LETTER

Using Molecules with Superior Water-Plasticity to Build Solid-Phase Molecular Self-Assembly: Room-Temperature Engineering Mendable and Recyclable Functional Supramolecular Plastics

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ABSTRACT: The brittleness of many supramolecular films in a dry environment has prevented their further application as supramolecular plastics. We report here the fabrication of supramolecular plastics displaying excellent dry-flexibility and mechanical strength through room-temperature solid-phase molecular self-assembly using water-locking polyelectrolyte and surfactant. Aided by mild mechanical pressure of about 0.5 MPa, the locked water enables the polyelectrolyte-bridged surfactant microdomains to merge into large mesophases to reduce the interface energy, which yields a transparent supramolecular film. The film still contains 2% water in a dry environment, which is capable of plasticizing the polyelectrolyte and surfactant; thus, it imparts excellent flexibility to the film. The dry film has a stress of 12 MPa and Young's modulus of 188 MPa with a strain of 24%. This mechanical strength is comparable to that of the commercial soft polyethylene plastics. Since the noncovalent interactions in the film can be activated by water under mild mechanical pressure within seconds, mending a broken film by pressing a wet patch with mild mechanical force onto the damage becomes possible. Complete recycling can be achieved under the same conditions. We envision the current room-temperature mechanical force driven water-based recyclable and mendable supramolecular plastics would be very promising in reducing white pollution and generating integrated materials.
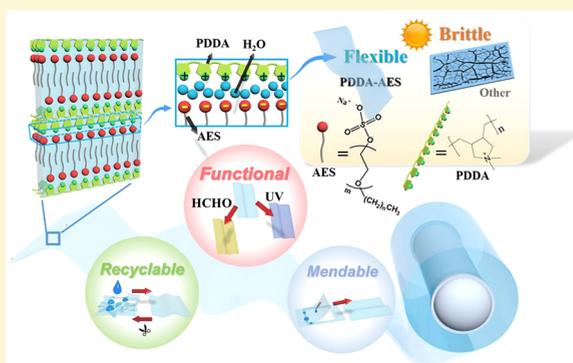
Owing to the severe energy consumption and environmental pollution caused by the excessive production of traditional plastics, supramolecular plastics with room-temperature engineering, recycling, and mending processes have attracted great attention.[1−10] Generally, they are fabricated with elegantly designed supramolecular building blocks,[11−15] followed by manufacturing through organic solvent evaporating process[14−19] or hot compression molding.[20−23] This approach is often tedious[13,14] and energy consuming.[24,25] So far, few supramolecular plastics can be manufactured without heating or organic solvent evaporating.[4−7]

