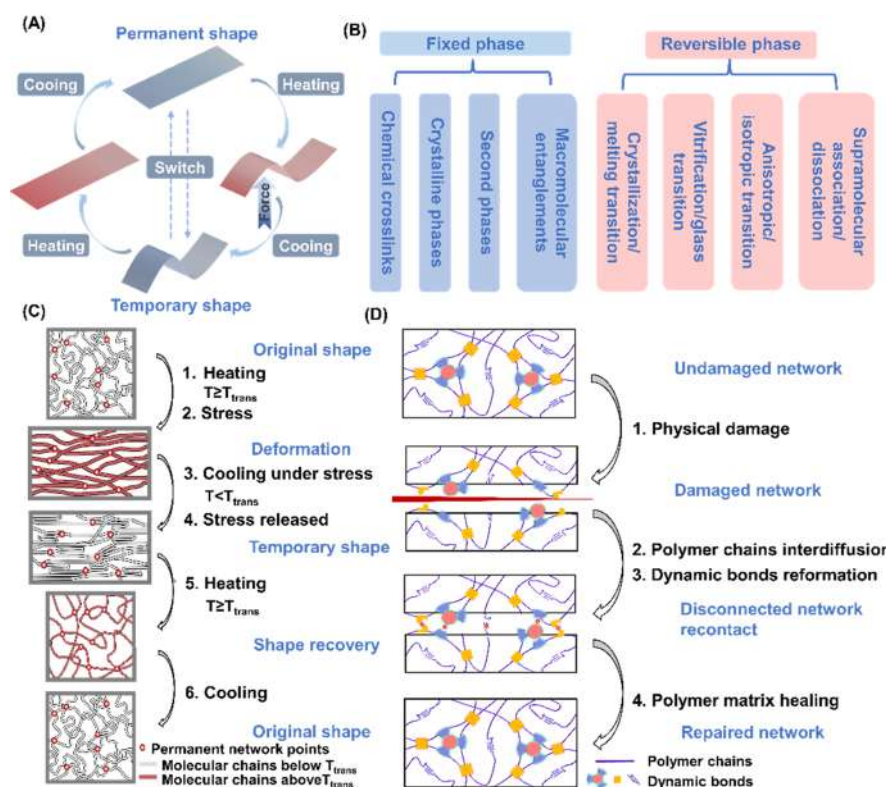
Figure 1. (A) Shape-memory cycle of SMPs. (B) The fixed phase and reversible phase that give rise to the shape memory effect (SME) of SMP. (C) Shape memory mechanism schematic diagram of glass transition SMP. (D) Self-healing mechanisms.

2. BASIC CONCEPTS OF SMPs AND SHPs

2.1. Basic Concepts of SMPs. The typical SME is not an intrinsic property exhibited by the polymer itself,[9] it is the result of molecular structure, reversible mobility changes, conformational entropy and programming.[10,11] Polymers exhibiting the SME require the presence of both a stationary phase and a reversible phase. Stationary phase refers to the three-dimensional network structure formed by chemical or physical cross-linking, which plays a crucial role in enabling permanent shape memory and storage by preventing the slip and creep of molecular chains. Reversible phases, responsive to external stimuli, play a pivotal role in fixing or releasing temporary shapes when triggered by stimuli.

The shape memory mechanism of unidirectional SMPs is the foundation for understanding all SMP deformation processes.[12] As shown in Figure 1A, taking thermally triggered dual-SMP as an example, under the appropriate stimulus, such as increasing the temperature, the dynamic interactions are disrupted, and the moving and deforming ability of polymers is enhanced. And it can be processed into a specific shape under the action of external forces. Maintain the external force, change the environmental conditions, such as lowering the temperature, and the dynamic interaction is reformed. At this time, the deformed shape can be maintained without external forces, and this shape is called the temporary shape. When conditions change again and the dynamic interaction is disrupted, the polymer reverts from its temporary shape to its permanent shape, completing one shape memory cycle. Due to the presence of two largely incompatible phases in the material, including a reversible phase that can change with temperature from a glassy state to a rubbery state and a fixed phase that holds the sample's initial shape, the material exhibits

shape memory. The fixed phase is formed by molecular entanglement, crystalline phase, chemical cross-linking, or interpenetrating network, determining the permanent shape of the polymer, while the reversible switch is composed of glass transition,[13] crystallization/melting transition,[14] anisotropic/isotropic liquid crystal transition,[15] or supramolecular association/dissociation[16] playing a role in fixing temporary shapes (Figure 1B). Taking the glass transition SMP as an example, the schematic diagram of molecular migration and chain conformational changes during the shape memory cycle is shown in Figure 1C.

The important quantities to be determined for describing shape memory properties of materials are the strain recovery rate ($R_r = \frac{\varepsilon - \varepsilon_{rec}}{\varepsilon} \times 100\%$, ε is the fixed strain after cooling and load removal, and ε_{rec} is the strain after recovery) and strain fixation rate ($R_f = \frac{\varepsilon}{\varepsilon_{load}} \times 100\%$, ε_{load} represents the maximum strain under load), which quantify the ability of materials to memorize permanent shapes and to fix temporary deformations, respectively. The thermoviscoelastic theoretical model is used to describe the thermodynamic behavior of the SMPs. In this model, molecular chains are treated as small springs, which intertwine when mixed because of their small diameter and relatively long length. At room temperature, the springs in SMPs are randomly arranged, resulting in a higher entropy. As the temperature increases, the polymers become more mobile, resulting in thermoviscoelasticity. In this case, the spring can be stretched and oriented by external forces, thereby reducing the polymer's entropy. If the temperature decreases while the external force remains constant, the polymer will lose its thermoviscoelasticity, hindering molecular motion and making it difficult for the springs to return to their original shape. This process converts the stress stored in the
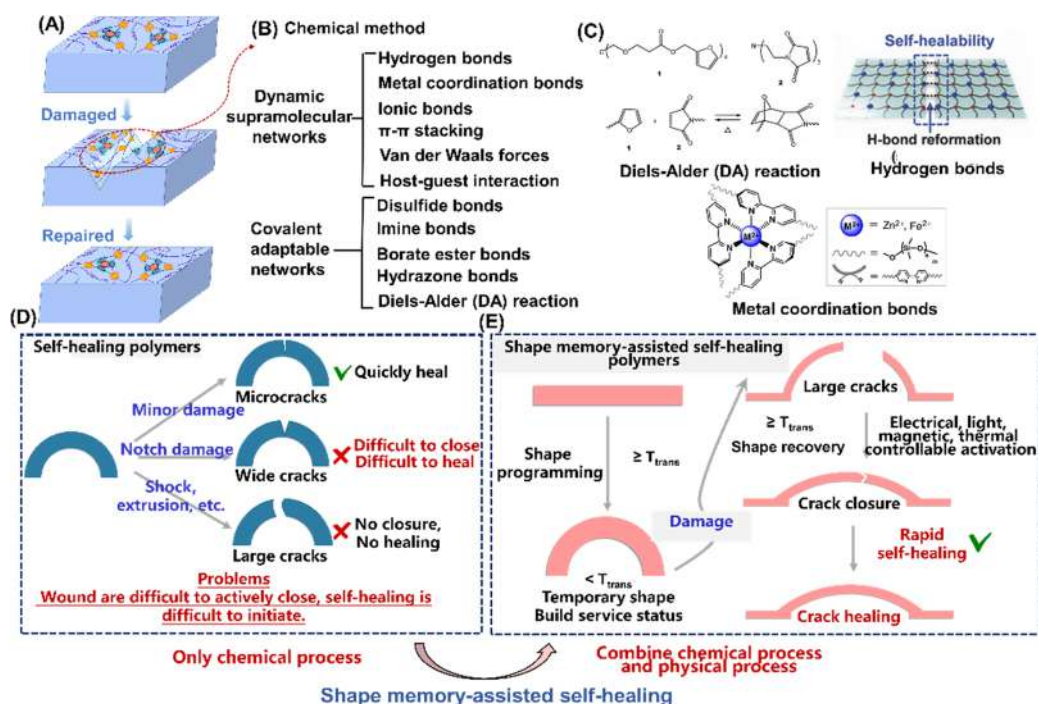
Figure 2. Intrinsic self-healing approach. (A) Schematic diagram of intrinsic self-healing process. (B) Chemical processes to achieve self-healing include supramolecular dynamic bonds and covalent bonds. (C) Self-healing through Diels−Alder (DA) reaction[31] (Reproduced with permission from ref 31. Copyright 2002, American Association for the Advancement of Science), hydrogen bonds[22] (Reproduced with permission from ref 22. Copyright 2018, Wiley-VCH) or metal coordination bonds[32] (Reproduced with permission from ref 32. Copyright 2016, American Chemical Society). (D) Problems with self-healing materials: wound are difficult to actively close, resulting in difficulties in repairing wide cracks or large cracks. (E) Shape memory-assisted self-healing (SMASH) polymers. External stimulation triggers shape recovery and promotes wound closure, achieving rapid self-healing.

