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Review

A Short Review on Polyethylene-based Ionomers: Synthesis, Structure, and Applications

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Cite This: *Chem Bio Eng.* 2025, 2, 156−170

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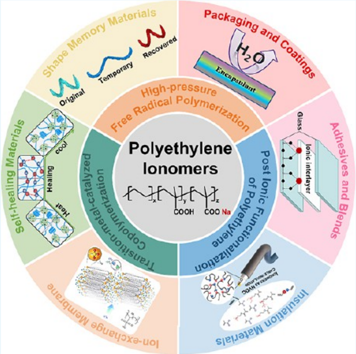
ABSTRACT: Polyethylene-based ionomers (PE ionomers) are polymers featuring polyethylene as the main chain structure with a small fraction of ionic functional groups pendant to the polyethylene backbone. Due to this combination of nonpolar covalent skeletons and polar ionic groups, PE ionomers can exhibit various properties, depending on their specific composition and structure, such as clarity, adhesivity, abrasiveness, enhanced mechanical strength, shape memory, and healable capabilities. These extraordinary properties have led to the broad applications of PE ionomers in the past decades for cosmetics packaging, coatings, blends, ion-exchange membranes, high voltage insulation materials, and adhesives and even hold great potential in the emerging fields of shape memory and healable smart materials. This review provides an in-depth overview of the latest progress in the field of PE ionomers, with a particular focus on diverse synthetic methods and structural models, as well as important related applications. The structure−property relationship is also discussed interstitially, providing ideas for the subsequent development of PE ionomers with novel structures and fresh applications.



KEYWORDS: *Polyethylene, Ionomers, Ionic Clusters, Surlyn Ionomers, Shape Memory and Healable Polymers*

1. INTRODUCTION

Ionomers typically refer to polymeric materials consisting of hydrocarbon backbone chains and a small amount (<15 mol %) of pendant ionic or ionizable groups or both. The hydrocarbon chain within ionomers is often composed of polyolefins, and the most studied pendant ionic or ionizable groups are ammonium groups or acid groups (such as carboxylic, sulfonic, or phosphoric acid groups), which can exist in either their unneutralized form (with ionizable property) or partially to fully neutralized form.[1−3] As a special class of high-value polymers, ionomer materials are emerging as rising stars of supramolecular materials and have gained increasing attention and expanding applications.[4] Three types of commercialized ionomers stand out as the most extensively utilized worldwide: (1) Surlyn ionomer, a class of copolymers of ethylene and (meth)acrylic acid (EAA or EMAA) partially neutralized with metals ions (e.g., zinc, sodium, and lithium), is renowned for optical transparency, toughness, excellent puncture strength, and superior adhesive properties. These distinguished attributes make it highly suitable for a wide range of applications in food packaging, electronics, and medical industries. (2) Nafion ionomer, a sort of branched fluorinated polymer with sulfonic acid groups, enjoys widespread applications in membrane technology to selectively transport protons, notably within the domain of fuel cell technology.[5] (3) Hypalon ionomer, a kind of thermoplastic elastomer derived from chloro-sulfonated polyethylene rubber, exhibits superb resistance to ultraviolet radiation and chemical agents. These qualities render them versatile for various applications in the construction industry, encompassing roofing materials and consumer products, such as inflatable rafts.

Among the three most widely used commercial ionomers, polyethylene-based ionomers (PE ionomers) with polyethylene as the hydrocarbon backbones are the main category of ionomers, containing the Surlyn and Hypalon ionomers.[6] Owing to the mismatch between the nonpolar polyethylene backbone and the polar pendant ionic groups in the PE ionomers, the ionic groups (or those associated with metal ions) tend to form ion-rich domains within the hydrophobic polyethylene matrix, which exert a significant influence on the mechanical properties and melt-flow characteristics of the resultant materials. As a result, PE ionomers possess various excellent properties, including superb abrasion resistance, high clarity, scratch and scuff resistance, impact resistance, chemical resistance, and adhesive performance. Moreover, the incorpo-

Received: August 23, 2024
Revised: October 31, 2024
Accepted: October 31, 2024
Published: November 4, 2024

https://doi.org/10.1021/cbe.4c00138
Chem Bio Eng. 2025, 2, 156−170

ration of ionic cross-linking within PE ionomer facilitates the dynamic rearrangement in response to damage and shape change via ions migration and redistribution. This property enables their utilization as healable and shape memory smart material.[7,8] More recently, a novel fluorescent eutectogel with high transparency, adhesion, and healable performance is fabricated via interfacial hydrogen bonding networks of EAA, expanding the multifunctional applications of ionomers in conformal information encryption and anticounterfeiting.[9] Although the ionic groups endow PE ionomers with distinctive properties and performance by comparing with the commonly utilized polyethylene, the synthesis of PE ionomers is significantly impeded by the limitations of high-pressure radical polymerization owing to the presence of a polar comonomer that inhibits the catalytic process. After more than 20 years of extensive research, several fine-designed catalysts that are more resistant to polar groups for ethylene copolymerization with polar comonomers have emerged, and thus the direct synthesis of PE ionomers has made great progress. In this case, many novel PE ionomers with multifunctional properties have been developed. Summarizing the recent progress on the synthesis, structure, and properties of PE ionomers is imperative, which could not only facilitate the design of advanced materials but also explore the application of PE ionomers.

Herein, we try to provide an in-depth overview that summarizes the recent progress in PE ionomers, with a particular focus on the existing diverse synthetic methods, structural theories, and important applications. A discussion of the corresponding relationship between the structure and performance will also be given. With this Review, we hope to spark new ideas and motivate new efforts for the subsequent development of the synthesis of new types of PE ionomers and the expansion of applications. It should be noted that this review covers only PE ionomers. Readers interested in ionomers based on other polymer matrix are referred to other excellent reviews.[4,7,10,11]

2. SYNTHESIS OF PE IONOMERS

As discussed, the PE ionomers are composed of a polyethylene backbone and pendant polar ionic groups. Traditionally, the synthesis of PE ionomers is restricted to high-pressure free radical copolymerization, but now the synthetic methods of PE ionomers have been explored to interconversion of reactive intermediate, direct catalytic copolymerization, olefin metathesis polymerization, and post ionic functionalization of inert polyethylene.[6]

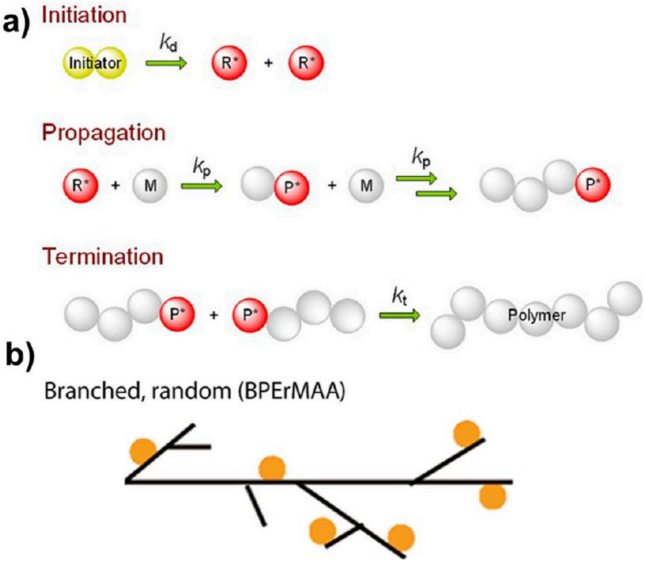


Figure 1. a) Schematic illustration showing the essential reaction steps of the free radical polymerization. Reproduced with permission.[13] Copyright 2021, Taylor & Francis. b) Branched PE ionomers produced using high-pressure polymerization with acid groups randomly spaced. Reproduced with permission.[17] Copyright 2010, American Chemical Society.

2.1. High-pressure Free Radical Polymerization. Normally, the free radical copolymerization of ethylene and a certain polar comonomer (e.g., acrylic acid, AA, or methacrylic acid, MAA) can produce an acidic-form PE ionomer. The copolymerization procedure is normally conducted under extremely high pressure (120−320 MPa) and high temperatures (160−320 °C) that are akin to the synthesis of low-density polyethylene (LDPE).[12] The detailed free radical polymerization mechanism of PE ionomer is illustrated in Figure 1a.[13] Primary radicals are produced from initiators, such as oxygen or organic peroxides, by thermally induced decomposition with the rate coefficient k_{d}. These active radicals could then react with monomers with rate coefficient k_{p} or may undergo mutual termination, by combination, or by disproportionation, i.e., by a hydrogen-transfer reaction, which produces saturated products and unsaturated products simultaneously. Therefore, the overall termination rate coefficient is composed of two terms: $k_{\mathrm{t}} = k_{\mathrm{t,comb}} + k_{\mathrm{t,disp}}$. Besides that, additional reactions, especially the chain-transfer reactions, widely exist during free radical polymerizations. Therefore, PE ionomers produced by free radical polymerization show highly branched topology structures together with wide molecular weight distribution, and high content of long-chain branches and short-chain branches (Figure 1b). Analogous to high-pressure ethylene homopolymerization, the chain structure and branch distribution of PE ionomers can also be modified by regulating polymerization parameters.[14,15] The relatively low reaction temperature and high pressure will obtain PE ionomers with relatively higher molecular weight and narrower molecular weight distribution. Different from the LDPE production, the content of the feed polar comonomer should be carefully controlled due to the significantly higher reactivity ratio of polar monomers. It is reported that the reactivity ratios of AA and MAA at 240 °C and 200 MPa are $r_{\mathrm{MAA}}= 11 \pm 3$ and $r_{\mathrm{AA}}= 8 \pm 2$.[12] It is also worth noting that the detailed relationships between operating conditions and the final material structure and properties of the polymer required further investigation.[16]

In the 1960s, DuPont commercialized PE ionomer under the trade name "Surlyn", which is synthesized through the free radical copolymerization of ethylene and (meth)acrylic acid, and followed by partial or full neutralization of the carboxylic acids with metals (especially alkali metals) (Figure 2a).[18,19] These materials are currently sold by Dow for high-end packaging and medical and sports applications. Besides the polymerization process, the neutralization process, which primarily encompasses the slurry method, solution method, or melting method, can also influence the structure or property of the final product. Sun et al.[20] synthesized healable and recyclable Surlyn materials by partially neutralizing poly(ethylene-*co*-methacrylic acid) (PEMA) with zinc ions, achieving a tensile strength of approximately 37 MPa, a

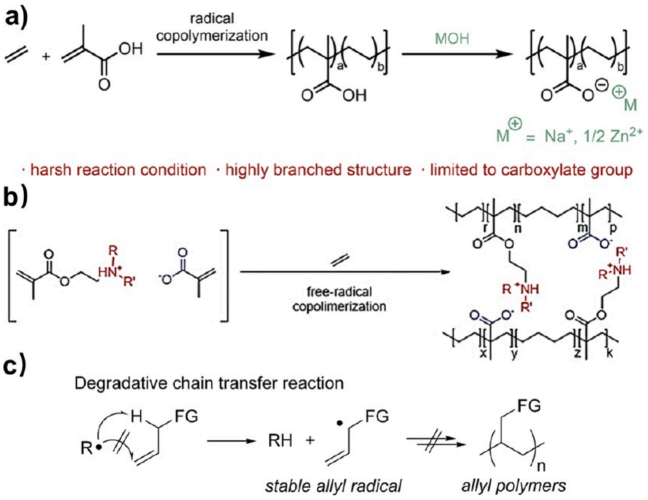


Figure 2. a) Synthesis route for commercially available Surlyn. Reproduced with permission.[6] Copyright 2023, American Chemical Society. b) Free radical polymerization reaction of novel PE ionomers that covalently bonded with cationic and anionic groups. Reproduced with permission.[21] Copyright 2023, Wiley-VCH. c) Degradative chain transfer reaction during the free radical polymerization. Reproduced with permission.[22] Copyright 2011, American Chemical Society.