Recently, we developed a strategy of solid-phase molecular self-assembly (SPMSA) for the large-scale fabrication of supramolecular plastics using commercially available surfactants (SA) and polyelectrolytes (PE).[26,27] Compared with the film casting method widely employed in creating various film materials,[28−33] the strategy of solid-phase molecular self-assembly avoids tedious solvent evaporating and allows fabrication of large-scale supramolecular films instantly by virtue of the spontaneous merging of the polymer-bridged nanometer-sized surfactant domains to reduce the interface energy under mild mechanical pressure.[26,27] However, similar
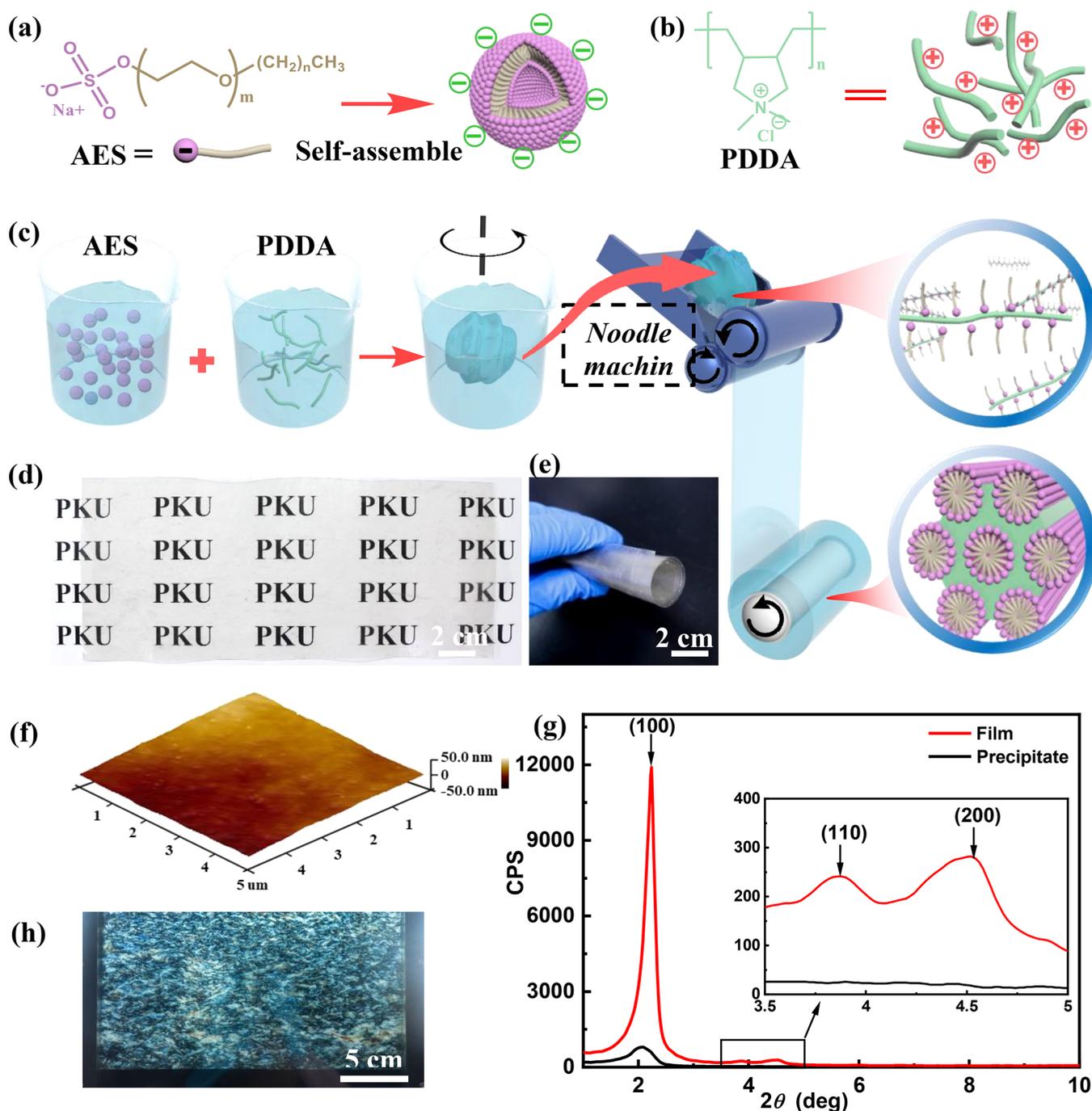
Figure 1. (a) Chemical structure of the anionic AES and the self-assembly of AES into vesicles. (b) Chemical structure of cationic PDDA. (c) Schematic illustration of the PDDA-AES film generation process. (d) A 240 mm × 100 mm × 0.3 mm PDDA-AES film fabricated by a noodle machine. (e) The PDDA-AES film can be rolled. (f) AFM image of the PDDA-AES film. (g) XRD pattern of the PDDA-AES precipitate and the film, respectively. (h) Birefringence of the film in part b observed in-between two vertically aligned 19 cm × 19 cm polarizers.

to other casted polyelectrolyte-based films, the resultant supramolecular films are fragile in a dry environment due to the loss of bonding water.[34] Although replacing water with ionic liquids would solve this dry-fragile problem,[26] the use of ionic liquid will inevitably increase the costs and has a risk of leaking of ionic liquids, which is disadvantageous for the creation of supramolecular plastics. Similarly, other approaches of imbedding water-locking small molecules would have the same problem.

