Smart Soft Materials

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Bending and Stretching Actuation of Soft Materials through Surface-Initiated Polymerization**

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Shape–memory materials (SMMs) and actuators possess the ability to respond to external stimuli such as temperature, electricity,[1] magnetic field, and light,[2] and change their shapes. During the process, energy is converted into mechanical deformation which makes them attractive for various applications in biomedical devices, deployable structures, artificial muscles, microdevices, sensors, etc.[3] Traditional SMMs and actuators rely on the properties of bulk material irrespective of their nature (e.g. polymers, metallic alloys, composite materials).[1–4] Very recently, polymer-brush-based nanoscale bending actuators were reported.[5] As a consequence of the strong interchain repulsion, the overcrowded polymer chains within the polymer brush can exert forces onto the underlying substrate and deform the substrate. However, there is no empirical evidence that bending observed on the nanoscale can be adapted for actuator applications on the macroscale. Furthermore, bending alone may not be sufficient to provide the desired macroscopic actuation; axial stretching may also be required.

Herein we demonstrate the bending and stretching of a soft polymeric substrate, plasticized poly(vinyl chloride) (pPVC, thickness 400 μm, Young's Modulus 6.89 MPa), on the macroscale by grafting a model hydrophilic polymer, poly(*N*,*N*-dimethylacrylamide) (PDMA), at high graft density on the pPVC surface. As shown in Figure 1 A, when PDMA chains were grafted on one side of the pPVC surface, bending of the substrate was observed. In contrast, when PDMA chains were grafted on both sides of the pPVC surface, stretching of the substrate was observed. Proof-of-concept bending and stretching actuators with relatively high actuator strain and reasonable force per unit length were developed based on this observation. The reversible bending and stretching can also be tailored to respond to various external stimuli by changing the chemical structures of the grafted polymer chains.

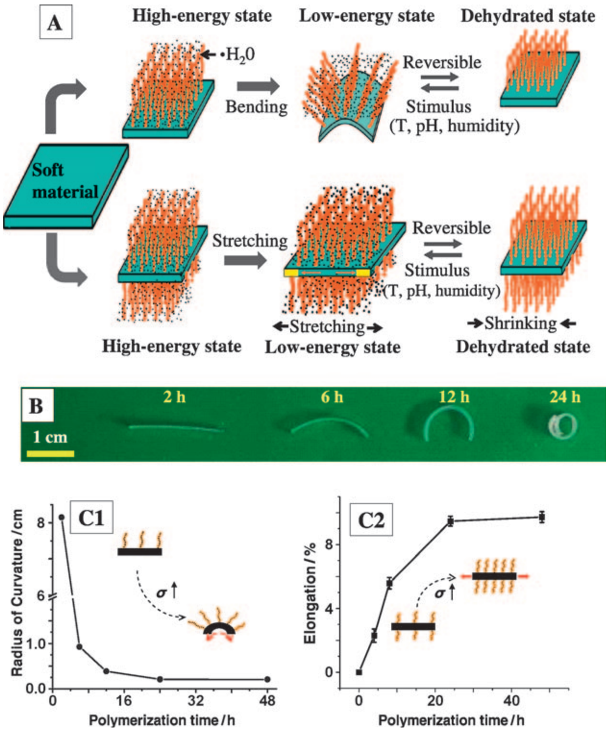

Figure 1. A) Illustration of bending and stretching of a soft material driven by the growth of polymer chains by SI-ATRP. B) Photographs showing the effect of the polymerization time on the bending of the plasticized PVC substrate. C) Effect of the polymerization time on bending (C1) and stretching deformation (C2; σ is the grafting density of the polymer brushes).

We first investigated the bending of the pPVC film on the macroscale. As a proof of concept, an initiator-modified pPVC substrate obtained by single-side atom-transfer radical polymerization (ATRP) without noticeable initial curvature was used (see the Supporting Information for sample preparation). The initiator-modified pPVC was precut into samples of 1.5 cm × 0.25 cm dimensions and they were used for surface-initiated ATRP (SI-ATRP) of *N*,*N*-dimethylacry-