Young's modulus of around 343 MPa. In these cases, Surlyn has attracted extensive research interest in industry and academia, but the ionic groups in Surlyn are currently still limited to carboxylate. More recently, a new type of ionomer has been obtained via high-pressure free radical copolymerization of ethylene in the presence of small amounts of ion-pair comonomers comprising amine-terminated methacrylate and methacrylic acid (Figure 2b).[21] Different from the commercially available Surlyn, the cationic and anionic groups are covalently bound to the backbone of the novel PE ionomer.

Although high-pressure free radical polymerization is the most widely used approach for producing PE ionomers, it still encounters several challenges. For example, harsh operating conditions (high temperature and high pressure) demand substantial energy consumption and maintenance costs. Importantly, the currently practiced free radical polymerization processes provide limited control over the polymer microstructure, which could produce ionomers with highly branched structures and wide molecular weight distributions. This limits the ionomer performance to some extent to LDPE type materials. Furthermore, the polar monomer of free radical polymerization processes is normally restricted. The polymerization of allyl monomers in free radical polymerization processes yields predominantly oligomers or polymers with low molecular weights due to the facile "degradative chain transfer" to the allyl monomers at the α-position of the polar groups, where the bond dissociation energy of the C−H bond adjacent to the polar group is relatively low, thereby diminishing the reactivity of the resultant allyl radical species (Figure 2c).[22] This significantly limits the diversity of the PE ionomers.

2.2. Transition-metal-catalyzed Copolymerization. To overcome the limitations of free radical copolymerization, several transition-metal-catalyzed copolymerization methods have been reported to access PE ionomers with potentially better control over material microstructures and properties.[23]

2.2.1. Interconversion of Reactive Polyethylene Intermediate. The copolymerization of ethylene with polar monomers is highly challenging owing to the formation of stable complexes between catalysts and polar groups, which may poison the catalyst and then inhibit polymerization to high polymers or cause undesirable side reactions, especially for early transition metal catalysts. The interconversion of the reactive polyethylene intermediate can be a feasible approach to the synthesis of PE ionomers by early transition metal catalysts. In this approach, the polar comonomer should be protected by the introduction of stabilizing groups, such as silane groups, to enhance compatibility with the catalysts. To achieve the final form of the PE ionomers, subsequent deprotection or ionization processes following the polymerization process are necessary. Based on this, Zhang et al.[24] demonstrated that silane protected amino-α-olefin comonomers could be copolymerized with ethylene via direct metallocene-mediated copolymerization because the sterically encumbered silyl-protecting groups can highly minimize the poisoning of the zirconium metallocene catalyst. After polymerization, the deprotection of the silyl-protecting groups under mild conditions yields primary amine-containing copolymers, which could be further protonated to yield ammonium PE ionomers (Figure 3a).[24] Compared with free radical polymerization, the interconversion of reactive polyethylene intermediate approach facilitates the incorporation of functional groups that can be ionized postpolymerization, expanding the range of ionic modifications beyond mere carboxylates, but it requires the synthesis of specialty monomers and/or ligands to avoid the diminishment of catalyst activity.[6]

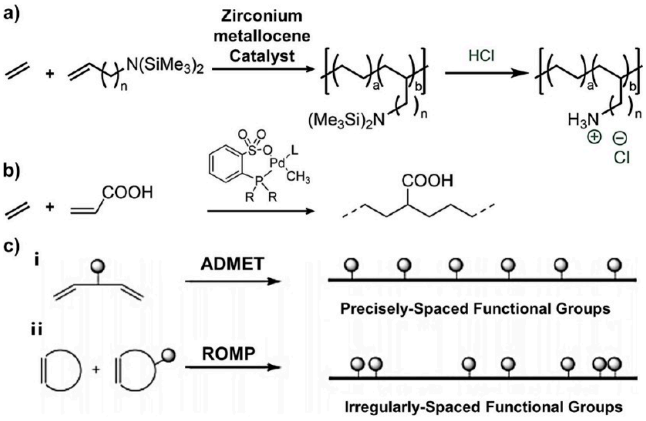


Figure 3. Synthesis of PE ionomers through transition-metal-catalyzed copolymerization. a) Interconversion of reactive polyethylene intermediate. Reproduced with permission.[24] Copyright 2011, American Chemical Society. b) Direct catalytic copolymerization by late-transition metal catalysts. Reproduced with permission.[26] Copyright 2011, American Chemical Society. c) Olefin metathesis polymerization of ADMET and ROMP. Reproduced with permission.[30] Copyright 2007, American Chemical Society.

2.2.2. Direct Catalytic Copolymerization. The direct catalytic copolymerization of ethylene with polar monomer to synthesize PE ionomers is always an appealing prospect due to its straightforward process. Compared with early transition metal catalysts, late-transition metal catalysts, such as Pd and Ni complexes with α-diimine ligands and Pd phosphine-sulfonate catalysts, are less oxophilic and occasionally tolerant enough for the coordination polymerization of polar monomers. The synthesis of PE ionomers by late transition metal catalysts has already been extensively investigated. Rünzi et al.,[25] Daigle et al.,[26] and Zhang et al.[27] have demonstrated successful examples of transition-metal-catalyzed copolymerization using phosphine sulfonate palladium catalysts (Figure 3b).[26] In these studies, a satisfactory AA incorporation rate of 3.0−9.6% was achieved, but with a relatively low molecular weight (Mn = 6100−8000 g/mol). Dai et al.[28] observed that sterically bulky α-diamine-based palladium catalysts could efficiently mediate the copolymerization of ethylene with AA, allyl acetic acid, and 10-undecenoic acid, producing branched, carboxylic acid-functionalized polyolefin materials. Furthermore, Xiang et al.[29] reported the synthesis of PE ionomer containing positively charged tetraalkylammonium ions and various counteranions (tetrafluoroborate BF_4^-, hexafluorophosphate PF_6^-, bis(trifluoro methane) sulfonamide Tf_2N^-, and hexafluoro antimonate SbF_6^-) through Pd-catalyzed copolymerization of ethylene with acrylic tetraalkylammonium-containing acrylate-type ionic liquid comonomers. The key to direct copolymerization indeed lies in the resistance of catalysts toward highly polar ionic groups, but the presence of polar ionic comonomers still significantly reduced the polymerization activity of catalysts, resulting in PE ionomers with relatively low molecular weight or highly branched microstructure of materials. Therefore, the meticulous design of catalysts can be a challenging task.

2.2.3. Olefin Metathesis Polymerization. PE ionomers with a controllable structure hold great appeal for specific applications. Two modes of olefin metathesis polymerization, acyclic diene metathesis (ADMET) and ring-opening metathesis polymerization (ROMP) have been proven to successfully synthesize a variety of strictly linear polyolefin ionomers. ADMET yields linear ionomers with precisely spaced functional groups along the polymer backbone, whereas ROMP yields linear ionomers with function groups irregularly spaced along the hydrocarbon chain (Figure 3c).[30] However, both ADMET and ROMP demand specialized polar monomers, such as alpha-omega dienes for ADMET and cyclic olefins with polar groups for ROMP (Figure 3c). Additionally, the olefin metathesis polymerization generates unsaturated products, typically requiring an additional hydrogenation process to yield the final PE ionomers. Using ADMET polymerization followed by catalytic hydrogenation, Wagner and colleagues synthesized carboxylate-containing PE ionomers with a range of AA contents (9−22 mol %) and molecular weights (Mn = 25−38 kDa) using Grubb's ruthenium catalysts.[30,31] The precise spacing of the carboxylate groups along the polymer chain was controlled by varying the number of methylene spacers in the initial diene monomer. Furthermore, ADMET polymerization is employed to yield PE ionomers containing imidazolium and sulfonate groups, with each ionic group precisely spaced along the polymer chain.[5,32] Additionally, they demonstrated that the ROMP of an appropriately functionalized cyclooctadiene, subsequently followed by the hydrogenation of the corresponding polyakenamer, to produce carboxylate-containing PE ionomers with tunable compositions (2−22 mol % AA; 12−93 kDa).[30] Similarly, Trigg et al.[5] synthesized PE ionomers through ADMET polymerization, featuring a sulfonic acid group precisely pendant to every twenty-first carbon atom along the chain with a number-average molecular weight (Mn) of 19.8 kg/mol and a dispersity index of 2.4. Besides, by using ADMET polymerization and subsequent deprotections and hydrogenation, the PE ionomers bearing precisely spaced carboxylic,[30] sulfonic,[33] phosphonic,[34] and boronic acid[35] functionalities were synthesized utilizing labile protecting groups or directly an ionic liquid that is compatible with ADMET polymerization conditions (for boronic acid).

2.3. Postionic Functionalization of Inert Polyethylene. Another strategy for synthesizing PE ionomers involves the ionic functionalization of inert polyethylene, which allows for the introduction of functionality to an existing polyethylene backbone, providing considerable flexibility in tuning the properties of the material. This approach has the potential to expand the variety of commercial polyethylene materials and facilitate the recycling and reuse of discarded polymer materials. Recently, the production of functional polyethylene via C−H functionalization has been extensively investigated.[36,37] Lee et al.[38] employed peroxides as hydrogen atom transfer (HAT) reagents for C−H functionalization of polyethylene to produce anhydride-functionalized polyethylene, which could undergo subsequent reactions with nucleophiles to produce PE ionomers. However, the C−H functionalization of polyethylene using peroxides often leads to relatively low selectivity, resulting in significant β-scission that adversely affects the molecular weight distribution and properties of the resultant product. Fazekas et al.[39] utilized an *O*-alkenylhydroxamate reagent that, under thermolysis, enables regioselective hydrogen atom transfer (HAT), subsequently facilitating functional group transfer to diverse linear and branched polyolefin substrates. To showcase the distinctive benefits of this approach, a primary alkyl halide was introduced onto linear low-density polyethylene (LLDPE), leading to the formation of an imidazolium polyolefin ionomer by displacement of the halide with methyl imidazole. The resultant imidazolium ionomers exhibited tensile properties akin to Surlyn, illustrating the capability of the postpolymerization modification approach to yield polymer materials comparable to high-value commercial ionomers. To provide a more versatile and efficient approach to access a broader range of PE ionomers via postpolymerization modification, Tran et al.[6] synthesized a series of PE ionomers via chemoselective C−H functionalization. The approach harnesses thiosulfates to facilitate group transfer onto polyethylene substrates, enabling the incorporation of pyridyl, benzo thiazolyl, and benz oxazolyl heteroarenes using an *O*-alkenylhydroxamate reagent (Figure 4). Note that pyridyl-functionalized polyethylene could be quantitatively transformed into pyridinium PE ionomers.

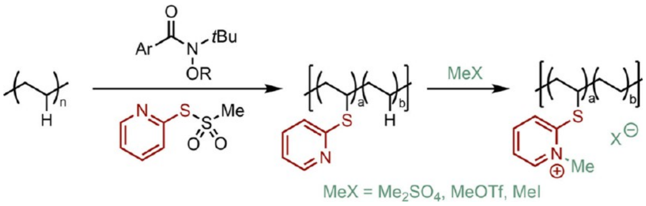


Figure 4. Synthesis of PE ionomer via postionic functionalization of inert polyethylene. Reproduced with permission.[6] Copyright 2023, American Chemical Society.