Herein we report that upon employment of polyelectrolyte and surfactant displaying superior water-plasticity, namely polydiallyldimethylammonium chloride (PDDA) and sodium alcohol ether sulfate (AES), the resultant supramolecular plastics can be made flexible enough even in a dry environment. Mechanical tests indicate that the stress of the film can be up to 12 MPa and the Young's modulus about 188 MPa while tolerating a strain of 24% at RH = 0 (zero relative humidity). This mechanical strength is comparable to that of
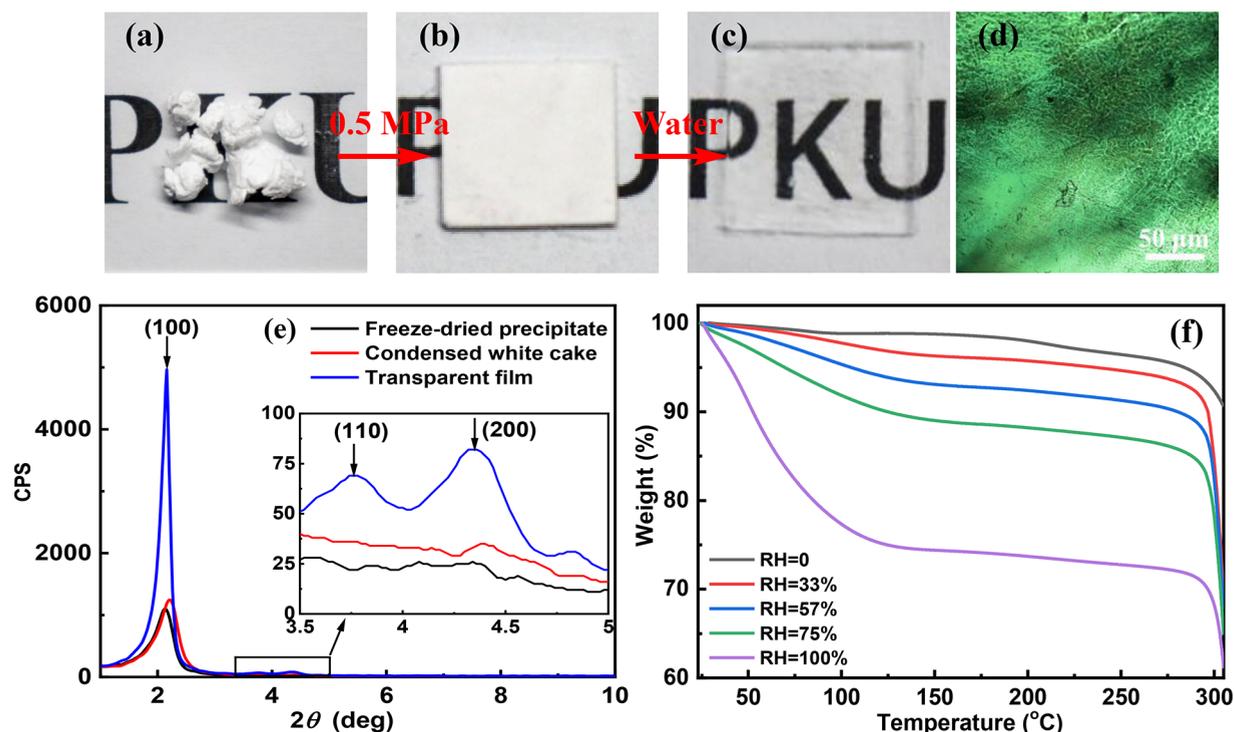
Figure 2. (a) The freeze-dried amorphous PDDA-AES precipitate was condensed to (b) a white cake and then became (c) a transparent film by treatment with water. (d) Birefringence of the film in part c. (e) XRD patterns of the freeze-dried precipitate, condensed white cake, and transparent film, respectively. (f) TGA curves for PDDA-AES films under different relative humidities.