molecular chain into elastic potential energy. Subsequently, when the temperature rises again, the spring releases the stored elastic potential energy, regaining thermoviscoelasticity. This process explains the role of molecular processes such as structural relaxation and stress relaxation in defining the SME and its time dependence. Phase transition theory is more suitable to explain the shape transformation behavior of SMP. Phase transition theory is more suitable for explaining the shape transformation behavior of SMPs. The phase composition of SMPs includes the frozen phase and the active phase, corresponding to the hard phase and the soft phase, respectively. In the frozen phase, further conformational movements of the contents are not possible, while the active phase can undergo deformation. During the programming process, conformational movements are stored in the active phase. As the temperature decreases, the active phase transitions into the frozen phase, at which point stress is not enough to drive the shape recovery. When the temperature increases, the frozen phase transforms into the active phase, releasing the stored stress. Phase transition theory explains the process of stress storage and release during the shape memory process.

2.2. Basic Concepts of SHPs. The discussion of SHPs in this article focuses on intrinsic SHPs, and extrinsic SHPs will not be the focus of this article. Intrinsic self-healing in SHPs can be broadly divided into three stages: damage sensing, material transfer to the injured area, and physical or chemical repair of the damaged area.[17,18] Typically, damaged areas self-healing through the interdiffusion of polymer chains and the rearrangement of dynamic bonds.[19] Figure 1B depicts a schematic diagram illustrating the mechanism of the self-healing process.

By controlling the main chain structure, molecular structure, and functional groups of the polymer, dynamic bonds can be tailored to create SHPs with varying strengths and responses to different temperatures and stimuli. Since the recovery of mechanical properties is related to the stability of materials in practical applications, most articles focus on the recovery efficiency of modulus, toughness, and other properties of materials under tension or compression through tensile testing or postimpact compression testing. The healing efficiency of the material is quantified by comparing the physical property before and after healing.[18,20,21] Tracking and monitoring the self-healing process through an optical microscope is a more intuitive method to qualitatively evaluate the self-healing efficiency, which can directly observe the crack closure during the healing process and roughly evaluate the self-healing. Fluorescence microscopy, nuclear magnetic resonance spectroscopy, and Raman spectroscopy can also track the diffusion of molecular chains during the healing process, which can be used to reveal the self-healing mechanism.

When quantifying self-healing efficiency, it is often necessary to manually cut scratches on its surface. However, the differences in the tools used during the cutting process, as well as variations in the force applied, can result in differences in the width and depth of the incision. Additionally, self-healing efficiency can also be influenced by various factors such as the time interval between the cutting and the beginning of healing and the roughness of the damaged surface, and these variations contribute to the lack of standardized testing methods for evaluating self-healing efficiency. Replacing

Table 1. Common Dynamic Bonds in Self-Healing Polymer Networks

manual cutting with the use of specific weights pressing on specific blades to create scratches on the sample surface may reduce the influence of uncontrollable variables, to some extent.

## 3. PHYSICAL AND CHEMICAL RULE IN HEALING PROCESS

Self-healing materials employ various repair methods to restore their structural integrity after physical damage. Intrinsic self-healing relies on the diffusion of polymer chains and the breakage and reorganization of dynamic bonds under external stimuli (Figure 2A). Common dynamic bonds include supramolecular dynamic bonds such as hydrogen bonds,[22,23] metal coordination bonds,[24,25] ionic bonds,[26] $\pi-\pi$ stacking, van der Waals forces,[27] host−guest interaction,[28] and others. Additionally, dynamic covalent bonds play a significant role in intrinsic self-healing, including disulfide bonds,[29] imine bonds,[30] hydrazone bonds, borate ester bonds, Diels−Alder (DA) reaction,[31] among others (Figure 2B, Table 1).

The primary advantage of intrinsic self-healing methods is the capability to repeat the self-healing processes. Ideally, SHPs can heal repeatedly at the same location while maintaining their self-healing ability. The concept of intrinsic self-healing was first proposed in 2002, using a thermally reversible DA reaction (Figure 2C, left).[31] The authors developed a material capable of self-healing at temperatures exceeding 120 °C. This discovery inspired research on self-healing polymer materials, and many other works have been reported. In 2018, Bao et al.[22] accomplished material self-healing by incorporating both strong and weak hydrogen bonds within the polymer matrix (Figure 2C, middle). In this system, strong hydrogen bonds maintain the material's elasticity, while the breakage and reorganization of weak hydrogen bonds effectively dissipate strain energy, imparting excellent notch insensitivity to the material. Consequently, large gaps are blocked during the

stretching process, preventing further tearing. Moreover, the material can achieve self-healing at room temperature after the fractured interface is artificially brought into proximity. Similarly, exploiting the versatility of metal−ligand interaction strength enables the attainment of high strength, high stretchability, and room temperature self-healing of cracks (Figure 2C, right).[32]

The chemical repair process, being highly tunable during synthesis, has been extensively studied for its role in contact repair. However, during material usage, wider or larger cracks often develop. In such cases, without external intervention, the damaged surfaces of the materials fail to effectively contact, impeding the initiation of physical or chemical adhesion necessary for healing and recovery from physical damage (Figure 2D). To address the challenge of damaged surfaces self-adhesion, the SME, capable of achieving shape control, is integrated into the SHP. The SME expedites the closure of wounds and cracks by bringing surfaces into spatial proximity, thereby broadening the scope of repairable wounds without human intervention. This advancement is invaluable for achieving effective and reproducible recovery from various forms and sizes of injuries (Figure 2E).