To date, besides the high-pressure free radical polymerization, the interconversion of reaction intermediate, direct catalytic copolymerization, olefin metathesis polymerization, and postionic functionalization of inert polyethylene have been employed to synthesize PE ionomers for various uses. Indeed, each of these methods exhibits its advantages and challenges,

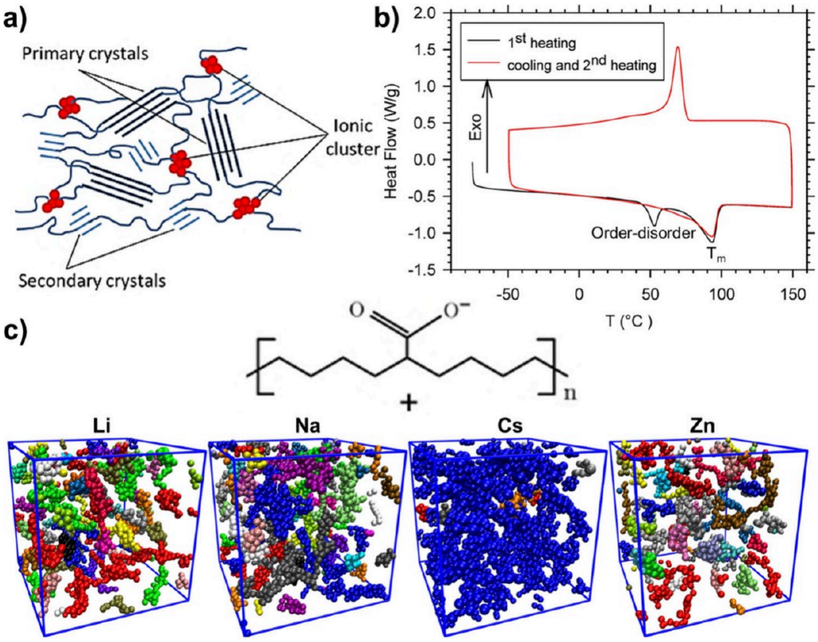


Figure 5. a) Schematic of the molecular structure of Surlyn 9520. Reproduced with permission.[44] Copyright 2017, American Chemical Society. b) DSC cooling and heating thermogram of Surlyn 9520. Reproduced with permission.[43] Copyright 2013, American Chemical Society. c) Visual representations of ionic aggregates. Selected examples of morphology were from atomistic molecular dynamics simulations. Different colors represent distinct aggregates. Reproduced with permission.[50] Copyright 2012, American Chemical Society.

therefore, needs to be chosen based on the specific requirements and constraints of the intended application.

3. STRUCTURE AND PROPERTIES OF PE IONOMERS

The molecular structures play an essential role in influencing the overall performance and functionality of the polymer materials. It is essential to recognize the distinct differences between polyethylene and PE ionomers that stem from their individual structural compositions. As the structure of novel PE ionomers is rarely studied in current references, this part mainly discusses the structure of a commercial PE ionomer (especially Surlyn ionomer).

In PE ionomers, ion pairs undergo microphase separation from the lower dielectric monomeric units of the polyethylene backbone. These ion pairs aggregate to form quadruplets, sextuplets, and higher aggregates, collectively termed multiplets wherein both unneutralized acid groups and ions reside. In the Eisenberg−Hird−Moore (EHM) model, the regions abundant in ions, referred to as ionic clusters, could also exist at sufficiently high ion concentrations, which has been proved through various techniques including small-angle X-ray scattering (SAXS).[40,41] As illustrated by the EHM model, the random ionomers typically exhibit tripartite microstructures, including a polyethylene crystalline phase, an amorphous polyethylene phase without the salt groups, and an ionic clusters phase.[42,43] The schematic of the tripartite microstructure of Surlyn 9520 is shown in Figure 5a.[44] Additionally, another morphological model parallels the tripartite microstructure and proposes that the carboxylic aggregates are uniformly dispersed within the amorphous phase (Yarusso and Cooper's liquid-like model).[42,45] Even though both models acknowledge that the ionic aggregates or clusters act as separate nanophases, resulting in the observation of two glass transition temperatures (T_g) within the nonpolar matrix. One T_g corresponds to the relevant homopolymer, while the other T_g signifies the constrained mobility in the vicinity of the acid or ionic aggregates.[42] In the case of commercial PE ionomer (Surlyn ionomer), the existence of ionic clusters significantly reduces PE chain mobility, resulting in a lower degree of crystallization compared to pure PE. Furthermore, the interaction between the PE chain and ionic clusters gives rise to two distinct crystalline polyethylene phases. It is widely acknowledged that the larger primary lamellae form initially, while the surrounding amorphous polymer can generate smaller secondary crystallites over time. Consequently, the PE ionomers exhibit two melting endothermic behavior in the DSC heating thermogram, attributed to the melting of the secondary (lower T_m) and primary crystallization (higher T_m) (Figure 5b).[43] While the existence of ionic aggregates or clusters is widely acknowledged, the basic questions of their size, internal structure, and distribution within the ionomers remain significantly uncertain. To illustrate the morphology of ionic clusters, a modified hard-sphere scattering (MHS) model, which approximates clusters with enhanced electron density as monodisperse spheres of radius, has been introduced.[46] Research demonstrated that the diameter of the ionic core in partial-neutralized EMAA is approximately 5 Å.[45] However, as for ionomers with higher acid and ionic contents, describing the ionic clusters as spherical appears to be an oversimplification.[46] Numerous studies show that the ionic clusters exhibit a nonspherical structure.[47] And ionomers prepared via solution neutralization and precipitation typically exhibit high spatial heterogeneity, which limits the applicability of the MHS model.[48] In fact, the structure of ionic clusters is influenced by several factors, including the size of ion pairs, the dielectric constant of the polymer, the distance between an ionic group and the polymer backbone, and the ion content (Figure 5c).[49,50] For example, Lueth et al.[51] demonstrated that in the melt state, ionomers with sulfonic acid groups could form larger and more elongated clusters compared to ionomers with carboxylic acid groups.

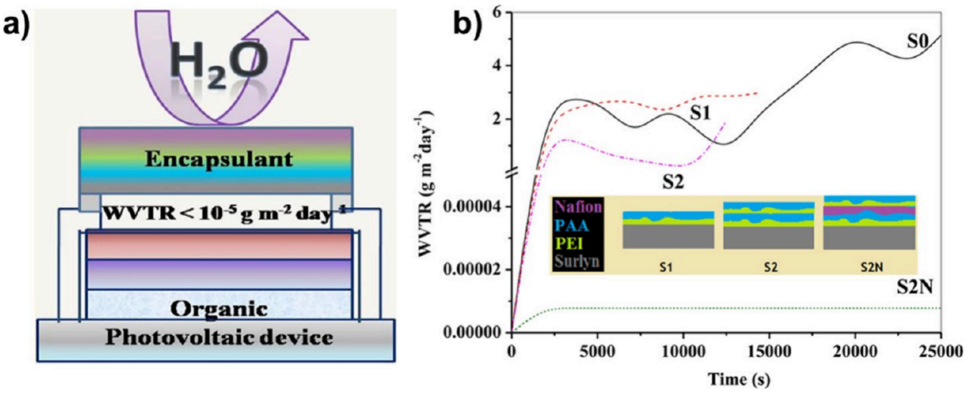


Figure 6. (a) Schematic for an organic photovoltaic device. (b) Water vapor barrier measurements from CRDS-based setup. Note that neat Surlyn is designed as S0, Surlyn/PEI/PAA is designed as S1, Surlyn/PEI/PAA/PEI/Surlyn is designed as S2, Surlyn/PEI/PAA/Nafin/PEI/Surlyn is designed as S2N. Reproduced with permission.[65] Copyright 2014, American Chemical Society.

4. APPLICATION OF PE IONOMERS

PE ionomers are the copolymer marriage of ethylene, unsaturated carboxylic acid, and metal salts. The excellent properties of PE ionomers depend on the interaction between the polyethylene matrix and the physical cross-links of ionic aggregates. The synergistic integration of their properties denotes those numerous functionalities and intriguing applications of typical polyethylene materials with high gloss and transparency properties and excellent mechanical properties that are also commonly applicable to PE ionomers, including food, medical vacuum packaging, cosmetic containers, golf ball shells and other sports equipment coatings.[52] Furthermore, the intrinsic features of the nonpolar covalent skeleton and polar ions cluster structure of PE ionomer endow it with superb compatibility with polar and nonpolar materials and excellent adhesion and have recently enabled fresh smart applications (e.g., shape-memory materials, healable materials).[1,2,53,54] The applications of PE ionomers are introduced and discussed in this section.

4.1. Packaging and Coatings. For packaging applications, three essential functions are generally included: containerization, protection, and merchandising.[4] It is well-known that LDPE has been widely used in packaging applications. Compared to LDPE where crystalline and amorphous phases are present, PE ionomers include additional ionic clusters. This intricate interaction between the hydrocarbon chains and ionic clusters endows PE ionomers with distinctive properties, such as low melt elasticity and high segmental viscosity (friction factor). Consequently, PE ionomers exhibit excellent properties in packaging applications, including grease resistance, puncture resistance, melt strength, thermal viscosity, high gloss, broad sealing range, capability for sealing over contaminated surfaces, remarkable transparency, excellent thermoformability, and inherent flexibility devoid of the necessity for plasticizers. Hog et al.[55] have demonstrated that Surlyn ionomers (Surlyn 1601 with Na and Surlyn 1652 with Zn) could maintain physical properties after irradiation at sterilizing doses (25−50 kGy). This indicates that Surlyn ionomers exhibit resilience even under sterilization conditions, thereby ensuring the safety and integrity of the packaged products. This finding suggests promising prospects for their application in the field of food packaging. Furthermore, PE ionomers are suitable for a diverse array of packaging techniques, such as thermoforming, skin packaging, blister packaging, and so on. Notably, applications such as golf ball covers, ski boots, and various other molding applications represent some of the most eye-catching uses of PE ionomers. Typically, to satisfy the requirements of packaging, different ionomers can be blended. For instance, golf balls are generally manufactured by a mixture of the two PE ionomers partly neutralized with either Zn or Na to ensure the best spin, bounce, speed, and durability. This approach effectively solves the cold cracking problems of Na-neutralized PE ionomers and the low rebound problems of Zn-neutralized PE ionomers. Dow has collaborated with Callaway Golf Company to develop the ERC Soft and Supersoft golf balls, featuring a hybrid cover made with a PARALOID impact modifier and SURLYN ionomers. This multimaterial design enhances performance, providing benefits like greater distance, softer feel, improved spin, and better control.[56] Besides that, in recent years, flexible packaging applications of PE ionomers have predominantly been directed toward food, medical vacuum fit packaging, high-end cosmetics containers, glass curtain walls, etc. Sessini et al. developed sandwich-type composites of Surlyn reinforced with woven nonwoven electrospun PLA fibers, demonstrating enhanced mechanical properties, hardness and wear resistance, making them suitable for active packaging applications.[57]

Recently, organic devices like light-emitting diodes and organic photovoltaic (OPV) devices are experiencing rapid development.[58−64] While these devices could be easily fabricated, the long-term stability of organic thin films is impeded by the extremely high sensitivity to moisture and oxygen, thus hampering their commercialization. The presence of moisture affects the active layer causing the change of morphology and/or delamination at the active layer/electrode interface and increasing the extent of oxidation, leading to the decreased current density.[65] Therefore, an encapsulant with high moisture and oxygen barrier properties while preserving high light transmittance is essential. Ideally, flexible moisture barrier materials should exhibit a water vapor transmission rate (WVTR) and oxygen transmission rate below 10^{-6} g m^{-2} day^{-1} and 10^{-5} cm^3 m^{-2} day^{-1}, respectively.[65] PE ionomer with inherently transparent, excellent adhesion, and ultralow permeable properties could be a promising candidate to meet the requirements (Figure 6). Kopanati et al.[62] demonstrated the feasibility of Surlyn/magnesium oxide nanocomposite films for the encapsulation of organic electronic devices. By optimizing the appropriate type and concentration of MgO, Surlyn/MgO composite films could achieve a low WVTR value of 0.008 $g{\cdot}m^{-2}{\cdot}d^{-1}$ while maintaining a visible light transmittance of 50–82%. Accelerated weathering tests exhibit significant prolongation of the lifetime of encapsulated OPV cells. Additionally, the blends of ionomers with poly(vinyl alcohol-*co*-ethylene),[60] TiO_2,[64] or cellulose nanofibers[61] have also been investigated as encapsulants, offering further avenues for enhancing stability and increasing the lifetime of the organic device.