the commercial soft polyethylene plastics, and we demoed the application of the resultant PDDA-AES films as a packing material. Most strikingly, the ionic interaction between PDDA and AES can be activated under the mild pressure exerted by a human finger in the presence of trace water, so that any broken film can be mended with a patch of the same material. Considering discarding package plastics is very common due to the unmendable breaking damage; this convenient mendable nature would prolong the service time of the plastic material. Furthermore, recycling of a seriously broken film with nondegrading of the mechanical strength is possible with a noodle machine in the presence of water. Since no phase transition and covalent bond formation are required, the entire engineering can be processed at room temperature, thus avoiding vast energy consumption. Furthermore, imbedding various functional chemicals into the supramolecular plastics is possible through a coprecipitation process, which allows fabrication of smart plastic devices that able detection of hazard gases. We show that the resultant plastic devices doped with different chemicals can be integrated to detect different hazardous gases, such as formaldehyde and hydrazine, orthogonally.

Figure 1a−c describes the film generation process with AES and PDDA. Both chemicals display superior hydrolyzation and water-plasticized ability, so that their commercial products are merely aqueous solutions of different concentrations.[35−38] Upon mixing the aqueous solution of AES and PDDA ($M_w \sim$ 400,000) at the charge balancing ratio, amorphous white precipitates occurred immediately. The precipitates were collected and loaded into a household noodle machine. A large-scale opaque plastic film was obtained immediately with this machinery process and became transparent within 30 min (Figure 1d and e). The thickness of the film can be

conveniently controlled between 0.1∼5 mm by setting the distance between the two rollers of the noodle machine. The surface of the film is very smooth with a small roughness of 3.66 nm revealed by AFM (Figure 1f).

XRD measurements (Figure 1g) revealed an intensified and sharpened peak at 2.1°, which is followed by two extra diffraction peaks. The three diffractions are with a spacing ratio of $1 : \sqrt{3} : \sqrt{4}$, respectively, corresponding to (100), (110), and (200) Miller indices of a 2D hexagonal mesostructure.[34,39,40] The distance obtained from the (100) diffraction is 3.94 nm, approximately two times the extending length of AES (2.5 nm, Figure S1), indicating AES has self-assembled into bilayers. TEM and DLS measurements suggest that AES itself in water self-assembled into vesicles (Figure S2). Obviously, the bilayer packing of AES chains is retained both in the precipitates and in the films. Different from the simple bilayer domains in the initial precipitate, the AES molecules, which were bonded electrostatically to the PDDA chains, rearranged into wormlike micelles and further packed into hexagonal phases in the film, as demonstrated in Figure 1c. The size of the hexagonal mesophases is about 800 nm, estimated from the width of the half height of the (001) diffraction.[26,41] In line with this large size of the mesophases, the film displays strong birefringence between two polarizers (Figure 1h).