Deng et al.[29] introduced disulfide bonds to obtain a polyurethane network capable of exhibiting SME and SHE independently and simultaneously. By preprogramming the temporary shape, scratches on the surface of the material can be completely repaired during the shape recovery process. This is attributed to the dynamic exchange of disulfide bonds (imparting self-healing properties) and the aggregation and chemical cross-linking of hard segments (imparting shape memory properties). Wei et al.[33] obtained a SMASH material that enhanced crack repair through a polymer system with a phase separation structure. These dynamic bonds not only undertake the task of self-healing during the healing process but also serve as fixed phases to complete the task of
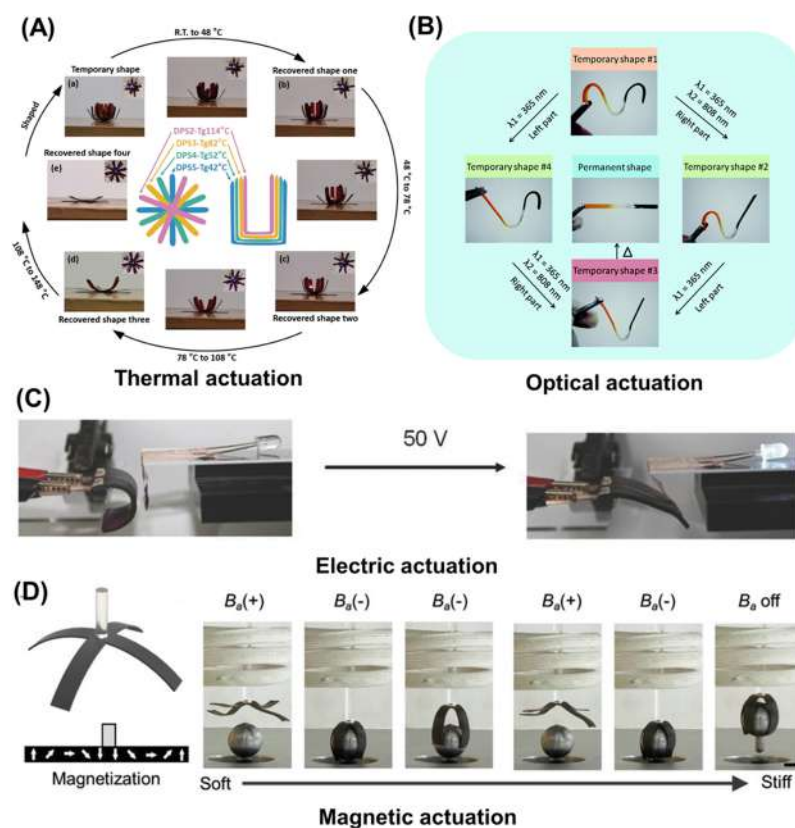
Figure 3. Shape memory effect (SME) under different external stimuli. (A) Thermal trigger shape memory cycle process. The structure consists of four materials with different response temperatures.[38] Reproduced with permission from ref 38. Copyright 2023, Wiley-VCH. (B) Photomanipulation of shape recovery processes of multicomposite.[39] Reproduced with permission from ref 39. Copyright 2015, Royal Society of Chemistry. (C) Electrically triggered SME, which is used as a shape memory connector.[40] Reproduced with permission from ref 40. Copyright 2015, Wiley-VCH. (D) Shape transforming and shape locking of SMP under superimposed magnetic fields.[41] Reproduced with permission from ref 41. Copyright 2019, Wiley-VCH.

remembering the original shape. This allows these materials to close the wound by returning to the original shape, which in turn triggers the recombination of dynamic bonds between interfaces to repair damage such as scratches and/or dents.

4. HOW TO TRIGGER SHAPE MEMORY BEHAVIOR

The SME can serve as a crucial support in overcoming the healing barriers between severely damaged interfaces. It is obvious that reasonable shape manipulation is vital to ensure the smooth execution of healing behavior in SMP-based devices postinjury. External stimuli such as heat, light, and electromagnetism have been widely employed to expedite the self-healing process between interfaces. Excitingly, these varied external stimuli also serve as ideal means to control the shape programming-recovery process of SMPs.[34−37] Here, we primarily delineate several commonly used diverse driving methods of SMPs, and we explore the effects of different driving methods on self-healing behavior.

4.1. Thermal-Driven SMPs. As shown in Figure 3A, Li et al.[38] synthesized a series of thermoset materials exhibiting shape memory properties. These materials provide adjustable stiffness and deformation characteristics at various T_{trans}. However, since the entire material must be uniformly heated during the process and the heating area cannot be precisely controlled, this method, while promoting material healing to some extent, lacks the ability to selectively target damaged areas.

4.2. Light-Driven SMPs. Shape memory behavior can be driven by photochemistry based on photocovalent cross-linking reactions. By absorbing the heat generated by optical radiation, a photothermal-driven shape memory behavior can be achieved. The latter is more conducive to playing a role in the repair process than the former. As shown in Figure 3B, Yu et al.[39] obtained photothermally driven SMPs. These materials enable remote control, noncontact operation, and localized actuation, which is significant for controllable local crack repair and remote-induced recovery. However, achieving effective photothermal conversion necessitates deep light penetration and proper filler distribution, as high filler concentrations can impede light penetration. Therefore, careful control of the filler concentration and dispersion is imperative.

4.3. Electroactive SMPs. As shown in Figure 3C, Zarek et al.[40] successfully developed a polymer exhibiting electrically responsive shape memory behavior. This material harnesses Joule heat generated by the passage of an electric current to remotely drive the SME. Consequently, when cracks occur within the material, this driving method significantly aids in internal material repair. Nevertheless, challenges persist in controlling independent shapes and achieving uniform conductive pathways.