Actually, the gas permeation mechanism through polymers involves the solution-diffusion mechanism.[60] In the case of PE ionomers, the predominant mode of penetrating (moisture or oxygen) transport is diffusion. The penetrant molecules first adhere to the polymer surface, dissolving into the matrix followed by diffusion through the matrix driven by concentration or pressure gradients. To decrease the diffusivity of penetrants like moisture or oxygen through ionomers, it is imperative to design a robust interactive matrix-permeant system. It is generally accepted that Zn-neutralized PE ionomers exhibit a lower water absorption rate owing to the dual effects of higher electric charge and larger ionic radius of Zn^{2+} ions in comparison to Na-neutralized PE ionomers. Typically, augmenting the ion content of ionomers also enhances their interaction with moisture.

4.2. Adhesives. PE ionomers exhibit exceptional adhesive properties with both organic and inorganic substrates, such as metals, glass, and polymers, primarily due to their ability to form strong interfacial bonds through multiple interactions, including ionic interactions of ionic clusters and hydrogen bonds of acid groups. This unique combination of bonding mechanisms makes them highly suitable as versatile adhesives.[66–70] Su et al.[70] used commercial Surlyn resin (Surlyn PC2200) as an ionic interlayer for laminated glass (Figure 7). The results reveal that the light-transmittance of the ionic interlayers is higher than polyvinyl butyral (PVB) interlayers and the bending strength was more than twice that of the laminated glass with the PVB interlayer (76.1 MPa vs. 30.3 MPa). The enhanced light-transmittance can be ascribed to the existence of ionic clusters in the ionic interlayer, and the improved bending strength can be ascribed to the much stronger ionic bonds between the PE ionomer interlayer and glass compared to the hydrogen bond in the PVB interlayer. Luo et al.[69] developed an EAA/Surlyn-Zn^{2+}/zinc stearate (St) blend system as an interlayer membrane for safety glass through blending and extrusion. The safety glass, prepared by the PE ionomer interlayer, exhibits 80.58% light transparency and an excellent yield strength of 73.1 MPa, coupled with superior glass adhesion properties with the absence of degumming in the broken glass during the bond strength test, suggesting the effectiveness of the PE ionomer interlayer in enhancing the mechanical and optical properties of safety glass (Figure 8). Significantly, unlike conventional glass, laminated glass features an ionomer film layer sandwiched between two sheets of glass, which imparts a considerable residual bearing capacity upon experiencing impact. This unique configuration effectively prevents the glass from fracturing and splashing, regulates the way crack propagation, maintains the glass's integrity upon impact, and ultimately enhances safety. D'Auria et al. developed an LDPE ionomer based on ion pair comonomers (IPC) recently. This newly developed ionomers significantly improved adhesion properties on aluminum substrates compared to conventional LDPE. Notably, the adhesives also exhibited thermal reversibility, making them ideal for applications that require easy disassembly.[71] Nowadays, PE ionomer resin represents key materials in the adhesives industry; the use of these materials as hot melt adhesives extends beyond mere bonding; they also enhance the structural integrity and performance of the end products, offering versatile and reliable solutions that meet rigorous performance demands.

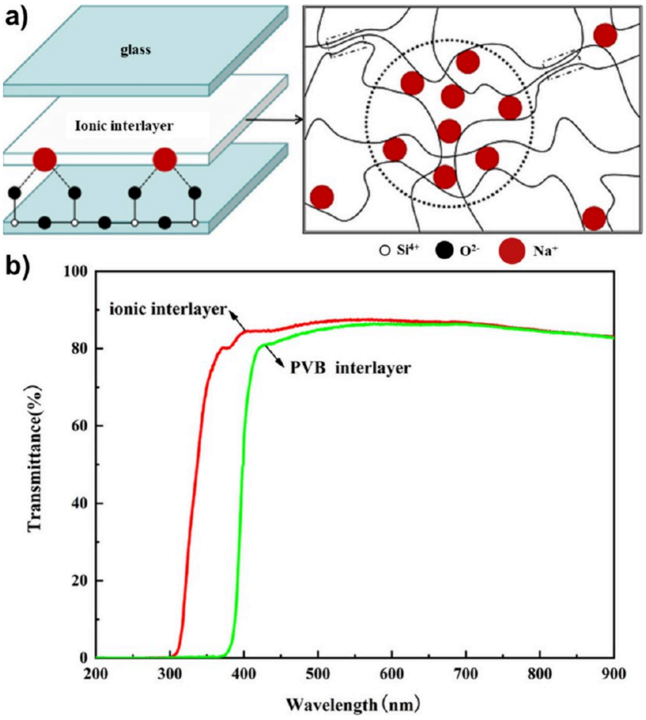


Figure 7. (a) Schematic illustration of the ionic interlayer membrane (Surlyn 1720) and (b) light transmittance of the ionic interlayer safety glass and PVB interlayer laminated glass. Reproduced with permission.[70] Copyright 2021, Springer Nature.

4.3. Ionomer Blends. Polymer blends could overcome the limitations inherent in a single material, thereby achieving the desired physicochemical properties of the final products. PE ionomers exhibit competitive strength, toughness, abrasion resistance, and optical performance, rendering them widely employed both as a matrix material for blending and as an additive to facilitate the process of blending modification.[72–79] However, diverse polymers typically exhibit incompatibility because the entropy of mixing is very small for polymers and the enthalpy is generally positive for incompatible components. One of the most effective methodologies to compatibilize two immiscible polymers lies in specific interactions, such as electrostatic, ionic, and hydrogen bonding. As discussed, PE ionomers are ion-containing polymers, with hydrocarbon backbones containing a relatively small number of acid groups (e.g., carboxylic, sulfonic, or phosphoric acids). Therefore, the ionomer contains both acid groups and ionic clusters, which can provide hydrogen bonding and ionic interactions, respectively. In this case, PE ionomers could be blended with other polymers via hydrogen bonding from the acid groups. Lee et al. have demonstrated the profound influence of the robust intermolecular hydrogen bonds between carboxylic acid and pyridine groups, facilitating a strong association between poly(2-vinylpyridine) and EMAA.[72] It is reported that EMAA containing at least 6–8 wt % MAA can be integrated with polyether through the formation of intermolecular dimers.[76] More importantly, the presence of ionic groups in

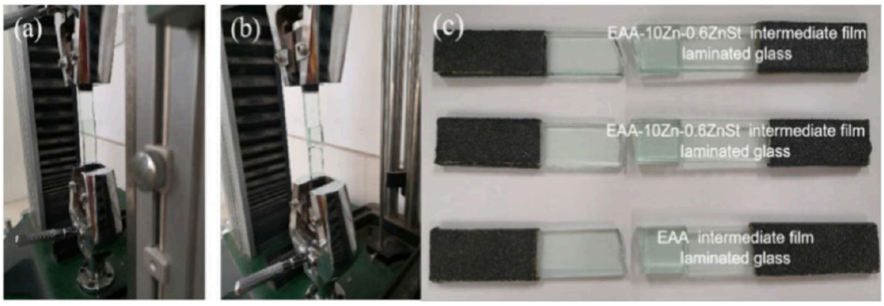


Figure 8. (a) Before tension, (b) after stretching, and (c) physical diagram of the EAA-10Zn-0.6ZnSt interlayer film and EAA interlayer film safety glass. Reproduced with permission.[69] Copyright 2022, Springer Nature.

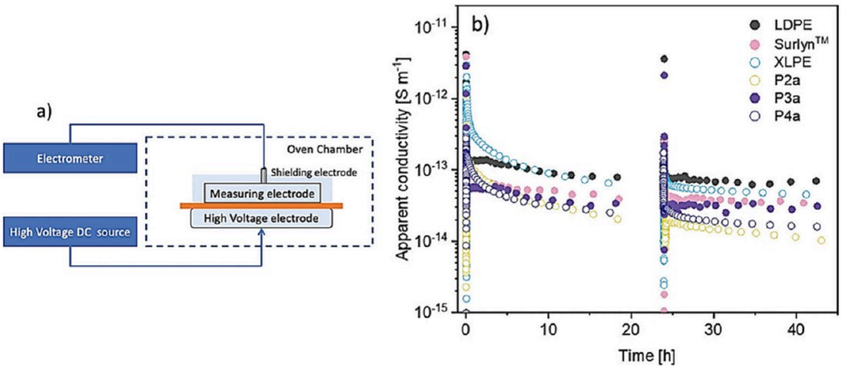


Figure 9. (a) Schematic of the setup used for leakage current measurements and (b) electrical conductivity of different samples at 70 °C and 30 kV/mm. Reproduced with permission.[21] Copyright 2023, Wiley-VCH.

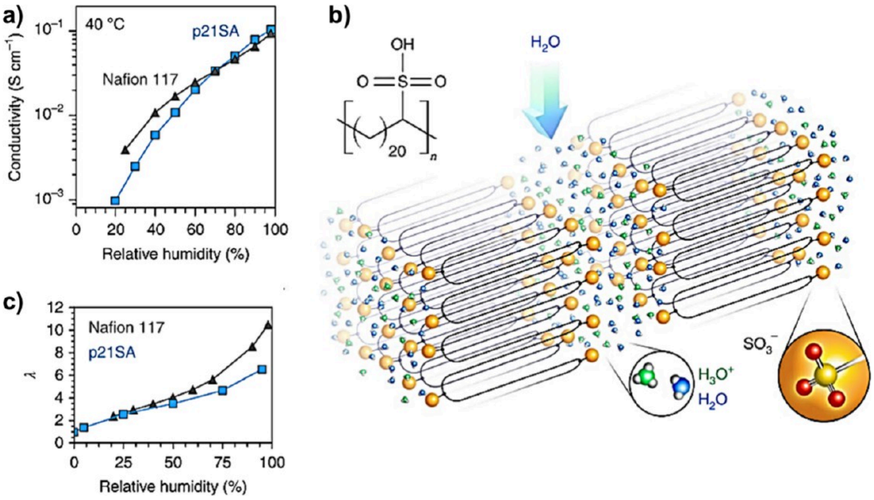


Figure 10. Sulfonated PE ionomers for ion-exchange membrane. (a) DC conductivity comparison of the sulfonated PE ionomer and Nafion 117 as a function of RH at 40 °C. (b) Chemical structure and schematic rendering of the secondary structure of hydrated sulfonated polyethylene ionomers, showing the crystalline backbones and acid-lined water layers. At the bottom right, the yellow atom is sulfur and the red atoms are oxygen. (c) Water uptake comparison of sulfonated polyethylene ionomers and Nafion 117 as a function of RH at 40 °C. λ is defined as the number of water molecules per sulfonic group and is measured with a sorption balance. Reproduced with permission.[5] Copyright 2018, Springer Nature.

PE ionomers could provide specific interaction with other ionic groups or polar groups through relatively strong ion−ion interactions (via proton-transfer or acid−base interactions), ion coordination, ion pair−ion pair interactions, ion−dipole interactions, ion-dipole interactions.[80] These interactions are typically highly exothermic and thus could lower the heat of mixing within polymer blends. Consequently, PE ionomers are a kind of promising material that could be blended with various polymers to enhance compatibility and mechanical performance.