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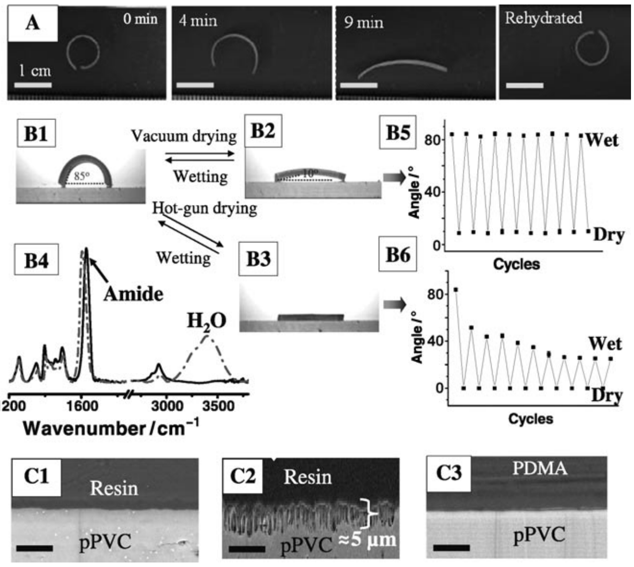

Figure 2. A) Effect of dehydration–rehydration on the bending of a pPVC substrate with PDMA chains grafted on one side (12 h SI-ATRP). B) Effect of different drying processes on the reversibility of the bending. B1) Photograph of a wet PDMA-grafted pPVC substrate, B2) photograph of the substrate dried under vacuum, B3) photograph of the substrate dried by a hot gun, B4) ATR-FTIR spectra of a PDMA-brush-grafted pPVC substrate dried in vacuum (dot-dashed line) and with a hot gun (solid line), B5 and B6) relationship of the bending angles to different wetting–drying cycles under different drying conditions (B5: vacuum drying, B6: hot-gun drying). C) Cross-sectional back-scattered electron SEM images of C1: unmodified pPVC, C2: pPVC grafted with PDMA (24 h SI-ATRP), and C3: spin-coated PDMA on pPVC. The scale bars in C1–C3 represent 5 µm.

lamide (DMA) for 2, 6, 12, and 24 h. As shown in Figure 1B, the pPVC substrates were deformed with increased polymerization time. All pPVC substrates curved in the direction of the side onto which the PDMA chains were grafted. Longer polymerization times resulted in a gradual decrease in the radius of the curvature of the substrates (Figure 1C1). The molecular weight (M_n: number-average molecular weight, M_w: weight-average molecular weight) of the PDMA chains formed in solution along with the surface-grafted chains remained constant after 2 h (M_n and M_w/M_n values were 1.5×10^6, 1.8×10^6, 2.1×10^6, 2.0×10^6 and 1.68, 1.75, 1.87, 2.00, respectively for 2, 6, 12, 24 h of SI-ATRP), suggesting that the increase in bending deformation can be attributed to the increase in graft density of the polymer chains (i.e. increase in chain–chain repulsion) on the surface. Although the direct measurement of the molecular weight is desirable,[6] the M_n values of the grafted PDMA chains were estimated from the solution polymers in the current study because the amide linkage between the polymer and the surface was cleaved incompletely. The presence of amide bonds in the PDMA also complicated the cleavage process. The gradual increase in the PDMA graft density and the ultrahigh molecular weight of the chains are consistent with our previous observation of SI-ATRP of DMA from unplasticized PVC in aqueous solution.[7]

A high degree of reversibility is essential for an ideal actuator design. Figure 2A shows the effect of dehydration–rehydration under atmospheric conditions on the bending–flattening of the PDMA-grafted pPVC substrate (12 h SI-ATRP). Under these conditions (45% relative humidity, 22 °C), the PDMA-grafted pPVC gradually dehydrated, flattened, and finally reached an equilibrium state after nine minutes. The dry sample reverted to its original shape upon rehydration within eight seconds (see video 1 in the Supporting Information). The flattening and bending of the PDMA-brush-grafted pPVC is due to conformational changes of the PDMA chains on the surface during the drying–wetting process. The chain dimensions of the grafted PDMA decreased during the drying process which resulted in reduced chain–chain interactions. During the rehydration, the polymer chains regained their original dimensions and the substrate reverted to its original shape. A control nontreated pPVC substrate did not show noticeable shape changes during the wetting–drying process (see video 2 in the Supporting Information).