4.4. Magnetism-Driven SMPs. As shown in Figure 3D, Ze et al.[41] used the Joule heat generated by magnetic field particles under a magnetic field to achieve shape memory behavior. The strong penetration of the magnetic field enables it to deeply penetrate the polymer, achieving the material's
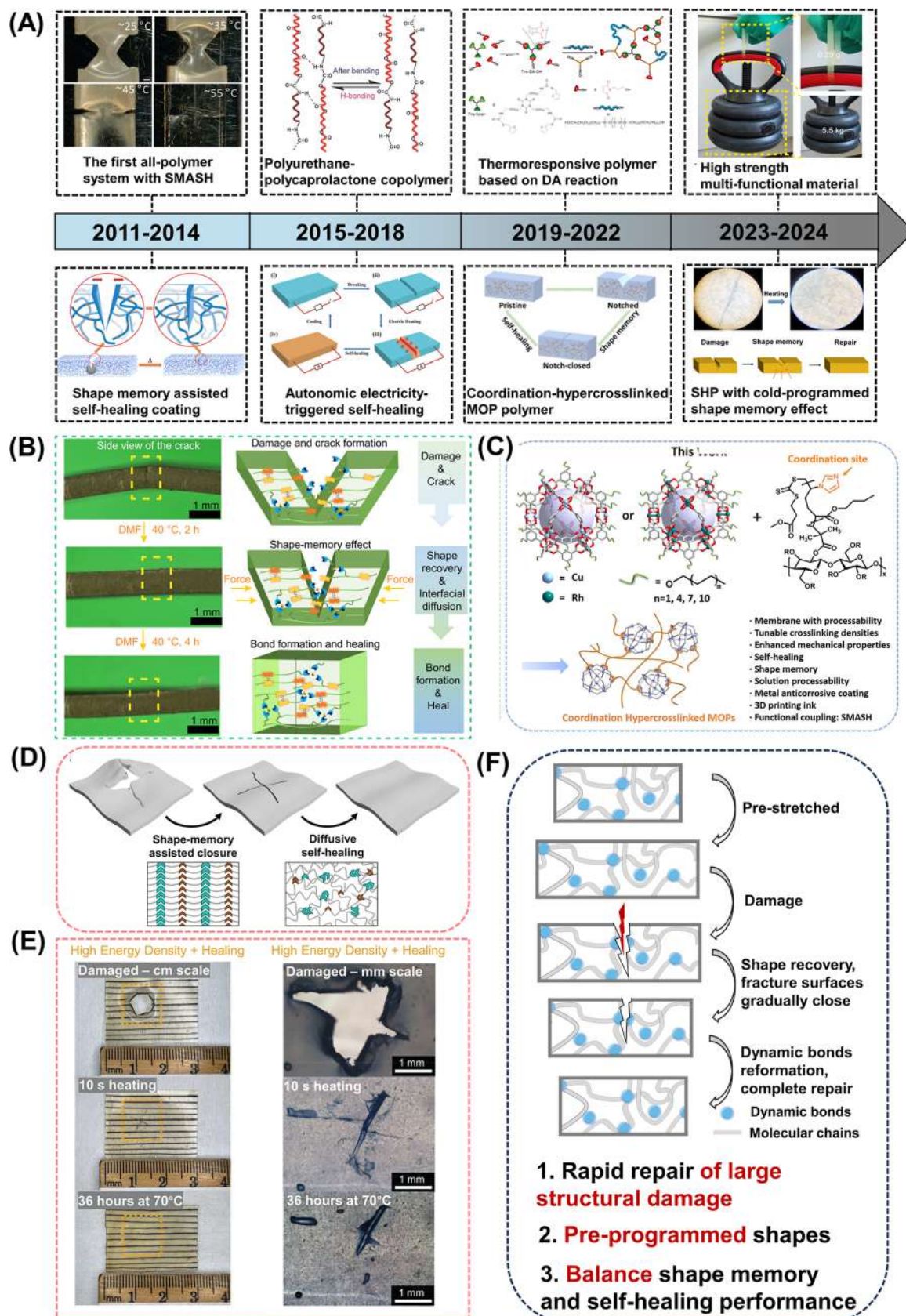
Figure 4. (A) Development of SMASH materials in recent years.[42−44,46,48,49,51,55] Reproduced with permission from ref 42. Copyright 2011, American Chemical Society. Reproduced with permission from ref 43. Copyright 2013, American Chemical Society. Reproduced with permission from ref 44. Copyright 2017, Wiley-VCH. Reproduced with permission from ref 46. Copyright 2020, Elsevier. Reproduced with permission from ref 48. Copyright 2024, Springer Nature. Reproduced with permission from ref 49. Copyright 2022, Wiley-VCH. Reproduced with permission from ref 51. Copyright 2018, Wiley-VCH. Reproduced with permission from ref 55. Copyright 2023, American Chemical Society. (B) Schematic

Figure 4. continued

diagram of solvent-assisted SMASH process.[48] Reproduced with permission from ref 48. Copyright 2024, Springer Nature. (C) Schematic illustration of MOP-cored coordination hyper-cross-linked network.[49] Reproduced with permission from ref 49. Copyright 2022, Wiley-VCH. (D) Schematic of the SMASH mechanism in high-energy-density SMASH polymer.[54] Reproduced with permission from ref 54. Copyright 2024, Elsevier. (E) SMASH of macroscopic punctures.[54] Reproduced with permission from ref 54. Copyright 2024, Elsevier. (F) Brief insights into the future development of SMASH materials.

deep self-healing. However, when they are employed for repairing materials in fields such as electronic or medical equipment, the powerful magnetic field required for this driving behavior may pose a risk of causing destructive effects on electronic devices or the human body.

In summary, by selecting the appropriate driving method, it is possible to achieve the localized repair of materials while achieving remote shape control. This controllable SMASH behavior will allow for novel approaches to critical real-world problem solving in the years to come. Moreover, in order to obtain satisfactory response stimulus SMASH behavior, it is usually necessary to add multifunctional nanofillers to the matrix, such as multiwalled carbon nanotubes, graphene derivatives, Fe_3O_4, SiO_2 nanoparticles, and montmorillonite. Nanomaterials such as carbon nanotubes and gold nanoparticles can generate photothermal effects and drive light-responsive shape memory behavior. Magnetic particles such as Fe_3O_4 can trigger SME under the influence of a magnetic field, generating Joule heating. While the addition of nanofillers enables remote actuation of SMPs, poor dispersion of fillers within the polymer matrix can adversely affect their performance. Therefore, it is essential to further improve the dispersion of nanofillers through appropriate dispersants, ultrasonic treatment, surface modification, etc., to enhance the bonding strength between nanofillers and polymers and the degree of filler dispersion within the matrix.

5. SHAPE MEMORY-ASSISTED SELF-HEALING

Using the unique SME of SMPs is an excellent approach to promote material self-healing. It enables not only the repair of microscopic cracks but also the filling of macroscopic cracks. When the material is damaged and the crack expands further under the action of external force, the material is stimulated to trigger a shape recovery process. The expanded crack can be gradually pulled closer until it is completely closed. After the crack is closed, the original properties of the material are restored through the diffusion of polymer chains and the reorganization of dynamic bonds. This SMASH behavior overcomes the limitation that the self-healing process requires manual intervention to bring the damaged interface into contact.

The SMASH process is mainly divided into two steps: wound closure mediated by SME and the recombination of dynamic bonds between interfaces. In shape memory materials, the reversible phase mainly includes crystal chain segment, glass transition temperature, metal−ligand interaction, and so on. The self-healing dynamic bonds mainly include supramolecular interactions (hydrogen bonds, metal−ligand bonds, host−guest interactions, etc.) and dynamic covalent bonds (imine bonds, D−A bonds, and disulfide bonds, etc.). Generally, the stationary phase of shape memory materials with SHE is dominated by dynamic bonds. These dynamic bonds undertake the task of memorizing the original shape and satisfying the SME. In order to implement the shape memory process, the shape transition temperature should be lower than

the dissociation temperature of the dynamic bonds to ensure efficient shape recovery for wound closure. In addition, after wound closure, the temperature should be appropriately raised to accelerate dynamic bond recombination at the damaged interface to achieve efficient healing.