Water plays a crucial role in the film formation process. Merely mechanical pressure is not able to transform the amorphous PDDA-AES precipitate into the transparent film. Figure 2a and b shows that the freeze-dried amorphous precipitate simply becomes a condensed white cake under mechanical pressure, and its XRD pattern almost remains unchanged upon exerting mechanical pressure (Figure 2e). However, the condensed white cake gradually became transparent upon dropping water (Figure 2c), which is
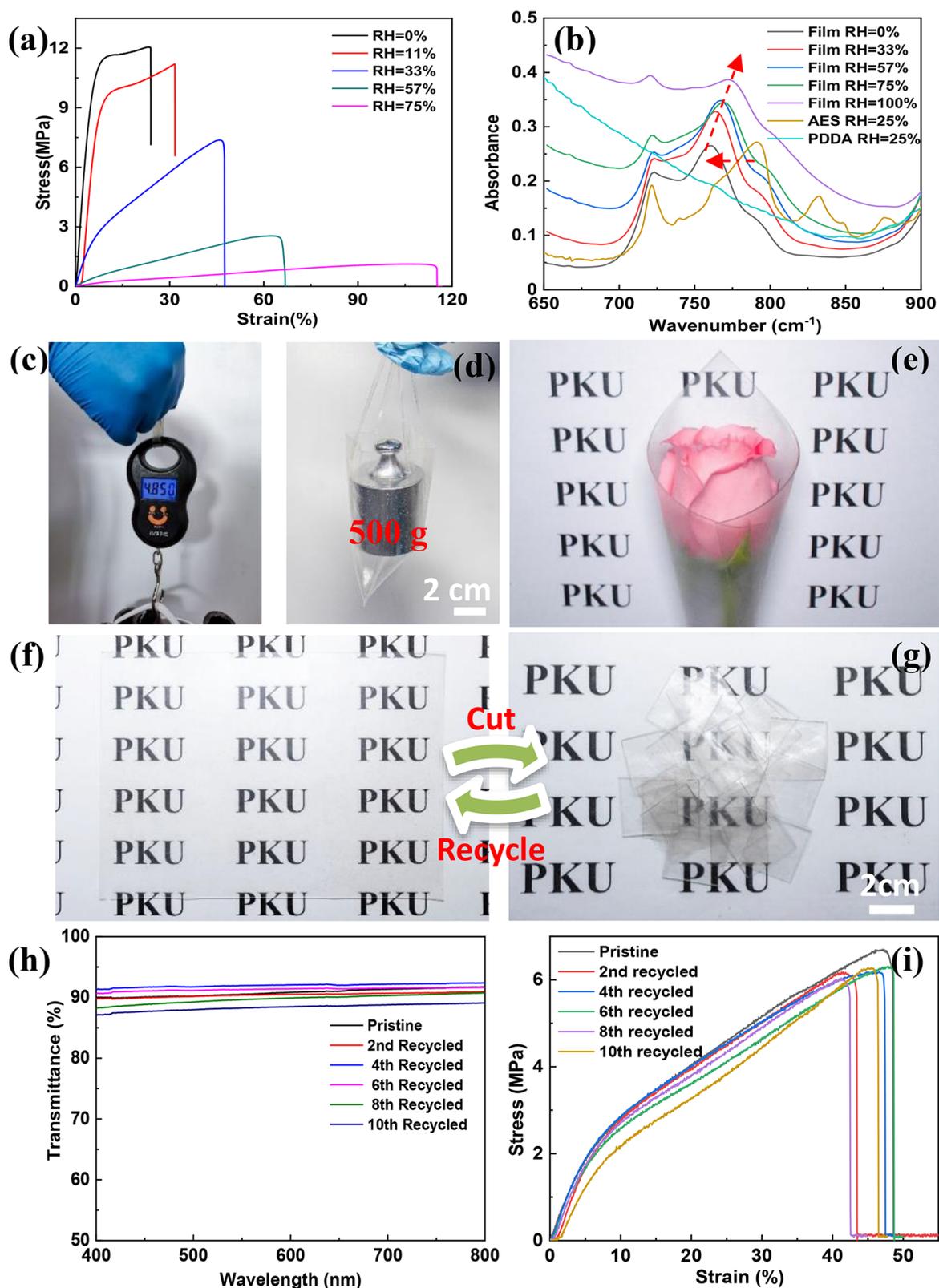
Figure 3. (a) Stress−strain curves for PDDA-AES films under different relative humidities. (b) FT-IR spectra of the stretching vibration of C−O−S in AES and the PDDA-AES films under different relative humidities. (c) Photo of the 1 cm width × 1 mm thick film loading a 4.85 kg weight at 40% RH. (d) Photo