To obtain quantitative information on the reversibility of the bending–flattening process, a wet PDMA-grafted pPVC substrate was dried by two approaches: vacuum drying (22 °C. 0.1 Pa, 15 minutes) and hot-gun drying (180 °C, 10 seconds). As shown in Figure 2B1, B2, and B5, the vacuum drying afforded a highly reversible bending–flattening process indicated by the minimal variation in the bending angles when the process was repeated (Figure 2B5). In contrast, hot-gun drying (complete drying) led to a gradual decrease in the bending angle (Figure 2B1, B3, B6) with repeated wetting–drying cycles, suggesting a more pronounced initial irreversibility. In the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum the water peak (3400 cm^{-1}) observed for the vacuum-dried substrate disappeared after hot-gun drying (Figure 2B4). The differences in the behavior of the substrate subjected to the two drying methods reflect the importance of the residual water for the reversibility of the bending–flattening process. One possible reason for the irreversible deformation in the case of hot-gun drying could be entanglement of the polymer chain. The residual water in the specimen after vacuum drying might have prevented such entanglement, resulting in the high reversibility of the process.

To verify that the covalently grafted PDMA chains are responsible for the bending, we examined the bending–flattening process of a pPVC substrate spin-coated with PDMA on one side. The M_n value of the spin-coated PDMA was comparable to that of the grafted chains and the thickness of the dry coating was approximately 31 µm. There was no bending observed for the spin-coated sample in the hydrated state and it bended slightly to the side of the PDMA coating upon drying, which is presumably due to the contraction of the PDMA layer. The structures of unmodified pPVC, the PDMA-grafted pPVC substrate (24 h SI-ATRP), and the pPVC spin-coated with PDMA were compared by scanning electron microscopy (SEM). The topography of the pPVC and the PDMA-grafted pPVC substrates is rougher than that of the spin-coated PDMA (see Figure 6S in the Supporting Information). Cross-sectional images of the samples are shown in Figure 2C. A sparsely spaced interface filled with vertically aligned fiberlike structures was observed for

PDMA-grafted pPVC (Figure 2C2). In contrast, unmodified PVC and spin-coated PDMA did not show any special interfacial features (Figure 2C1 and 2C3). The thickness of the PDMA-grafted layer on the pPVC was approximately 5 μm as determined by SEM (approximately 1% of the thickness of the pPVC substrate), correlating well with the ultrahigh molecular weight of the PDMA chains.

To understand the experimental observations better and to illustrate the application of this shape–memory mechanism for the generation of bending and stretching actuator devices (Figure 3), we applied engineering principles. An engineering analysis of the experimentally observed bending deformations has been performed by using beam theory.[8a] The polymer-brush layer grafted onto the surface is assumed to exert an in-plane membrane force, f per unit width, at the polymer-brush–substrate interface, in the plane of the interface as shown in Figure 3A (the details of the engineering model and the analysis are described in the Supporting Information). This allows two deformations. In the first case, the substrate bends when either the upper or the lower surface alone is coated. This bending is similar to the observation by Stoney and co-workers of the bending of nickel-plated metal strips as a result of residual stresses.[8b,c,9] In the second case, the substrate stretches when the same polymer-brush structure is present on both sides (Figure 3B). Consequently, both stretching and bending actuation of the substrate is possible with the polymer-brush coatings. Based on the engineering analysis of the deformations we estimate a membrane force of 24 $\mathrm{N\,m^{-1}}$ for a polymerization time of 4 h and a M_n value of 1.6×10^6 for bending actuators (see Figure S8 in the Supporting Information). For the stretching case, the estimated force per unit length (FPL) for the upper and lower surfaces was 18.3 and 12.9 $\mathrm{N\,m^{-1}}$, respectively. A detailed calculation of the force density is provided in the Supporting Information. When the polymerization time was increased from 4 to 24 h, much higher values of 74.7 and 67.3 $\mathrm{N\,m^{-1}}$ were deduced for the upper and the lower surfaces, respectively (see Figure S10 in the Supporting Information). This is attributed to the increase in graft density with increasing polymerization time.[7] The elastic modulus of the pPVC did not change significantly after PDMA chains had been grafted on the surface.