SMASH is commonly observed in biological systems, such as wound closure in leaves.[17] In synthetic polymers, exploiting the viscoelastic qualities of the glass transition in polymers enables the gradual autonomous closure and repair of wounds. When the force causing the injury is released, the SME can restore entropic energy and close the wound. However, not all SME exhibited by polymers can effectively promote self-healing. Factors such as viscoelasticity and the surface energy of the material need to be considered. Viscoelastic shape memory behavior driven by the stored conformational entropy after damage is highly conducive to self-healing. Additionally, using surface energy or surface tension to drive shallower wounds and reduce the newly generated surface area after an injury can also promote material healing.

In 2011, Rodriguez et al.[42] first proposed an all-polymer system with SMASH capability. They developed this polymer system by blending a cross-linked polycaprolactone network (n-PCL) with linear polycaprolactone (l-PCL). The shape memory properties in this system are derived from n-PCL, where the chemical cross-linking sites act as hard segments and crystallization serves as a reversible phase. On the other hand, the self-healing property is attributed to the diffusion of l-PCL. This SMASH material is capable of restoring seemingly permanent deformation below or at the reversible transformation temperature. The authors refer to this effect as Reversible Plasticity Shape Memory (RPSM). In current research, this form of shape memory is frequently utilized to facilitate self-healing processes.

Since the concept of SMASH was proposed, SMASH materials have garnered increased attention in various polymer systems and response modes, leading to more research endeavors (Figure 4A). Their versatility and potential applications in polymer coatings,[43] electronic devices, and biomedical fields have garnered considerable attention.

Rehman et al.[44] synthesized polyurethane-polycaprolactone copolymers (PUPCL), which featured a chemically cross-linked stationary phase and a high-temperature elastic transient phase. The melting point of PUPCL served as the critical temperature to trigger the shape memory properties. The shape memory property of the material showed no significant reduction after repeated cycling tests, demonstrating high stability. Additionally, based on its SMASH performance, it achieved a remarkable 95.1% self-healing efficiency. Furthermore, Heo et al.[45] and Nguyen et al.[46] both developed polymers exhibiting SMASH behavior based on the DA reaction. Upon heating for several hours, the cracks gradually closed and the broken DA bonds were rebuilt, completing the self-healing process.

Polymer systems incorporating metal coordination bonds have emerged as another promising approach for constructing

SMASH polymers. Xie et al.[47] developed a SMASH elastomer utilizing metal coordination interactions of Zn(II)-carboxyl and Zn(II)-pyridine. By presetting the temporary shape, the elastomer exhibited robust SMASH behavior, enabling rapid closure and repair of destructive cracks. Wang et al.[48] utilized coordination bonds and hydrogen bonds as sacrificial bonds for staged energy dissipation, achieving not only SMASH behavior but also improved mechanical properties. However, due to its high hardness of 76.37 MPa, solvent drops were required to be added to the cracks during the healing process of this material to enhance self-healing efficiency (Figure 4B). Without the addition of solvent, the material's recovery efficiency was less than 40%. Liu et al.[49] fabricated a class of coordination-hyper-cross-linked MOP polymers using a macromonomer coordination cross-linking method with metal−organic cages as building units with high connectivity (Figure 4C). This coordination network exhibited excellent mechanical properties and could be repeatedly bent, twisted, or stretched without damage.

In addition to direct heating, SMASH can also be driven by light, electricity, or magnetism. Bai et al.[50] reported NIR light-triggered SMASH composites incorporating graphene oxide. Under the irradiation of 1.4 W cm^{-2} NIR light, the crack interface gradually closed due to the light-induced SME. After the crack was closed, under 2.5 W cm^{-2} NIR light irradiation, the dynamic bonds reorganized, thereby achieving light-induced self-healing of large cracks. Pu et al.[51] reported electrically driven SMSAH composites based on polyurethane and carbon nanotubes (CNTs). CNTs were wrapped on the surface of polyurethane, rendering the composites excellent conductivity. When the material was damaged, its resistance increased, and heat production increased. With the increase of temperature, SMASH behavior was triggered to complete the healing of damage. The effective recovery of electrical conductivity and mechanical properties enables this electrically driven SMASH composite to provide programmable shape control, extend service life, and enhance practicality, making it highly applicable in bionic electronic sensors. Huang et al.[52] reported a thermoplastic vulcanizate with thermal/magnetic/light-triggered SMASH behavior. Through prestretching, the materials achieved high healing efficiency. However, the sample without prestretching could not achieve perfect surface contact, resulting in local cracks still existing.

Since indirect drives such as light and magnetic drives are essentially indirect thermal drives, they cannot avoid the aging problems caused by local high temperatures during the long-term use of materials. Utilizing other nonthermal stimuli, such as redox agents, solvents, and water, to trigger SMASH behavior is a direction worthy of further research. This stimulation method is currently mostly used in hydrogels but is less common in elastomers. Jiang et al.[53] prepared a moisture-induced SMASH polymer by introducing hydrogen bonds and host−guest interactions in semi-interpenetrating polymer networks. The moisture-induced SMASH behavior of this material placed high demands on the hygroscopicity of the network. Sufficient moisture caused the hydrogen bond network to loosen, releasing stored deformation energy, restoring the shape of the material and facilitating the closure necessary for self-healing. The development of nonheat-triggered SMASH capabilities holds significant potential in biomedical applications such as drug delivery and soft robotics.

It can be seen that SMASH materials have broad application prospects in the fields such as wearable electronic products, smart biomedical devices, soft robots, and space-deployable structures. Smart devices built on SMASH can quickly recover their original performance after damage. Previous research on SMASH focused on the effective repair of micrometer cracks. However, the damage scale of the device often spans the centimeter level or even the meter level, which poses a challenge for the practical application of SMASH. According to our investigation, there are no insights or reviews on the repair of centimeter-scale and above damage for SMASH. Repairing destructive damage with SMASH is significant but challenging. Rodriguez et al.[42] demonstrated that combining shape memory behavior with conventional self-healing abilities helps close small scratches and nanoindentations. However, the degree of self-healing is limited to minor scratches, because the low energy density of SMPs restricts the driving force for large fragments, thereby preventing the closure of macroscopic wounds.

High-energy-density SMPs may be an important alternative to address the performance deficiencies mentioned above. However, it is a great challenge to realize high-energy-density SMPs with both high recovery stress and large recoverable strain. Typically, the recovery stress generated when an SMP returns to its initial state is determined by the entropy energy stored in the network, which is controlled by the density and strength of the network connections. Since the density of connections in the entangled network is predetermined by the entangled molecular weight of the polymer, SMPs typically store entropy energy of the same order of magnitude as their entangled platform modulus (∼1 MPa), thus providing an upper limit for achievable recovery stress. To address these issues, Bao et al.[54] designed high-energy-density shape memory polymers via strain-induced supramolecular nanofibers, which combined shape memory behavior with achievable terminal flow temperature to rapidly self-heal large puncture injuries, which was previously only possible with capsule- and vascular-based self-healing mechanisms.