of the 2 mm width × 0.3 mm thick string loading a 500 g weight at 60% RH. (e) Application demonstation of AES-PDDA films as a packing film. (f and g) Demonstration of the recycling process of the PDDA-AES film. (h) UV−vis transmission spectra of the PDDA-AES films after multiple generations of recycling. (i) Stress−strain curves of the PDDA-AES films after multiple generations of recycling.
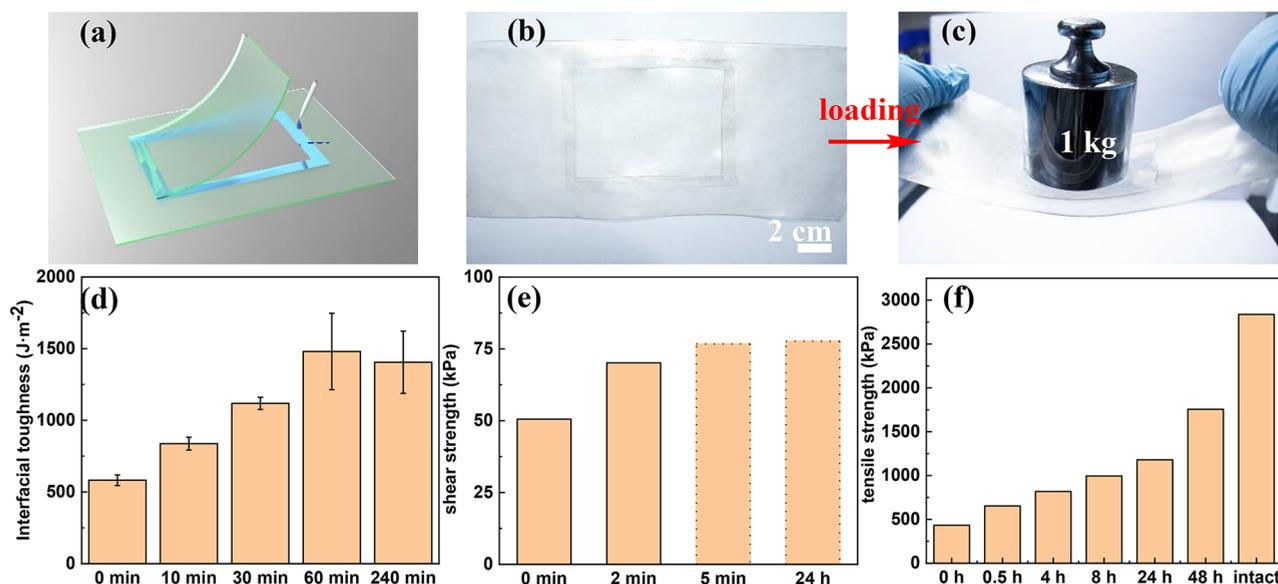
Figure 4. (a) Schematic illustration of the mending process of a broken PDDA-AES film. (b) Photo of a broken film with a 6 cm × 9 cm hole after being mended with a patch. (c) Photo of the mended film in part b loading with a 1 kg weight. (d−f) Water-triggered self-adhesion performance of the PDDA-AES films: (d) interfacial toughness, (e) shear strength, and (f) tensile strength versus adhesion time.