4.4. High Voltage Insulation Materials. High voltage direct-current (HVDC) power cables are essential components of modern electrical power grids. The most sophisticated HVDC cables feature an extruded insulation layer sandwiched between the inner conductor and the outer shielding.[21,81] The predominant insulation material used in these cables is cross-linked low-density polyethylene (XLPE).[82] XLPE exhibits a low electrical conductivity ($\sigma_{DC} \approx 3 \times 10^{-14}$ S/m) at an electric field strength of 30 kV/mm and 70 °C, ensuring efficient performance under high-voltage conditions. Since the

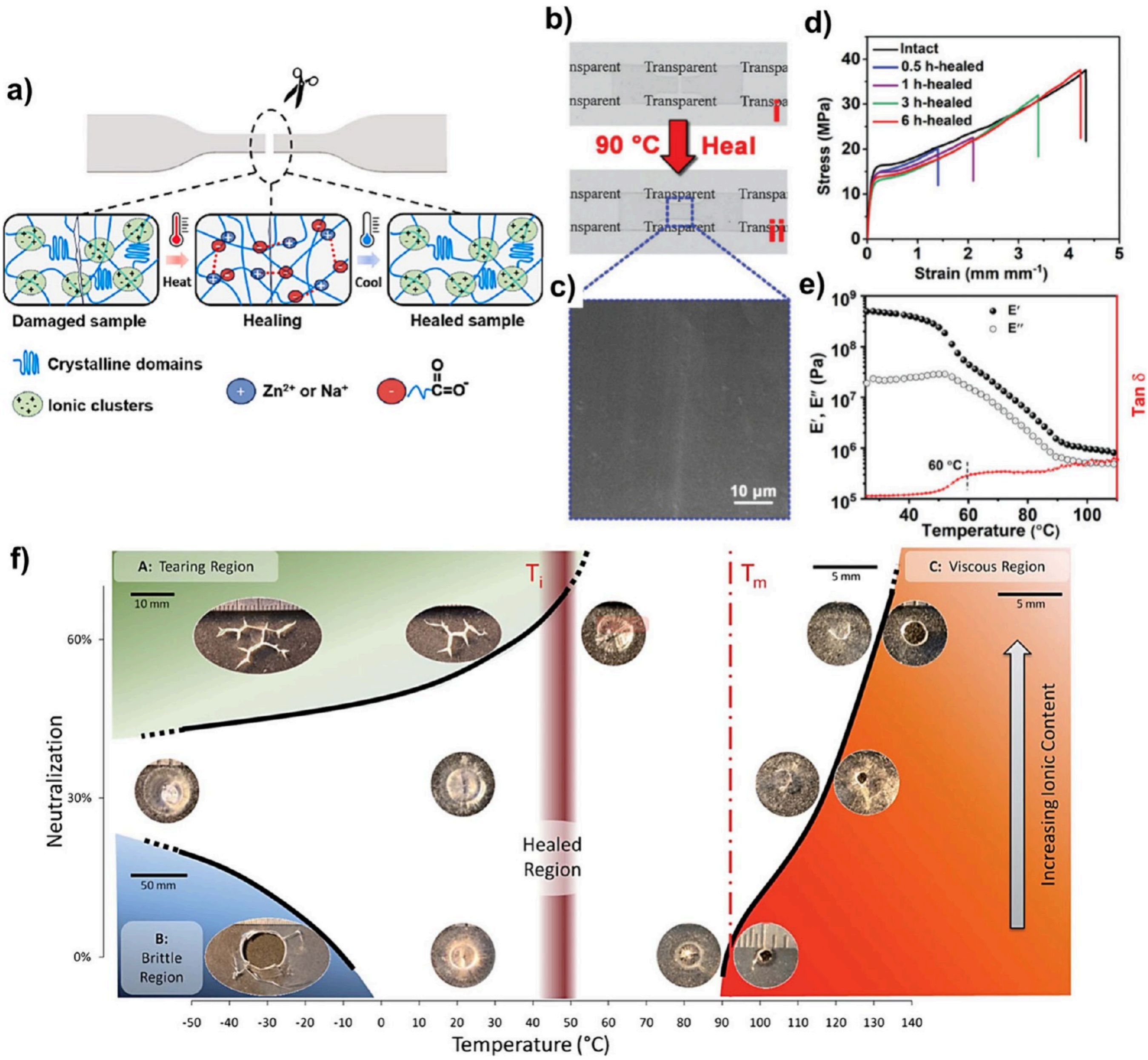


Figure 11. a) Schematic showing the possible mechanism of the healing behavior. Reproduced with permission.[1] Copyright 2023, Elsevier. b) Digital images of the PEMA/$Zn_{0.5}$ composite being (i) cut into two pieces and (ii) being healing upon healing at 100 °C for 6 h. c) SEM image of the healed PEMA/$Zn_{0.5}$ composite. d) Stress−strain curves of the intact, 0.5, 1, 3, and 6 h-healed PEMA/$Zn_{0.5}$ composites. e) DMA curves of the PEMA/$Zn_{0.5}$ composite. Reproduced with permission.[20] Copyright 2020, Wiley-VCH. f) Self-healing "phase diagram" showing ballistic puncture-reversal of sodium-based PE ionomer as a function of temperature and ionic content. Note that the central healing region means successful puncture-reversal, while the fringe areas prove unsuccessful. Reproduced with permission.[88] Copyright 2013, Royal Society of Chemistry.

ionic clusters in ionomers could effectively trap electrons injected from the electrodes owing to the strong electron affinity. Additionally, the carbonyls in the carboxyl groups could serve as hopping sites for charge transport, allowing for the uniform distribution of negative charge postdischarge. Actually, PE ionomer blends have been designed for insulation in direct current cables.[80] Recently, D'Auria et al.[21] synthesized a novel PE ionomer from ethylene and ion pair comonomers (amine-terminated methacrylate and methacrylic acid) via high-pressure free radical polymerization. The resulting materials maintain characteristics like XLPE in terms of crystallinity, melting temperature, rubber plateau modulus, and thermal conductivity but are still melt-processable. Furthermore, the preparation process of the ionomers generates no byproducts such as water, methane, and cumyl alcohol that result from peroxide cross-linking during the production of XLPE, which will cause premature aging of the dielectrics under severe conditions. Consequently, the ionomers exhibit promising insulating properties with an electrical conductivity of 6×10^{-14} S/m at 30 kV/mm and 70 °C and have the potential to be an alternative to XLPE for high-voltage insulation (Figure 9).

4.5. Ion-exchange Membrane.

As is well-known, Nafion (perfluoro-sulfonate ionomers) membrane exhibits excellent proton-transport performance, as the sulfonic acid functional groups in perfluoro-sulfonate ionomers tend to form ionic

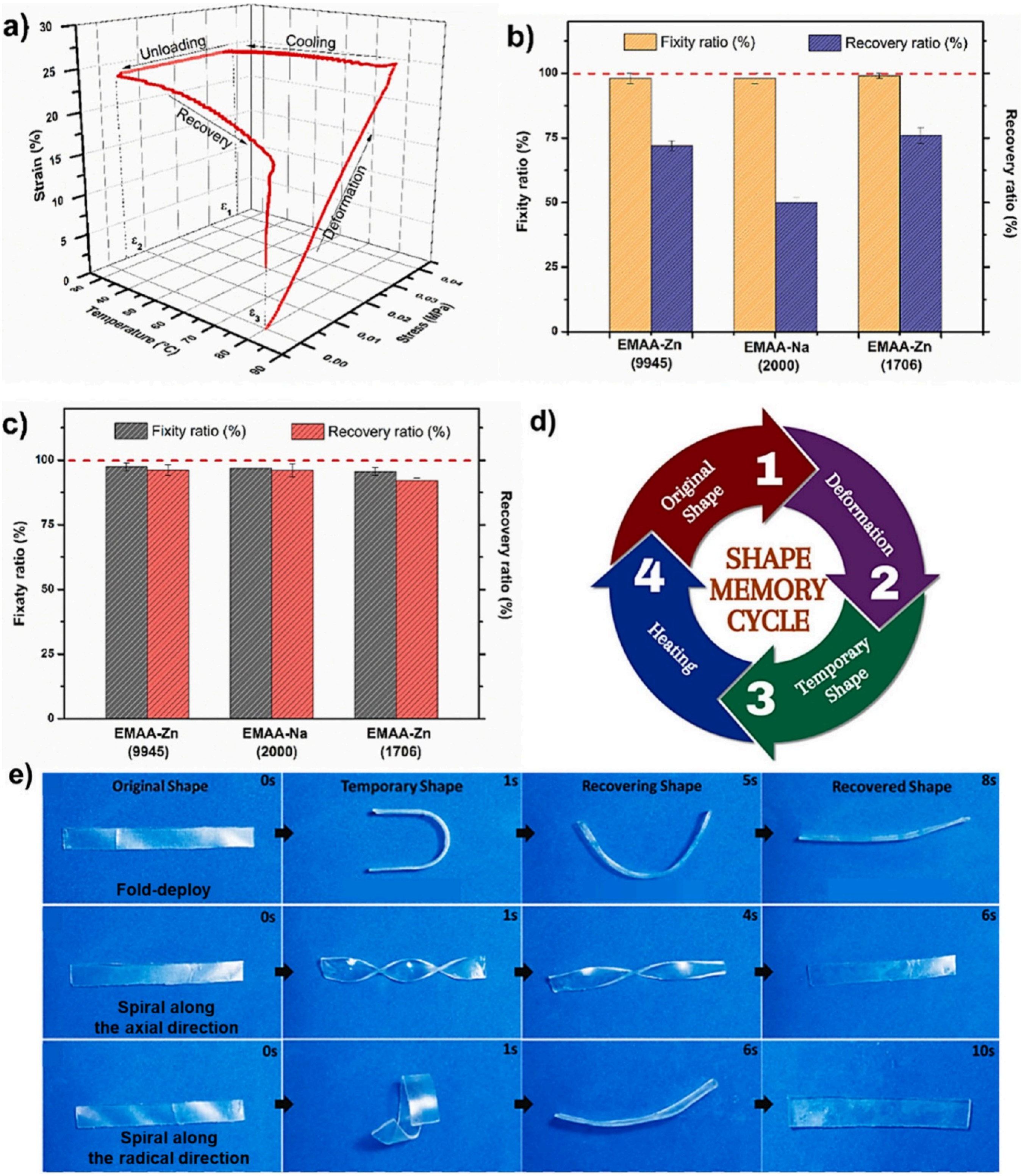


Figure 12. (a) 3D diagram of the shape memory cycle of EMAA-Zn (9945). (b) Shape memory properties of ionomers obtained in torsion mode. (c) Shape memory properties of ionomers obtained in fold-deploy, at a switching temperature of 80 °C. (d) Representative shape memory cycle on polymers, and (e) recovery processes of EMAA-Zn (9945) with various temporary shapes in the water bath (80 °C). Reproduced with permission.[1] Copyright 2023, Elsevier.

domains containing water (i.e., forming inverted micelle cylinders) and the hydrophobic, semicrystalline polytetrafluoroethylene-like matrix percolates into the sulfonate-lined water channels, giving high conductivity.[5,24,83−85] However, few researchers have explored the application of the PE ionomer as an ion-exchange membrane. Recently, Trigg et al.[5] synthesized sulfonated polyethylene ionomers with precisely positioned sulfonic acid groups pendant to every twenty-first carbon atom via acyclic diene metathesis polymerization. The controlled chain folding results in highly uniform hydrated acid layers of subnanometer thickness, contributing to remarkable proton conductivity (Figure 10). Surprisingly, the proton conductivity of sulfonated polyethylene matches that of the benchmark fuel cell membrane, Nafion 117. It is noteworthy that the polyethylene with periodic pendant carboxyl groups could be also synthesized,[84] while the PE ionomers with sulfonic acid groups, which are highly hygroscopic moieties, produce higher proton conductivity than PE ionomers with carboxyl acid groups.