■ CONCLUSION AND INSIGHTS

As previously discussed, SHPs are intelligent materials that can autonomously repair damage and reinstate their original functionality upon being damaged. This process hinges on triggering the rearrangement of dynamic bonds and the diffusion of polymer chains under external stimuli. However, predominant research on SHPs predominantly centers on their efficacy in contact repair, often overlooking their requirement of independently facilitating the closure of wounds during the repair process. Consequently, when confronted with larger or broader cracks, SHPs often necessitate external intervention to align the damaged surfaces for the subsequent self-healing procedure to proceed at the interface. This reliance on external forces poses constraints on their practical applicability. This problem can be effectively solved by coupling the SME in SHPs and utilizing the shape recovery process to achieve the automatic closure of the damaged interface.

While significant progress has been made in developing SMASH materials, numerous challenges persist. First, achieving both shape memory and self-healing capabilities typically demands distinct material properties and structural designs. SHPs necessitate highly reversible phase change behavior, effective Ttrans, and exceptional mechanical properties to ensure reliable triggering and shape recovery. Conversely, SMPs require good plasticity to autonomously mend the damaged components. Due to differences, integrating shape

memory properties into self-healing materials may impact their self-healing performance, potentially requiring additional measures such as the addition of solvent to complete the self-healing process, which has evidenced in prior studies (Figure 4B). Thus, striking a balance between the triggering temperature of SME and self-healing efficiency, as well as reconciling the mechanical strength and self-healing speed of the material, emerges as pressing issues demanding resolution.

Moreover, achieving the coupling of shape memory and self-healing performance typically demands intricate regulation and optimization of the material's structure and composition. The design and preparation of such materials often entail the selection of various raw materials, including polymers, metal complexes, and organic small molecules. Additionally, careful consideration must be given to the type and density of dynamic bonds. These can complicate large-scale material synthesis. Therefore, it is essential to simplify the synthesis process by reducing the number of synthesis steps and additional chemical modification processes, removing complex molecular architectures, and developing a simpler, more cost-effective synthesis method to achieve multifunctional integration for large-scale application of SMASH materials.

In addition, SMASH materials are currently extensively used in wearable electronic sensors, drug delivery, anticorrosion coatings, and other fields. In addition to self-healing and shape memory properties, different application scenarios impose additional performance criteria on materials. For example, electronic sensors require stable conductivity, medical applications require biocompatibility, and anticorrosion coatings require good hydrophobicity, compactness, and so on. It is extremely challenging to balance these diverse performance requirements to obtain excellent multifunctional materials while ensuring good shape recovery and self-healing efficiency. Therefore, it is necessary to carry out further research to understand the synergistic or antagonistic interactions among various mechanisms, analyze the individual and synergistic effects of parameters such as polymer systems and filler types on different properties, and obtain multifunctional materials that meet different application requirements.

Furthermore, in application environments such as anticorrosive coatings or artificial skin, it is difficult to guarantee a relatively flat interface. In the face of the diversity of contact surfaces, SMASH polymers not only achieve a good fit at the interface but also prevent the penetration of corrosive agents and other external environments into the damaged area, thus performing as a protective barrier. Therefore, considering the service status of the materials during actual use, programming the temporary shape of the materials, and logically designing to ensure the effective implementation of SMASH behavior according to usage requirements are also challenges that SMASH materials need to face in the next stage.

Lastly, most of the currently developed SMASH polymers can only repair micrometer-scale cracks such as scratches or dents and often have poor repair ability for large structural damages. The rapid repair of large structural damage is an urgent challenge in the future development of SMASH polymers. By summarizing the advanced literature, we propose two methods to achieve large crack repair: presetting temporary shapes and preparing high-energy-density elastomers. Presetting temporary shapes can provide a guided target for the material, helping it automatically return to its original shape after damage. This orientation helps the self-healing process proceed in the expected direction and improves the

effectiveness of repairing large area damage. High-energy-density elastomers possess high recovery stress and large recoverable strain, which can drive the repair of large area damage, thereby enhancing repair effectiveness. Based on these approaches, it is of great significance to develop new ways to realize the efficient repair of large structural damage to address multiple modes of damage in practical applications.

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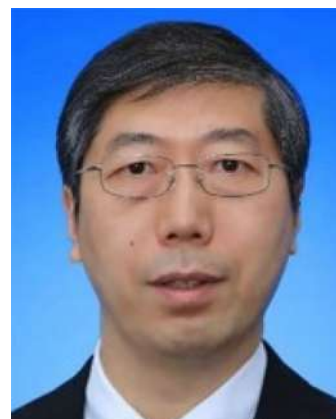
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■ REFERENCES

(1) Wu, D. Y.; Meure, S.; Solomon, D. Self-Healing Polymeric Materials: A Review of Recent Developments. *Prog. Polym. Sci.* **2008**, *33*, 479−522.

(2) Chen, J.; Zeng, H. Mussel-Inspired Reversible Molecular Adhesion for Fabricating Self-Healing Materials. *Langmuir* **2022**, *38*, 12999−13008.

(3) Toohey, K. S.; Sottos, N. R.; Lewis, J. A.; Moore, J. S.; White, S. R. Self-Healing Materials with Microvascular Networks. *Nat. Mater.* **2007**, *6*, 581−585.

(4) Cash, J. J.; Kubo, T.; Bapat, A. P.; Sumerlin, B. S. Room-Temperature Self-Healing Polymers Based on Dynamic-Covalent Boronic Esters. *Macromolecules* **2015**, *48*, 2098−2106.

(5) Liu, X.; Wu, J.; Tang, Z.; Wu, J.; Huang, Z.; Yin, X.; Du, J.; Lin, X.; Lin, W.; Yi, G. Photoreversible Bond-Based Shape Memory Polyurethanes with Light-Induced Self-Healing, Recyclability, and 3D Fluorescence Encryption. *ACS Appl. Mater. Interfaces* **2022**, *14*, 33829−33841.

(6) S, A.; Banerjee, S. S. Shape Memory Behavior and Self-Healing Effects of Dynamically Vulcanized TPU/ENR Thermoplastic Elastomeric Blends. *ACS Appl. Polym. Mater.* **2023**, *5*, 10446−10457.

(7) Boynton, N. R.; Dennis, J. M.; Dolinski, N. D.; Lindberg, C. A.; Kotula, A. P.; Grocke, G. L.; Vivod, S. L.; Lenhart, J. L.; Patel, S. N.; Rowan, S. J. Accessing Pluripotent Materials Through Tempering of Dynamic Covalent Polymer Networks. *Science* **2024**, *383*, 545−551.

(8) Ping, Z.; Xie, F.; Gong, X.; Zhang, F.; Zheng, J.; Liu, Y.; Leng, J. Tailoring Photoweldable Shape Memory Polyurethane with Intrinsic Photothermal/Fluorescence Via Engineering Metal-Phenolic Systems. *Adv. Funct. Mater.* **2024**, 2402592.

(9) Behl, M.; Lendlein, A. Shape-memory polymers. *Memory Polymers. Mater. Today* **2007**, *10*, 20−28.

(10) Hornat, C. C.; Urban, M. W. Shape Memory Effects in Self-Healing Polymers. *Prog. Polym. Sci.* **2020**, *102*, 101208.