accompanied by the intensified and sharpened (001) diffraction (Figure 2e) and strong birefringence (Figure 2d). This means that it is water that has triggered rearrangement of the AES molecules to form a large mesophase. TGA measurements suggest that the film contains at most 26% water when equilibrated in an environment with 100% relative humidity (RH) (Figure 2f), which is much higher than the 10% water in other surfactant−polyelectrolyte films.[26,27,41] Even for the low humidity of RH = 0, there is still 2% water in the film. Clearly, this small amount of water is sufficient to plasticize the film, which renders the film with sufficient flexibility even in a dry environment, which avoids the brittleness caused by the loss of water.

The mechanical strength of the AES-PDDA film is comparable to some soft plastics such as low-density polyethylene (LDPE).[42] The broken stress of the film at 0% RH is 12 MPa, and the Young's modulus is 188 MPa (Figure 3a). It is noticed that while most water-based supramolecular films become fragile in a dry environment,[5,27,33,41] the AES-PDDA film can still endure a strain of 24% at RH = 0. Control experiments revealed that as the PDDA-AES film was replaced by other combinations, such as PSS-CTAB, the resultant film would be fragile at RH = 0 (Figure S3). Furthermore, when either PDDA or AES is replaced by other cationic polyelectrolyte and anionic surfactants, the resultant films would also become fragile (Figure S4). It is noticed that the water contents in all these films at RH = 0 are comparable, indicating only the combination of PDDA-AES can be easily plasticized by the small content of retaining water. Therefore, sufficient water-plasticity of both components is required for the creation of dry-flexible supramolecular plastics.

With increasing humidity, the water content in the PDDA-AES films increases correspondingly, as revealed in the TGA curves (Figure 2f) and FT-IR spectra (Figure S5). These enhanced water contents significantly weaken the electrostatic interactions between PDDA and AES, as manifested by the FT-IR spectra in Figure 3b. The stretching vibration of C−O−S in AES occurs at 761 cm^{-1} in the PDDA-AES film at RH = 0, whereas it shifts gradually to 791 cm^{-1} as the RH increases to

100%. This weakened ionic interaction between AES and PDDA renders enhanced mobility for the polymer chains, so that the broken stress decreases with the increasing humidity, but still in the order of MPa even at the high humidity of 75%. At the extremely high saturated relative humidity of 100%, the film still remains intact and has the considerable broken stress of 0.1 MPa, which is a sufficiently high value for many flexible materials.[43,44] Strikingly, the broken stress would recover to its original state of 12 MPa after drying (Figure S6). At 40% RH, which is a typical weather condition popular for drylands,[45] the 1 cm width × 1 mm thick film can sustain a load of 4.85 kg (Figure 3c). Even at a higher RH of 60%, the 2 mm width × 0.3 mm thick string can sustain a load of 500 g (Figure 3d). These data demonstrate that the mechanical strength of the current film is sufficient for practical daily application. Figures 3e and S7 demonstrate the use of an AES-PDDA film as a packing film and package bag, respectively. Clearly, both the excellent mechanical strength and the transparency are satisfied for the purpose of different package applications.

Furthermore, the important role of water in the film generation process endows the film with excellent room-temperature recyclable and engineering abilities. As the films were cut into small pieces, they rejuvenate into new ones upon being wetted by drops of water and then repeatedly pressed at room temperature (Figure 3f and g). Both the transparency (Figure 3h) and the mechanical strength (Figure 3i) of the films were not fatigued after 10 recycling cycles. XRD patterns showed that the molecules in the reprocessed film also form a hexagonal mesostructure (Figure S8), which confirmed the extraordinary recyclability of PDDA-AES films at the molecular level.

This excellent room-temperature water-facilitated engineering capability under a mild mechanical pressure of only 0.5 MPa, which can be easily exerted by fingers, allows facilely mending a broken film. Here, water works as a plasticizer and triggers films to adhere themselves through activating the dynamic molecular rearrangement under mechanical pressure. Figure 4a illustrates the two-step mending process: (1) wetting the interfaces between the damage and the patch; (2) pressing