4.6. Healable Smart Materials. Healable materials have emerged as a prominent domain of investigation, encompassing a diverse range of novel materials.[20,86] These materials exhibit the extraordinary ability to repair external damages by harnessing their inherent structural properties, when subjected to specific external stimuli such as light, heat, stress, etc. The ionic clusters within PE ionomers provide special physical cross-linking, order-to-disorder transition, and ion hopping at elevated temperatures, exhibiting unique viscoelastic properties. Consequently, PE ionomers demonstrate superior healing property and could be used as healable smart materials.[11,20,86−95] For a detailed healing process, the ionomers may undergo three stages.[1] When the PE ionomer is cut off, the dynamic ionic cross-linking network is initially disrupted. Subsequently, upon contact with the incisions, they are heated to a specific temperature, typically T_g or a semicrystalline area, to maintain them in a molten state. In this particular state, the fractured ionic clusters will undergo unique interaction, leading to the diffusion and entanglement of the polymer chains, ultimately fostering the reconstitution of the cross-linked network. Consequently, with the formation of new ionic clusters, the two fractured segments shall be reconnected on a macroscopic scale and the mechanical properties of the affected area are continuously restored (Figure 11a−e).[1,20] However, the self-healing mechanism differs depending on the type of neutralizing metal ions.[1,88] Zinc-based PE ionomers have revealed superior healing properties due to the dynamic coordination interactions between carboxylate groups and zinc ions, leading to the efficient reformation of ionic clusters postdamage, while the healable performance of sodium-based PE ionomer relies on the migration of Na^+ ions within the polymer matrix to promote reversible ionic interactions. Different healing mechanisms will influence the overall efficiency and performance of healable ionomers. It is generally accepted that the EMAA neutralized with zinc exhibits superior healable properties compared to sodium-ion-neutralized ionomer.[1,53]

Moreover, the neutralization degree also plays a crucial role in self-healing properties.[1] Kalista et al.[91] have demonstrated that several EMAA (neutralization degree of 0%) exhibits unique ability of self-healing after being punctured by a projectile, with the punctured areas subsequently withstanding pressures excess of 3 MPa. Then, they[88] further explored how the degree of neutralization influences the temperature range for activation of the healing process, revealing that 30% of acid groups neutralized with sodium ions exhibited the broadest temperature range for self-healing (Figure 11f).

4.7. Shape Memory Smart Materials. Shape memory polymers (SMPs) are a category of intelligent materials endowed with the remarkable capability to maintain a temporary configuration and subsequently revert to its original shape when exposed to an external stimulus (such as heat, light, electric or magnetic fields) via the dynamic cross-linking points.[7,96] The ionic clusters within PE ionomers generally serve as the permanent cross-linked network that could persist to relatively high temperatures (>150 °C), while the polyethylene crystalline domains offer the temporary network (see Figure 5a).[44] This inherent feature of PE ionomers could autonomously adjust shape in response to external temperature or other stimuli and holds significant potential for widespread application prospects in diverse fields, such as medical equipment, smart textiles, microelectronic devices, and home automation.[1,87,96−101] For example, Dolog et al.[43] investigated the shape memory behavior of zinc-neutralized PE ionomer (Surlyn 9520), revealing the shape memory recovery efficiency (R) of approximately 89% because the cross-linking can significantly strengthen the permanent network, and the multiple-shape memory performance was achieved by choosing two or more switching temperatures within the broad melting transition range of 60−100 °C. Moreover, Lu et al.[99] demonstrated that EMAA partially neutralized with sodium (Surlyn 8940) exhibits both one-way multishape memory effect and tunable two-way shape-memory effect. The mechanism of the 2W-SME is a crystallization-melting-driven process featuring reversible elongation by cooling and contraction by heating without repeated programming. Importantly, the shape memory property of ionomers can be enhanced through the modification of the structure of ionic clusters or polyethylene crystalline domains. The ionomers prepared with multivalent cations exhibit superior shape memory properties compared to those with monovalent cations, owing to the robust dipole−dipole interactions.[101] For example, the sodium-based PE ionomer exhibited relatively poor shape memory behavior, with fixity (F) and recovery (R) values of about 80% and 45%, respectively, while ionomers neutralized by utilizing multivalent cations showcased fixity and recovery values surpassing 90% that were reproducible across multiple shape memory cycles. For instance, zinc, with a valence of +2, can establish more robust bonds with carboxylate groups compared to sodium with a valence of +1, resulting in a stronger shape memory effect in zinc-based ionomers (Figure 12).[1] In addition, 3D or 4D printing technologies have emerged as a transformative approach for fabricating materials with specialized functionalities in the field of shape-memory materials. These advanced printing techniques allow for precise control over the architecture of the material, enabling the design of complex, customized structures that can respond dynamically to external stimuli such as temperature, light, or magnetic fields. Zhao et al.[44] demonstrate the shape memory behavior of 3D printed objects with fused deposition modeling (FDM) using Surlyn 9520. Li et al.[102,102] illustrate the potential of 4D printed shape memory polymers (Surlyn 9910) in the design and manufacturing of intelligent devices for elastic-wave control and vibration isolation. With the progress of research, the possibilities for innovation in the design and application of shape-memory materials appear boundless, promising a new era of materials engineered to meet the precise needs of future challenges.

5. CONCLUSION

In this review, we have systemically summarized the recent progress in the synthesis, structure, diverse properties, and broad applications of PE ionomers. Generally, PE ionomers could be synthesized by free radical copolymerization, transition-metal-catalyzed copolymerization, and postionic functionalization of inert polyethylene. The use of such preparation methods has facilitated the exploration of numerous robust PE ionomers with diverse chemical structures. These PE ionomers have been proven to be endowed with many extraordinary properties, including remarkable transparency, excellent thermoformability, puncture resistance, melt strength, thermal viscosity, high gloss, grease resistance, a broad sealing range, and inherent flexibility. Notably, these advantageous properties make PE ionomers unique from classical and widely used polyolefin materials. PE ionomers thus represent a quite promising class of ion-containing polymer materials that exhibit great potential in many practical and frontier applications such as packaging, coatings, blends, ion-exchange membranes, high voltage insulation materials, adhesives, shape memory polymer, healable polymer materials, and so forth.

Despite significant advancements over recent years, research on PE ionomers remains in its infancy, with myriad unexplored possibilities. First of all, the development of novel synthesis methods must be a continual priority. While numerous unsaturated acids have been employed to synthesize PE ionomers, achieving precise and directional synthesis remains a formidable challenge due to the inherent complexities of controlled polymerization. The recent innovations in controlled polymerization techniques and computational modeling, although promising, still fall short of fully enabling the precise assembly of supramolecular structures. These methods often struggle with accurately predicting molecular interactions under varying polymerization conditions, thereby limiting their efficacy in guiding the targeted synthesis of PE ionomers. Future research must therefore focus on advancing polymerization techniques and computational models that not only enhance structural control but also integrate cross-disciplinary insights from chemistry, materials science, and computational science.

Moreover, the analysis of the microstructure of ionic clusters faces several challenges including technical limitations, data complexity, and the difficulty of controlling experimental conditions. The microstructural analysis of ionic clusters is particularly challenging due to their nanoscale dimensions, intricate architecture, and susceptibility to environmental influences. Although high-resolution techniques, such as atomic force microscopy (AFM) and transmission electron microscopy (TEM) offer direct observation and characterization, they are often constrained by difficulties in data interpretation and the need for stringent experimental controls. Developing advanced in situ techniques capable of analyzing the dynamic behavior of ionic clusters in real-time, combined with sophisticated computational simulations, will be crucial to overcoming these challenges. Additionally, it is imperative to address the effects of varying experimental conditions on the structure of ionic clusters and refine data processing methods to enhance reliability and reproducibility. By comprehensively integrating these innovative approaches, we could more effectively tackle the challenges associated with the microstructural analysis of ionic clusters, thereby promoting the development of this field.

In conclusion, PE ionomers represent a new class of promising ion-containing polymer materials with numerous possibilities. While numerous commercially relevant acid- and ion-containing polymer ionomers exist, exploring their structures and properties, and delving deeper into their tunable attributes could unveil novel or enhanced desirable properties, which can pave the way for next-generation applications. These proposed opportunities and challenges facing the field of PE ionomers require the collaborative and sustained contributions of individuals from diverse backgrounds. We hope this review will appeal to researchers, potentially sparking new interests and creating fresh opportunities that will lead to a boom in this field in the near future.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support and encouragement of the Key Projects of the Ministry of Industry and Information Technology of China (TC220A04W-3, 188).

REFERENCES

(1) Cunha, R. B. d.; Agrawal, P.; Brito, G. d. F.; Mélo, T. J. A. d. Exploring Shape Memory and Self-Healing Behavior in Sodium and Zinc Neutralized Ethylene/Methacrylic Acid (EMAA) Ionomers. *J. Mater. Res. Technol.* **2023**, *27*, 7304−7317.

(2) El Choufi, N.; Mustapha, S.; Tehrani-Bagha, A. R.; Grady, B. P. Self-Healability of Poly(ethylene-co-methacrylic acid): Effect of Ionic Content and Neutralization. *Polymers* **2022**, *14* (17), 3575.

(3) Laschewsky, A. Structures and Synthesis of Zwitterionic Polymers. *Polymers* **2014**, *6* (5), 1544−1601.

(4) Zhang, L.; Brostowitz, N. R.; Cavicchi, K. A.; Weiss, R. A. Perspective: Ionomer Research and Applications. *Macromol. React. Eng.* **2014**, *8* (2), 81−99.

(5) Trigg, E. B.; Gaines, T. W.; Marechal, M.; Moed, D. E.; Rannou, P.; Wagener, K. B.; Stevens, M. J.; Winey, K. I. Self-Assembled Highly Ordered Acid Layers in Precisely Sulfonated Polyethylene Produce Efficient Proton Transport. *Nat. Mater.* **2018**, *17* (8), 725−731.

(6) Tran, Q. H.; Neidhart, E. K.; Sheiko, S. S.; Bras, W.; Leibfarth, F. A. Polyolefin Ionomer Synthesis Enabled by C-H Thioheteroarylation. *Macromolecules* **2023**, *56* (21), 8920−8927.

(7) Cavicchi, K. A.; Pantoja, M.; Cakmak, M. Shape Memory Ionomers. *J. Polym. Sci. B Polym. Phys.* **2016**, *54* (14), 1389−1396.

(8) Mirabedini, S. M.; Alizadegan, F. Ionomers as Self-Healing Materials. *Self-Healing polymer-based systems* **2020**, 279−291.

(9) Li, C.; Liu, J.; Qiu, X.; Yang, X.; Huang, X.; Zhang, X. Photoswitchable and Reversible Fluorescent Eutectogels for Conformal Information Encryption. *Angew. Chem., Int. Ed.* **2023**, *62* (46), No. e202313971.

(10) Grady, B. P. Review and Critical Analysis of the Morphology of Random Ionomers Across Many Length Scales. *Polym. Eng. Sci.* **2008**, *48* (6), 1029−1051.

(11) Stephen, J.; Kalista, J. Self-Healing Ionomers. *Encyclopedia of Polymer Science and Technology* **2002**, 73−100.

(12) Buback, M.; Wittkowski, L. High-Pressure Free-Radical Copolymerization of Ethene with Methacrylic Acid and Ethene with Acrylic Acid, 2. Ethene Reactivity Ratios. *Macromol. Chem. Phys.* **2000**, *201* (4), 419−426.

(13) Buback, M.; Kattner, H. Detailed Analysis of Radical Polymerisation Kinetics by Pulsed-laser Techniques. *Mol. Phys.* **2021**, *119* (17−18), 1939452.

(14) Ehrlich, P.; Mortimer, G. A. Fundamentals of the Free-Radical Polymerization of Ethylene. *Adv. Polym. Sci.* **1970**, *7*, 386−448.

(15) Machi, S.; Kise, S.; Hagiwara, M.; Kagiya, T. Mechanisms of Propagation, Transfer, and Short-Chain Branching Reactions in the Free-Radical Polymerization of Ethylene. *J. Polym. Sci., Part A-1: Polymer Chem.* **1967**, *5* (12), 3115−3128.

(16) Dietrich, M. L.; Sarmoria, C.; Brandolin, A.; Asteasuain, M. Modeling Low-Density Polyethylene (LDPE) Production in Tubular Reactors: Connecting Polymerization Conditions with Polymer Mmicrostructure and Rheological Behavior. *Macromol. React. Eng.* **2022**, *16* (4), 2200003.

(17) Seitz, M. E.; Chan, C. D.; Opper, K. L.; Baughman, T. W.; Wagener, K. B.; Winey, K. I. Nanoscale Morphology in Precisely Sequenced Poly(ethylene-co-acrylic acid) Zinc Ionomers. *J. Am. Chem. Soc.* **2010**, *132* (23), 8165−8174.

(18) Walther, B. W.; Neubauer, A. C.; Kim, E. K.; Pavlicek, C. L.; Diehl, C. F. Process for Producing High Quality Ionomers. US7645836B2, 2010.

(19) Richard, W. R. Process of Crosslinking Polymers. US3404134A, 1968.