It is instructive to compare the polymer-brush actuator with other existing actuators based on two mechanical indices for actuator performance: force per unit length and actuator strain. The actuator force per unit length is deduced from the engineering analysis. Actuator strain is the maximum strain the actuator undergoes. The FPL versus actuator strain diagram is shown in Figure 3E, wherein actuators drawn from an actuator data base[8d] are compared with polymer-brush-based actuators. It can be observed that there is a trade-off between FPL and actuator strain in general for all actuators. Actuators with high FPL, such as piezoelectric materials, cannot provide large strains. Shape–memory metals such as Ni–Ti are attractive due to their larger strains. The polymer-brush-based actuators developed herein are shown to provide even higher actuator strain (typically 10%) and moderate force per unit length: slightly better than some electroactive polymers. This comparison diagram underlines the potential for polymer-brush actuators in soft material systems. We note that graft density and molecular weight govern the FPL and actuator strain, and the data reported here is for the experiments we conducted.

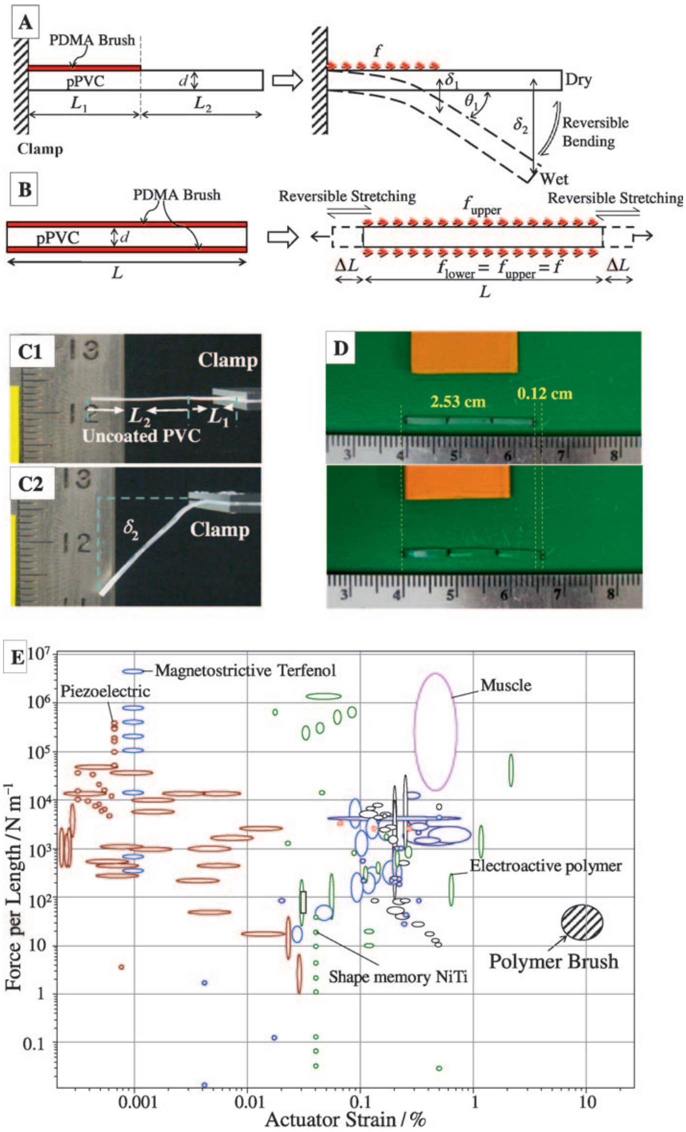

Figure 3. A) Engineering model to describe the bending behavior of pPVC substrates with PDMA grafted on one side. The length of the coated and uncoated segment was denoted as $L1$ and $L2$, respectively. B) Engineering model predicting the stretching of pPVC coated with PDMA on both sides. C) Photographs of the pPVC substrate with PDMA-grafted on one side under dry (C1) and wet (C2) conditions. D) Photograph of the stretching actuator based on a PDMA-brush-grafted pPVC sample. Comparison of the length of the pPVC surfaces grafted with PDMA on both sides under dry (top) and wet (bottom) conditions. E) Comparison of the polymer-brush actuator to other available actuators with regard to two performance indices: force per unit length and actuator strain.