the patch to the wetted damage for seconds. As a demo, a 6 cm × 9 cm hole was made on a film, which was mended by gluing a patch with water (Figure 4b). The photo in Figure 4c shows that this mended film can sustain a load of 1 kg. To quantitatively evaluate the water-triggered self-adhesion performance of the PDDA-AES films, we conducted three different types of mechanical tests according to the literature,[46] measuring the interfacial toughness by peel tests, the shear strength by shear tests, and the tensile strength by tensile tests. Peel tests revealed that the interfacial toughness is up to 1480 J·m^{-2} after 1 h of adhesion (Figure 4d). The shear strength would reach a stable value of 75 kPa within 5 min (Figure 4e), while the tensile strength gradually increased to 1756 kPa within 2 days (Figure 4f). Compared with the original film, about 64% of the tensile strength was recovered. However, the loading experiment in Figure 4c indicates that this tensile strength is sufficient to extend their lifetimes and reduces their deposing rates as daily used plastic materials. Furthermore, since both PDDA and AES are degradable in the natural environment[47−49] (Figure S9) and the ionic bindings between PDDA and AES can be weakened by water and brine solution (Figures 3b and S10), when they reach the end of their life span, the supramolecular plastics are theoretically degradable.

Besides the potential of replacing conventional plastics for daily packaging, these room-temperature water activatable supramolecular plastics can also be made into orthogonal sensors for detection of toxic gases by integrating supramolecular plastics doping with different sensing chemicals. As our previous work showed, this polyelectrolyte−surfactant supramolecular material is a multifunctional platform because of the alternatively arranged hydrophobic/hydrophilic domains.[24] Since van der Waals interactions are universal between different molecules, almost all functional molecules, regardless of their hydrophobicity, can be doped into the film by coprecipitation, rendering it an open platform toward diversified functions. Each piece of functional plastic is an independent device and performs its functions, respectively. The facile processing approach and the excellent water-enabled self-adhesion ability allow the creation of intelligent plastic sensors by integrating the devices together through water gluing. As a demo we doped spiropyrane and ammonium acetylacetone into the films (Figure 5a and b). With the aid of water, these pieces of plastics can be glued together and exhibit responsiveness for both UV light and formaldehyde (Figure 5c) by virtue of the UV responsive ring-opening reaction[50,51]
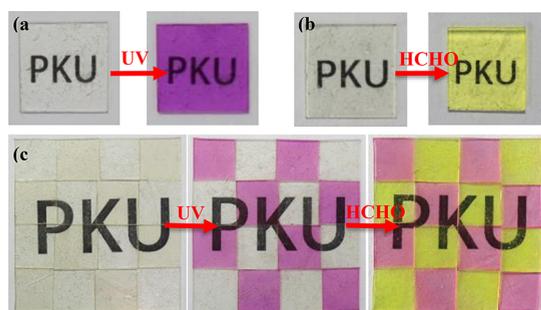
and the color displaying reaction between acetylacetone and formaldehyde[52] (Figure S11).

The excellent transparency, mechanical strength, recyclability, and mendability and its facile fabrication from commercial industrial materials make it possible to use the current AES-PDDA supramolecular plastics to replace conventional plastics in the field of packing. Since disposable packages are one of the main origins of white pollution, we envision that the AES-PDDA film is very promising in solving the global energy and environmental problems triggered by plastic problems.

■ ASSOCIATED CONTENT

ⓈⅠ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.1c00724.

> Materials; methods including details for precipitate and film formation, fabrication of integrated functional films, relative humidity control, mechanical tests, and characterizations of the films; supplementary figures for AES molecular structure, TEM and DLS of AES aqueous solution, stress-strain curves of CS-AES, PDDA-SDS, and PDDA-SDBS films, XRD patterns of the pristine film and recycled film, and reaction equations of spiropyrane and ammonium acetylacetone (PDF)

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Figure 5. (a) Spiropyrane doped film with UV light responsiveness. (b) Ammonium acetylacetone doped film with formaldehyde responsiveness. (c) The spiropyrane and ammonium acetyacetone integrated film shows both UV light and formaldehyde responsiveness. Each individual film is 1 cm × 1 cm in size.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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