(11) Ni, C.; Chen, D.; Yin, Y.; Wen, X.; Chen, X.; Yang, C.; Chen, G.; Sun, Z.; Wen, J.; Jiao, Y.; Wang, C.; Wang, N.; Kong, X.; Deng, S.; Shen, Y.; Xiao, R.; Jin, X.; Li, J.; Kong, X.; Zhao, Q.; Xie, T. Shape Memory Polymer with Programmable Recovery Onset. *Nature* **2023**, *622*, 748−753.

(12) Luo, L.; Zhang, F.; Wang, L.; Liu, Y.; Leng, J. Recent Advances in Shape Memory Polymers: Multifunctional Materials, Multiscale Structures, and Applications. *Adv. Funct. Mater.* **2024**, *34*, 2312036.

(13) Jia, Y.; Ying, H.; Zhang, Y.; He, H.; Cheng, J. Reconfigurable Poly(urea-urethane) Thermoset Based on Hindered Urea Bonds with Triple-Shape-Memory Performance. *Macromol. Chem. Phys.* **2019**, *220*, 1900148.

(14) Behl, M.; Kratz, K.; Zotzmann, J.; Nöchel, U.; Lendlein, A. Reversible Bidirectional Shape-Memory Polymers. *Adv. Mater.* **2013**, *25*, 4466−4469.

(15) Shen, W.; Liu, J.; Du, B.; Zhuo, H.; Chen, S. Thermal- and Light-Responsive Programmable Shape-Memory Behavior of Liquid Crystalline Polyurethanes with Pendant Photosensitive Groups. *J. Mater. Chem. A* **2021**, *9*, 15087−15094.

(16) Li, J.; Viveros, J. A.; Wrue, M. H.; Anthamatten, M. Shape-Memory Effects in Polymer Networks Containing Reversibly Associating Side-Groups. *Adv. Mater.* **2007**, *19*, 2851−2855.

(17) Wang, S.; Urban, M. W. Self-Healing Polymers. *Nat. Rev. Mater.* **2020**, *5*, 562−583.

(18) Blaiszik, B. J.; Kramer, S. L. B.; Olugebefola, S. C.; Moore, J. S.; Sottos, N. R.; White, S. R. Self-Healing Polymers and Composites. *Annu. Rev. Mater. Res.* **2010**, *40*, 179−211.

(19) Cooper, C. B.; Root, S. E.; Michalek, L.; Wu, D.; Lai, H.-Y.; Khatib, M.; Oyakhire, S. T.; Zhao, B.; Qin, J.; Bao, Z. Autonomous Alignment and Healing in Multilayer Soft Electronics Using Immiscible Dynamic Polymers. *Science* **2023**, *380*, 935−941.

(20) Li, B.; Cao, P.-F.; Saito, T.; Sokolov, A. P. Intrinsically Self-Healing Polymers: From Mechanistic Insight to Current Challenges. *Chem. Rev.* **2023**, *123*, 701−735.

(21) Yang, Y.; Ding, X.; Urban, M. W. Chemical and Physical Aspects of Self-Healing Materials. *Prog. Polym. Sci.* **2015**, *49−50*, 34−59.

(22) Kang, J.; Son, D.; Wang, G. J. N.; Liu, Y.; Lopez, J.; Kim, Y.; Oh, J. Y.; Katsumata, T.; Mun, J.; Lee, Y.; Jin, L.; Tok, J. B. H.; Bao, Z. Tough and Water-Insensitive Self-Healing Elastomer for Robust Electronic Skin. *Adv. Mater.* **2018**, *30*, 1706846.

(23) Xu, J. H.; Chen, J. Y.; Zhang, Y. N.; Liu, T.; Fu, J. J. A Fast Room-Temperature Self-Healing Glassy Polyurethane. *Angew. Chem., Int. Ed.* **2021**, *60*, 7947−7955.

(24) Zhang, Y.; Chen, J.; Zhang, G.; Xv, J.; Xv, J.; Hu, Y.; Guo, H.; Guo, F.; Fu, J.; Jiang, W. Mechanically Robust, Highly Adhesive and Autonomously Low-Temperature Self-Healing Elastomer Fabricated Based on Dynamic Metal-Ligand Interactions Tailored for Functional Energetic Composites. *Chem. Eng. J.* **2021**, *425*, 130665.

(25) Mei, J. F.; Jia, X. Y.; Lai, J. C.; Sun, Y.; Li, C. H.; Wu, J. H.; Cao, Y.; You, X. Z.; Bao, Z. A Highly Stretchable and Autonomous Self-Healing Polymer Based on Combination of Pt···Pt and π−π Interactions. *Macromol. Rapid Commun.* **2016**, *37*, 1667−1675.

(26) Duan, N.; Sun, Z.; Ren, Y.; Liu, Z.; Liu, L.; Yan, F. Imidazolium-Based Ionic Polyurethanes with High Toughness, Tunable Healing Efficiency and Antibacterial Activities. *Polym. Chem.* **2020**, *11*, 867−875.

(27) Urban, M. W.; Davydovich, D.; Yang, Y.; Demir, T.; Zhang, Y. Z.; Casabianca, L. Key-and-Lock Commodity Self-Healing Copolymers. *Science* **2018**, *362*, 220−225.

(28) Wang, Z.; An, G.; Zhu, Y.; Liu, X.; Chen, Y.; Wu, H.; Wang, Y.; Shi, X.; Mao, C. 3D-Printable Self-Healing and Mechanically Reinforced Hydrogels with Host−Guest Non-Covalent Interactions Integrated into Covalently Linked Networks. *Mater. Horiz.* **2019**, *6*, 733−742.

(29) Deng, X.-Y.; Xie, H.; Du, L.; Fan, C.-J.; Cheng, C.-Y.; Yang, K.-K.; Wang, Y.-Z. Polyurethane Networks Based on Disulfide Bonds: from Tunable Multi-Shape Memory Effects to Simultaneous Self-Healing. *Sci. China Mater.* **2019**, *62*, 437−447.

(30) Wang, P.; Yang, L.; Dai, B.; Yang, Z.; Guo, S.; Gao, G.; Xu, L.; Sun, M.; Yao, K.; Zhu, J. A Self-Healing Transparent Polydimethylsiloxane Elastomer Based on Imine Bonds. *Eur. Polym. J.* **2020**, *123*, 109382.

(31) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A Thermally Re-mendable Cross-Linked Polymeric Material. *Science* **2002**, *295*, 1698−1702.

(32) Rao, Y.-L.; Chortos, A.; Pfattner, R.; Lissel, F.; Chiu, Y.-C.; Feig, V.; Xu, J.; Kurosawa, T.; Gu, X.; Wang, C.; He, M.; Chung, J. W.; Bao, Z. Stretchable Self-Healing Polymeric Dielectrics Cross-Linked Through Metal-Ligand Coordination. *J. Am. Chem. Soc.* **2016**, *138*, 6020−6027.

(33) Wei, H.; Yao, Y.; Liu, Y.; Leng, J. A Dual-Functional Polymeric System Combining Shape Memory with Self-Healing Properties. *Compos. Part B-Eng.* **2015**, *83*, 7−13.