To explore the application of this shape-change phenomenon further, we used two other external stimuli, namely temperature and pH. To generate SMMs and actuators sensitive to temperature, a classical temperature-sensitive polymer, poly(*N*-isopropylacrylamide) (PNIPAm), and its copolymer with PDMA were used. As shown in Figure 4A,

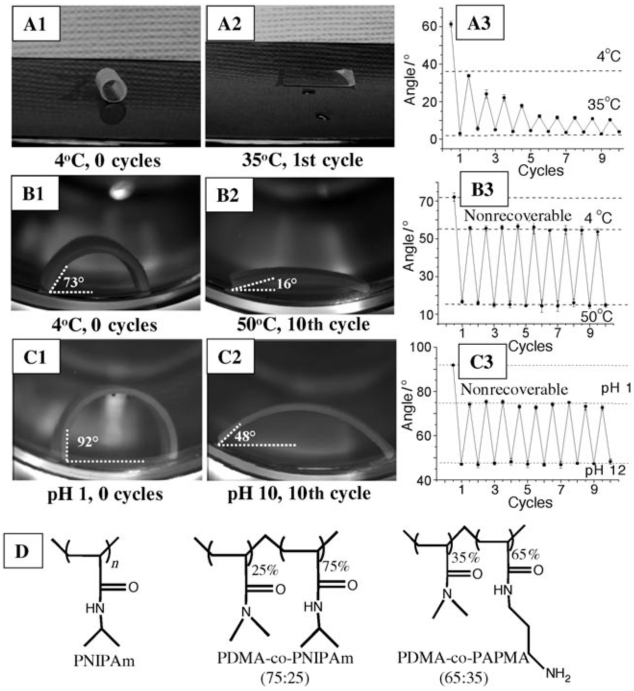

Figure 4. Effect of different stimuli on the bending of polymer-brush-grafted pPVC substrates. A) Photographs of the PNIPAm-grafted pPVC substrate at different temperatures (A1, A2); A3: Relationship of bending of angles and heating–cooling cycles. B) Photographs of PDMA-co-PNIPAm-brush-grafted pPVC substrate at different temperatures (B1, B2); B3: Relationship of bending angles and heating–cooling cycles. C) Photographs of PDMA-co-PAPMA-brush-grafted pPVC substrate at different pH values (C1, C2); C3: Relationship of bending angles and pH-change cycles. D) Chemical structures of three polymers.

when a PNIPAm-grafted pPVC substrate (stored at 4 °C after polymerization) was heated to 35 °C and then cooled to 4 °C, an irreversible bending–flattening process was observed. The phase transition of the grafted PNIPAm may have resulted in chain entanglement, which is not reversed upon cooling (Figure 4 A3), similar to the complete drying of a PDMA brush seen earlier (Figure 2 B6). To overcome this, we used poly(*N*-isopropylacrylamide-*co*-*N*,*N*-dimethylacrylamide) (PNIPAm-co-PDMA; 75:25), resulting in a nearly reversible bending–flattening process during the heating–cooling cycles (Figure 4 B3). The value of the bending angle was lowered by about 25 % during the first cycle and remained constant afterwards. The reversibility of the process may be because the PDMA component remains hydrated during the collapse of the copolymer chains induced by a temperature change. Similarly, the grafting of a pH-sensitive copolymer, poly(*N*,*N*-dimethylacrylamide-*co*-aminopropyl-methacrylamide) (PDMA-*co*-PAPMA), resulted in a pH-sensitive substrate (Figure 4 C). Again, the introduction of a neutral PDMA component in the copolymer significantly improved the reversibility of the process.

In summary, we have illustrated a novel and universal mechanism of generating soft shape–memory materials based on bending and stretching actuators through the surface modification of soft polymeric substrates. We anticipate that this will give a new direction in the generation of soft shape–memory materials and devices. We have demonstrated that conformational changes at the nanoscale associated with the grafted polymer chains (polymer brushes) can be transformed to the macroscale. The deformation of the grafted soft polymeric materials can be achieved by external stimuli such as humidity, temperature, and pH, and possibly other stimuli. We have also demonstrated the application of this mechanism for the generation of proof-of-concept bending and stretching actuators. The achieved force per unit length and the actuation strains make these soft material systems potential candidates for artificial muscles and components in hitherto unexplored applications in biomedical sciences and nanotechnology.

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[9] While Stoney's analysis is concerned with the initial curvature resulting from residual stresses, we are interested in the reversible curvature owing to forces induced by polymer chains on the substrate.