(20) Zhan, S.; Wang, X.; Sun, J. Rediscovering Surlyn: A Supramolecular Thermoset Capable of Healing and Recycling. *Macromol. Rapid Commun.* **2020**, *41* (24), No. e2000097.

(21) D'Auria, S.; Pourrahimi, A. M.; Favero, A.; Neuteboom, P.; Xu, X. D.; Haraguchi, S.; Bek, M.; Kádár, R.; Dalcanale, E.; Pinalli, R.; Müller, C.; Vachon, J. Polyethylene Based Ionomers as High Voltage Insulation Materials. *Adv. Funct. Mater.* **2023**, *33* (36), 2301878.

(22) Ito, S.; Kanazawa, M.; Munakata, K.; Kuroda, J.; Okumura, Y.; Nozaki, K. Coordination-Insertion Copolymerization of Allyl Monomers with Ethylene. *J. Am. Chem. Soc.* **2011**, *133* (5), 1232−1235.

(23) Boffa, L. S.; Novak, B. M. Copolymerization of Polar Monomers with Olefins Using Transition-Metal Complexes. *Chem. Rev.* **2000**, *100* (4), 1479−1493.

(24) Zhang, M.; Kim, H. K.; Chalkova, E.; Mark, F.; Lvov, S. N.; Chung, T. C. M. New Polyethylene Based Anion Exchange Membranes (PE-AEMs) with High Ionic Conductivity. *Macromolecules* **2011**, *44* (15), 5937−5946.

(25) Rünzi, T.; Fröhlich, D.; Mecking, S. Direct Synthesis of Ethylene-Acrylic Acid Copolymers by Insertion Polymerization. *J. Am. Chem. Soc.* **2010**, *132* (50), 17690−17691.

(26) Daigle, J. C.; Piche, L.; Claverie, J. P. Preparation of Functional Polyethylenes by Catalytic Copolymerization. *Macromolecules* **2011**, *44* (7), 1760−1762.

(27) Zhang, D.; Chen, C. Influence of Polyethylene Glycol Unit on Palladium-and Nickel-Catalyzed Ethylene Polymerization and Copolymerization. *Angew. Chem., Int. Ed.* **2017**, *56* (46), 14672−14676.

(28) Dai, S.; Chen, C. Palladium-Catalyzed Direct Synthesis of Various Branched, Carboxylic Scid-Functionalized Polyolefins: Characterization, Derivatization, and Properties. *Macromolecules* **2018**, *51* (17), 6818−6824.

(29) Xiang, P.; Ye, Z. Hyperbranched Polyethylene Ionomers Containing Cationic Tetralkylammonium Ions Synthesized by Pd-Diimine-Catalyzed Direct Ethylene Copolymerization with Ionic Liquid Comonomers. *Macromolecules* **2015**, *48* (17), 6096−6107.

(30) Baughman, T. W.; Chan, C. D.; Winey, K. I.; Wagener, K. B. Synthesis and Morphology of Well-Defined Poly(ethylene-co-acrylic acid) Copolymers. *Macromolecules* **2007**, *40*, 6564−6571.

(31) Middleton, L. R.; Trigg, E. B.; Schwartz, E.; Opper, K. L.; Baughman, T. W.; Wagener, K. B.; Winey, K. I. Role of Periodicity and Acid Chemistry on the Morphological Evolution and Strength in Precise Polyethylenes. *Macromolecules* **2016**, *49* (21), 8209−8218.

(32) Aitken, B. S.; Lee, M.; Hunley, M. T.; Gibson, H. W.; Wagener, K. B. Synthesis of Precision Ionic Polyolefins Derived from Ionic Liquids. *Macromolecules* **2010**, *43* (4), 1699−1701.

(33) Gaines, T. W.; Bell, M. H.; Trigg, E. B.; Winey, K. I.; Wagener, K. B. Precision Sulfonic Acid Polyolefins via Heterogenous to Homogenous Deprotection. *Macromol. Chem. Phys.* **2018**, *219* (11), 1700634.

(34) Opper, K. L.; Fassbender, B.; Brunklaus, G.; Spiess, H. W.; Wagener, K. B. Polyethylene Functionalized with Precisely Spaced Phosphonic Acid Groups. *Macromolecules* **2009**, *42* (13), 4407−4409.

(35) Simocko, C.; Young, T. C.; Wagener, K. B. ADMET Polymers Containing Precisely Spaced Pendant Boronic Acids and Esters. *Macromolecules* **2015**, *48* (16), 5470−5473.

(36) Williamson, J. B.; Lewis, S. E.; Johnson, R. R., 3rd; Manning, I. M.; Leibfarth, F. A. C-H Functionalization of Commodity Polymers. *Angew. Chem., Int. Ed.* **2019**, *58* (26), 8654−8668.

(37) Ciccia, N. R.; Shi, J. X.; Pal, S.; Hua, M.; Malollari, K. G.; Lizandara-Pueyo, C.; Risto, E.; Ernst, M.; Helms, B. A.; Messersmith, P. B.; Hartwig, J. F. Diverse Functional Polyethylenes by Catalytic Amination. *Science* **2023**, *381* (6665), 1433−1440.

(38) Lee, J. A.; Kontopoulou, M.; Parent, J. S. Synthesis and Characterization of Polyethylene-Based Ionomer Nanocomposites. *Polymer* **2005**, *46* (14), 5040−5049.

(39) Fazekas, T. J.; Alty, J. W.; Neidhart, E. K.; Miller, A. S.; Leibfarth, F. A.; Alexanian, E. J. Diversification of Aliphatic C-H Bonds in Small Molecules and Polyolefins through Radical Chain Transfer. *Science* **2022**, *375* (6580), 545−550.

(40) Yarusso, D. J.; Cooper, S. L. Microstructure of Ionomers: Interpretation of Small-Angle X-ray Scattering Data. *Macromolecules* **1983**, *16* (12), 1871−1880.

(41) Eisenberg, A.; Hird, B.; Moore, R. B. A New Multiplet-Cluster Model for the Morphology of Random Ionomers. *Macromolecules* **1990**, *23* (18), 4098−4107.

(42) Peiffer, D. G. Structure and Properties of Blends Containing Ethylene-Methacrylate Copolymers. *J. Polym. Sci. B Polym. Phys.* **1992**, *30* (9), 1045−1053.

(43) Dolog, R.; Weiss, R. A. Shape Memory Behavior of a Polyethylene-Based Carboxylate Ionomer. *Macromolecules* **2013**, *46* (19), 7845−7852.

(44) Zhao, Z.; Peng, F.; Cavicchi, K. A.; Cakmak, M.; Weiss, R. A.; Vogt, B. D. Three-Dimensional Printed Shape Memory Objects Based on an Olefin Ionomer of Zinc-Neutralized Poly(ethylene-co-

methacrylic acid). *ACS Appl. Mater. Interfaces* **2017**, *9* (32), 27239−27249.

(45) Kutsumizu, S.; Tagawa, H.; Muroga, Y.; Yano, S. Small-Angle X-ray Scattering Investigation of Noncrystalline Poly(ethylene-co-methacrylic acid) Ionomers. *Macromolecules* **2000**, *33* (10), 3818−3827.

(46) Register, R. A. Morphology and Structure-Property Relationships in Random Ionomers: Two Foundational Articles from *Macromolecules*. *Macromolecules* **2020**, *53* (5), 1523−1526.

(47) Buitrago, C. F.; Bolintineanu, D. S.; Seitz, M. E.; Opper, K. L.; Wagener, K. B.; Stevens, M. J.; Frischknecht, A. L.; Winey, K. I. Direct Comparisons of X-ray Scattering and Atomistic Molecular Dynamics Simulations for Precise Acid Copolymers and Ionomers. *Macromolecules* **2015**, *48* (4), 1210−1220.

(48) Vanhoorne, P.; Register, R. A. Low-Shear Melt Rheology of Partially-Neutralized Ethylene-Methacrylic Acid Ionomers. *Macromolecules* **1996**, *29* (2), 598−604.

(49) Bolintineanu, D. S.; Stevens, M. J.; Frischknecht, A. L. Influence of Cation Type on Ionic Aggregates in Precise Ionomers. *Macromolecules* **2013**, *46* (13), 5381−5392.

(50) Hall, L. M.; Seitz, M. E.; Winey, K. I.; Opper, K. L.; Wagener, K. B.; Stevens, M. J.; Frischknecht, A. L. Ionic Aggregate Structure in Ionomer Melts: Effect of Molecular Architecture on Aggregates and the Ionomer Peak. *J. Am. Chem. Soc.* **2012**, *134* (1), 574−87.

(51) Lueth, C. A.; Bolintineanu, D. S.; Stevens, M. J.; Frischknecht, A. L. Hydrogen-Bonded Aggregates in Precise Acid Copolymers. *J. Chem. Phys.* **2014**, *140* (5), 054902.

(52) Esmaeilirad, M.; Jiang, Z.; Harzandi, A. M.; Kondori, A.; Tamadoni Saray, M.; Segre, C. U.; Shahbazian-Yassar, R.; Rappe, A. M.; Asadi, M. Imidazolium-Functionalized Mo_3P Nanoparticles with an Ionomer Coating for Electrocatalytic Reduction of CO_2 to Propane. *Nat. Energy* **2023**, *8* (8), 891−900.

(53) García-Huete, N.; Post, W.; Laza, J. M.; Vilas, J. L.; León, L. M.; García, S. J. Effect of the Blend Ratio on the Shape Memory and Self-Healing Behaviour of Ionomer-Polycyclooctene Crosslinked Polymer Blends. *Eur. Polym. J.* **2018**, *98*, 154−161.

(54) Wang, Q.; Li, Y.; Xiao, J.; Xia, L. Intelligent *Eucommia Ulmoides* Rubber/Ionomer Blends with Thermally Activated Shape Memory and Self-Healing Properties. *Polymers* **2023**, *15* (5), 1182.

(55) Hoh, G.; Cumberbatch, G. M. Stability of Surlyn® Ionomer Films to Ionizing Radiation. *J. Plast. Film Sheeting* **1991**, *7* (3), 221−246.

(56) Dow. PARALOID Impact Modifiers Enhance Performance of Callaway Golf Balls. *Additives for Polymers* **2021**, *2021* (2), 2−3.

(57) Sessini, V.; López Galisteo, A. J.; Leonés, A.; Ureña, A.; Peponi, L. Sandwich-Type Composites Based on Smart Ionomeric Polymer and Electrospun Microfibers. *Front. Mater.* **2019**, *6*, 301.

(58) Seethamraju, S.; Ramamurthy, P. C.; Madras, G. Reactive Interlayer Based Ultra-Low Moisture Permeable Membranes for Organic Photovoltaic Encapsulation. *Phys. Chem. Chem. Phys.* **2015**, *17* (35), 23165−23172.

(59) Seethamraju, S.; Ramamurthy, P. C.; Madras, G. Organic Passivation Layer on Flexible Surlyn Substrate for Encapsulating Organic Photovoltaics. *Appl. Phys. Lett.* **2014**, *105* (10), 104102.

(60) Seethamraju, S.; Ramamurthy, P. C.; Madras, G. Ionomer Based Blend as Water Vapor Barrier Material for Organic Device Encapsulation. *ACS Appl. Mater. Interfaces* **2013**, *5* (10), 4409−4416.

(61) Lertngim, A.; Phiriyawirut, M.; Wootthikanokkhan, J.; Yuwawech, K.; Sangkhun, W.; Kumnorkaew, P.; Muangnapoh, T. Preparation of Surlyn Films Reinforced with Cellulose Nanofibres and Feasibility of Applying the Transparent Composite Films for Organic Photovoltaic Encapsulation. *R. Soc. Open Sci.* **2017**, *4* (10), 170792.

(62) Kopanati, G. N.; Seethamraju, S.; Ramamurthy, P. C.; Madras, G. A Surlyn/Magnesium Oxide Nanocomposite as an Effective Water Vapor Barrier for Organic Device Encapsulation. *RSC Adv.* **2015**, *5* (41), 32580−32587.