(34) Liu, J.; Huang, Y.-S.; Liu, Y.; Zhang, D.; Koynov, K.; Butt, H.-J.; Wu, S. Reconfiguring Hydrogel Assemblies Using a Photocontrolled Metallopolymer Adhesive for Multiple Customized Functions. *Nat. Chem.* **2024**, *16*, 1024.

(35) Zhou, S.-W.; Zhou, D.; Gu, R.; Ma, C.-S.; Yu, C.; Qu, D.-H. Mechanically Interlocked [c2] Daisy Chain Backbone Enabling Advanced Shape-Memory Polymeric Materials. *Nat. Commun.* **2024**, *15*, 1690.

(36) Zhu, Y.; Deng, K.; Zhou, J.; Lai, C.; Ma, Z.; Zhang, H.; Pan, J.; Shen, L.; Bucknor, M. D.; Ozhinsky, E.; Kim, S.; Chen, G.; Ye, S.-h.; Zhang, Y.; Liu, D.; Gao, C.; Xu, Y.; Wang, H.; Wagner, W. R. Shape-Recovery of Implanted Shape-Memory Devices Remotely Triggered Via Image-Guided Ultrasound Heating. *Nat. Commun.* **2024**, *15*, 1123.

(37) An, S.-C.; Lim, Y.; Jun, Y. C. Rapid and Selective Actuation of 3D-Printed Shape-Memory Composites Via Microwave Heating. *Sci. Rep.* **2023**, *13*, 18179.

(38) Li, Y.; Zhang, F.; Liu, Y.; Leng, J. A Tailorable Series of Elastomeric-To-Rigid, Selfhealable, Shape Memory Bismaleimide. *Small* **2024**, *20*, 2307244.

(39) Yu, L.; Wang, Q.; Sun, J.; Li, C.; Zou, C.; He, Z.; Wang, Z.; Zhou, L.; Zhang, L.; Yang, H. Multi-Shape-Memory Effects in a Wavelength-Selective Multicomposite. *J. Mater. Chem. A* **2015**, *3*, 13953−13961.

(40) Zarek, M.; Layani, M.; Cooperstein, I.; Sachyani, E.; Cohn, D.; Magdassi, S. 3D Printing of Shape Memory Polymers for Flexible Electronic Devices. *Adv. Mater.* **2016**, *28*, 4449−4454.

(41) Ze, Q.; Kuang, X.; Wu, S.; Wong, J.; Montgomery, S. M.; Zhang, R.; Kovitz, J. M.; Yang, F.; Qi, H. J.; Zhao, R. Magnetic Shape Memory Polymers with Integrated Multifunctional Shape Manipulation. *Adv. Mater.* **2020**, *32*, 1906657.

(42) Rodriguez, E. D.; Luo, X.; Mather, P. T. Linear/Network Poly (ε-caprolactone) Blends Exhibiting Shape Memory Assisted Self-Healing (SMASH). *ACS Appl. Mater. Interfaces* **2011**, *3*, 152−161.

(43) Luo, X.; Mather, P. T. Shape Memory Assisted Self-Healing Coating. *ACS Macro Lett.* **2013**, *2*, 152−156.

(44) Ur Rehman, H.; Chen, Y.; Hedenqvist, M. S.; Li, H.; Xue, W.; Guo, Y.; Guo, Y.; Duan, H.; Liu, H. Self-Healing Shape Memory PUPCL Copolymer with High Cycle Life. *Adv. Funct. Mater.* **2018**, *28*, 1704109.

(45) Heo, Y.; Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **2014**, *24*, 5261−5268.

(46) Nguyen, L. T.; Pham, H. Q.; Thi Phung, D. T.; Truong, T. T.; Nguyen, H. T.; Chanh Duc Doan, T.; Dang, C. M.; Le Tran, H.; Mai, P. T.; Tran, D. T.; Nguyen, T. Q.; Ho, N. Q.; Nguyen, L.-T. T. Macromolecular Design of a Reversibly Crosslinked Shape-Memory Material with Thermo-Healability. *Polymer* **2020**, *188*, 122144.

(47) Xie, F.; Ping, Z.; Xu, W.; Zhang, F.; Dong, Y.; Li, L.; Zhang, C.; Gong, X. A Metal Coordination-Based Supramolecular Elastomer with Shape Memory-Assisted Self-Healing Effect. *Polymers* **2022**, *14*, 4879.

(48) Wang, X.; Xu, J.; Zhang, Y.; Wang, T.; Wang, Q.; Li, S.; Yang, Z.; Zhang, X. A Stretchable Mechanically Robust Polymer Exhibiting Shape-Memory-Assisted Self-Healing and Clustering-Triggered Emission. *Nat. Commun.* **2023**, *14*, 4712.

(49) Liu, J. J.; Li, J. M.; Qiao, S.; Wang, Z. F.; Zhang, P. H.; Fan, X. Q.; Cheng, P.; Li, Y. S.; Chen, Y.; Zhang, Z. J. Self-Healing and Shape Memory Hypercrosslinked Metal-Organic Polyhedra Polymers via Coordination Post-Assembly. *Angew. Chem.Int. Ed.* **2022**, *61*, No. e202212253.

(50) Bai, Y.; Zhang, J.; Wen, D.; Gong, P.; Liu, J.; Ju, J.; Chen, X. A Reconfigurable, Self-Healing and Near Infrared Light Responsive Thermoset Shape Memory Polymer. *Compos. Sci. Technol.* **2020**, *187*, 107940.

(51) Pu, W.; Fu, D.; Wang, Z.; Gan, X.; Lu, X.; Yang, L.; Xia, H. Realizing Crack Diagnosing and Self-Healing by Electricity with a Dynamic Crosslinked Flexible Polyurethane Composite. *Adv. Sci.* **2018**, *5*, 1800101.

(52) Huang, J.; Cao, L.; Yuan, D.; Chen, Y. Design of Novel Self-Healing Thermoplastic Vulcanizates Utilizing Thermal/Magnetic/Light-Triggered Shape Memory Effects. *ACS Appl. Mater. Interfaces* **2018**, *10*, 40996−41002.

(53) Jiang, Z. C.; Xiao, Y. Y.; Kang, Y.; Li, B. J.; Zhang, S. Semi-IPNs with Moisture-Triggered Shape Memory and Self-Healing Properties. *Macromol. Rapid Commun.* **2017**, *38*, 1700149.

(54) Shi, Y.; Cooper, C. B.; Nogusa, T.; Lai, J.-C.; Lyu, H.; Khatib, M.; Xu, C.; Michalek, L.; Bao, Z. Shape-Memory-Assisted Self-Healing of Macroscopic Punctures Via High-Energy-Density Periodic Dynamic Polymers with Tunable Actuation Temperature. *Matter* **2024**, *7*, 2108−2124.

(55) Xia, B.; Li, Z.; Lin, T.; Gao, M.; Zhao, C.; Wu, X.; Lin, C.; Wang, J. Self-Healing, Recyclable Syndiotactic 1, 2-Polybutadiene-Based Thermadapt Shape Memory Polymers with Cold-Programmed Shape Memory Effect. *ACS Appl. Polym. Mater.* **2024**, *6*, 102−114.