(63) Kopanati, G. N.; Seethamraju, S.; Ramamurthy, P. C.; Madras, G. Water Vapor Barrier Material by Covalent Self-Assembly for Organic Device Encapsulation. *Ind. Eng. Chem. Res.* **2014**, *53* (46), 17894−17900.

(64) Kopanati, G. N.; Ramamurthy, P. C.; Madras, G. TiO_2/EVOH Based Reactive Interlayer in Surlyn for Organic Device Encapsulation. *Mater. Res. Express* **2016**, *3* (2), 025302.

(65) Seethamraju, S.; Rao, A. D.; Ramamurthy, P. C.; Madras, G. Layer-by-Layer Assembly of Nafion on Surlyn with Ultrahigh Water Vapor Barrier. *Langmuir* **2014**, *30* (48), 14606−14611.

(66) Zhang, X.; Liu, H.; Maharaj, C.; Zheng, M.; Mohagheghian, I.; Zhang, G.; Yan, Y.; Dear, J. P. Impact Response of Laminated Glass with Varying Interlayer Materials. *Int. J. Impact Eng.* **2020**, *139*, 103505.

(67) Samieian, M. A.; Cormie, D.; Smith, D.; Wholey, W.; Blackman, B. R. K.; Dear, J. P.; Hooper, P. A. On the Bonding between Glass and PVB in Laminated Glass. *Eng. Fract. Mech.* **2019**, *214*, 504−519.

(68) Martín, M.; Centelles, X.; Solé, A.; Barreneche, C.; Fernández, A. I.; Cabeza, L. F. Polymeric Interlayer Materials for Laminated Glass: A review. *Constr. Build. Mater.* **2020**, *230*, 116897.

(69) Luo, H.; Su, Y.; Wang, X.; Helal, M. H.; Ibrahim, M. M.; Huang, M.; El-Bahy, S. M.; Jiang, Q. Preparation and Properties of Ethylene-Acrylic Acid co Polymer/Surlyn-Zn^{2+}/Zinc Stearate Blends Ionic Interlayer Membrane. *Adv. Compos. Hybrid Mater.* **2022**, *5* (3), 2078−2091.

(70) Su, Y.; Yang, J.; Wang, X.; Ma, Y.; Pan, D.; Vupputuri, S. Surlyn Resin Ionic Interlayer-Based Laminated Glass: Preparation and Property Analysis. *Adv. Compos. Hybrid Mater.* **2022**, *5* (1), 229−237.

(71) D'Auria, S.; Neuteboom, P.; Pinalli, R.; Dalcanale, E.; Vachon, J. Polyethylene Ionomers as Thermally Reversible and Aging Resilient Adhesives. *Eur. Polym. J.* **2024**, *211*, 113000.

(72) Lee, J. Y.; Painter, P. C.; Coleman, M. M. Hydrogen Bonding in Polymer Blends. 4. Blends Involving Polymers Containing Methacrylic Acid and Vinylpyridine Groups. *Macromolecules* **1988**, *21* (4), 954−960.

(73) Kumar S. Mural, P.; Jain, S.; Madras, G.; Bose, S. Improving Antifouling Ability by Site-Specific Silver Decoration on Polyethylene Ionomer Membranes for Water Remediation: Assessed Using 3D Micro Computed Tomography, Water Flux and Antibacterial Studies. *RSC Adv.* **2016**, *6* (91), 88057−88065.

(74) Ali, S.; Iqbal, O.; Ding, S.; Li, N.; Guo, H. Interaction Between the Phase Separation and Flow-Induced Crystallization Process in Polyethylene/Ethylene-Methacrylic Acid Ionomers (Surlyn) Blends During the Film Blowing: An In-Situ Synchrotron Radiation X-ray Scattering Study. *Polymer* **2022**, *248*, 124819.

(75) Okamoto, M.; Shinoda, Y.; Kinami, N.; Okuyama, T. Nonisothermal Crystallization of Poly(ethylene terephthalate) and Its Blends in the Injection-Molding Process. *J. Appl. Polym. Sci.* **1995**, *57* (9), 1055−1061.

(76) Coleman, M. M.; Lee, J. Y.; Serman, C. J.; Wang, Z.; Painter, P. C. Poly(ethylene-co-methacryl acid)-Polyether Blends. *Polymer* **1989**, *30* (7), 1298−1307.

(77) Kim, Y. J.; Lee, H. M.; Park, O. O. Processabilities and Mechanical Properties of Surlyn-Treated Starch/LDPE Blends. *Polym. Eng. Sci.* **1995**, *35* (20), 1652−1657.

(78) López GonzalezNúñez, R. G.; Vázquez-Fletes, R. C.; Ortega-Gudiño, P.; Vázquez-Lepe, M. O.; Rodrigue, D.; González-Núñez, R. Rotational Molding of Compatibilized PA6/LLDPE Blends. *Polym. Eng. Sci.* **2021**, *61* (4), 1007−1017.

(79) Tang, X.; Liu, C.; Keum, J.; Chen, J.; Dial, B. E.; Wang, Y.; Tsai, W. Y.; Bras, W.; Saito, T.; Bowland, C. C.; Chen, X. C. Upcycling of Semicrystalline Polymers by Compatibilization: Mechanism and Location of Compatibilizers. *RSC Adv.* **2022**, *12* (18), 10886−10894.

(80) Suh, K. S.; Hwang, S. J.; Lee, C. R. Charge Behavior in Polyethylene-Ionomer Blends. *IEEE Trans. Dielectr. Electr. Insul.* **1997**, *4* (1), 58−63.

(81) Pourrahimi, A. M.; Hoang, T. A.; Liu, D.; Pallon, L. K.; Gubanski, S.; Olsson, R. T.; Gedde, U. W.; Hedenqvist, M. S. Highly Efficient Interfaces in Nanocomposites Based on Polyethylene and Zno Nano/Hierarchical Particles: A Novel Approach toward Ultralow

Electrical Conductivity Insulations. *Adv. Mater.* **2016**, *28* (39), 8651−8657.

(82) Meng, F. B.; Chen, X.; Shi, Y.; Hong, Z.; Zhu, H.; Muhammad, A.; Paramane, A.; Wang, Y.; Huang, R.; Deng, X. Spraying Core-Shell ZnO to Achieve High Insulation Performance for HVDC Cable Factory Joints. *ACS Appl. Energy Mater.* **2022**, *5* (6), 7681−7691.

(83) Xing, Y.; Liu, L.; Fu, Z.; Li, Y.; Li, H. Preparation of an Integrated Membrane Electrode Assembly for Proton Exchange Membrane Fuel Cells Using a Novel Wet-Bonding Strategy. *Energy Fuels* **2023**, *37* (16), 12360−12368.

(84) Trigg, E. B.; Stevens, M. J.; Winey, K. I. Chain Folding Produces a Multilayered Morphology in a Precise Polymer: Simulations and Experiments. *J. Am. Chem. Soc.* **2017**, *139* (10), 3747−3755.

(85) Huang, H. C.; Zacharia, N. S. Polyelectrolyte Multilayers and Complexes to Modify Secondary Interactions in Ethylene-co-methacrylic Acid Ionomers. *ACS Macro Lett.* **2012**, *1* (1), 209−212.

(86) Penco, M.; Rhaman, A.; Spagnoli, G.; Janszen, G.; Di Landro, L. Novel System with Damage Initiated Autonomous Healing Property Based on Heterogeneous Blends of Ethylene-methacrylic Acid Ionomer. *Mater. Lett.* **2011**, *65* (14), 2107−2110.

(87) Ahn, D.; Sun, J.; Han, S.; Lee, J.; Jeong, S.; Cha, S.; Noh, S.; Choi, H.; Ren, B.; Yoon, H.; Kim, H.; Park, J. J. Controllable Physical Synergized Triboelectricity, Shape Memory, Self-Healing, and Optical Sensing with Rollable Form Factor by Zn Cluster. *Adv. Sci.* **2022**, *9* (18), No. e2200441.

(88) Kalista, S. J.; Pflug, J. R.; Varley, R. J. Effect of Ionic Content on Ballistic Self-Healing in EMAA Copolymers and Ionomers. *Polym. Chem.* **2013**, *4* (18), 4910−4926.

(89) Zhu, Y.; Rahbar-Rastegar, R.; Li, Y.; Qiao, Y.; Si, C. Exploring the Possibility of Using Ionic Copolymer Poly (ethylene-co-methacrylic) Acid as Modifier and Self-Healing Agent in Asphalt Binder and Mixture. *Appl. Sci.* **2020**, *10* (2), 426.

(90) Rahman, M. A.; Spagnoli, G.; Grande, A. M.; Di Landro, L. Role of Phase Morphology on the Damage Initiated Self-Healing Behavior of Ionomer Blends. *Macromol. Mater. Eng.* **2013**, *298* (12), 1350−1364.

(91) Kalista, S. J.; Ward, T. C.; Oyetunji, Z. Self-Healing of Poly(ethylene-co-methacrylic acid) Copolymers Following Projectile Puncture. *Mech. Adv. Mater. Struct.* **2007**, *14* (5), 391−397.

(92) Silva, P. A. P.; da Silva, A. B.; Santos, J. P. F.; Oréfice, R. L. Self-Healing Polymer Blend Based on PETG and EMAA. *J. Appl. Polym. Sci.* **2021**, *138* (14), No. e50148.

(93) Kalista, S. J., Jr; Ward, T. C. Thermal Characteristics of the Self-Healing Response in Poly(ethylene-co-methacrylic acid) Copolymers. *J. R. Soc. Interface* **2007**, *4* (13), 405−411.

(94) Deng, Y.; Zhang, Q.; Feringa, B. L.; Tian, H.; Qu, D. H. Toughening a Self-Healable Supramolecular Polymer by Ionic Cluster-Enhanced Iron-Carboxylate Complexes. *Angew. Chem., Int. Ed.* **2020**, *132* (13), 5316−5321.

(95) Varley, R. J.; van der Zwaag, S. Towards an Understanding of Thermally Activated Self-Healing of an Ionomer System During Ballistic Penetration. *Acta Mater.* **2008**, *56* (19), 5737−5750.

(96) Delaey, J.; Dubruel, P.; Van Vlierberghe, S. Shape-Memory Polymers for Biomedical Applications. *Adv. Funct. Mater.* **2020**, *30* (44), 1909047.

(97) Selezneva, E. V.; Bakirov, A. V.; Sedush, N. G.; Bystrova, A. V.; Chvalun, S. N.; Demco, D. E.; Möller, M. How Shape Memory Effects can Contribute to Improved Self-Healing Properties in Polymer Materials. *Macromolecules* **2021**, *54* (5), 2506−2517.

(98) Zhang, Y.; Li, H.; Li, C.; Chen, X.; Lesser, A. Investigation of “Zn^{2+} Salt-Bondings” Cross Linked ENR with Shape Memory Effect via Ionic Interactions. *Polym. Eng. Sci.* **2019**, *59* (S1), 367−374.

(99) Lu, L.; Li, G. One-Way Multishape-Memory Effect and Tunable Two-Way Shape Memory Effect of Ionomer Poly(ethylene-co-methacrylic acid). *ACS Appl. Mater. Interfaces* **2016**, *8* (23), 14812−14823.

(100) Zende, R.; Ghase, V.; Jamdar, V. A Review on Shape Memory Polymers. *Polym. Plast. Technol. Mater.* **2023**, *62* (4), 467−485.

(101) Shi, Y.; Weiss, R. A. Sulfonated Poly(ether ether ketone) Ionomers and Their High Temperature Shape Memory Behavior. *Macromolecules* **2014**, *47* (5), 1732−1740.

(102) Li, B.; Zhang, C.; Peng, F.; Wang, W.; Vogt, B. D.; Tan, K. T. 4D Printed Shape Memory Metamaterial for Vibration Bandgap Switching and Active Elastic-Wave Guiding. *J. Mater. Chem. C* **2021**, *9* (4), 1164−1173.