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Shape Memory Polymer Thin Films Deposited by Initiated Chemical Vapor Deposition

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Introduction. Shape memory polymers (SMPs) are smart materials displaying a mechanical response when triggered by an external stimulus.[1,2] The SMPs have the unique ability to "remember" and return to a specific shape which is acquired during the deposition. In the case when the stimulus is heat, recovery to the initial shape will happen when a "transition temperature" is reached, a specific temperature where the polymer switches from a hard or "glassy" state to a soft or "rubbery" state.

Compared to shape memory alloys, the SMPs are cheaper, easier to fabricate, have better recoverability, and can be tuned over a wide range.[3] However, alloys are able to exert a larger force when shape recovery occurs.

As bulk materials, SMPs have been extensively studied for applications including stents, specific drug delivery systems, smart textiles, or data storage.[4−9] This work concentrates on SMP thin films, 1−3 μm in thickness, deposited using initiated chemical vapor deposition (iCVD). The iCVD technique is a bottom-up film growth approach for conformal coatings, compatible with real-time deposition monitoring,[10] and therefore offers a high degree of control over the geometry and thickness of the SMPs.

In SMPs, the shape memory effect results from the specific combination of two monomer types. The "cross-linker" is responsible for the shape recovery and connects individual chains with one another. A second "switching" component allows the temporary shape fixation. When a polymer is too heavily cross-linked, it cannot be deformed into a new shape without breaking the bonds, thereby losing its shape-memory properties. However, a too weakly cross-linked polymer may not have enough restoring force to recover from a temporary shape. Changing the specific combination of the two components, the copolymer permits tuning of the SMP properties. An example is the ability to shift the transition temperature by changing the amount of cross-linker.[16]

The iCVD process is a free-radical polymerization process where resistively heated filaments create the free radicals by thermal decomposition of the initiator molecules in the vapor phase. These radicals then react with the monomers adsorbed on the surface, initiating chains which subsequently form a thin polymer film on the surface. A major advantage of the iCVD process is the fact that the surface can remain at relatively low temperatures (typically < 50 °C), and the method does not require any solvents since the whole process takes place in the vapor and solid phase. Therefore, iCVD enables coating of solvent or temperature sensitive substrates (i.e., paper, membranes, and polymers) with good uniformity.[10−15]

In this work fabrication of free-standing SMP thin films using iCVD is demonstrated for the first time. iCVD enables to control the cross-linking degree of the deposited films which is critical for deposition of the SMPs. Furthermore, ultrathin free-standing SMP films can be deposited using iCVD. The glass transition temperature of the deposited films is measured using dynamic mechanical analysis (DMA). The shape recovery behavior of the films is also demonstrated using DMA and scanning electron microscopy (SEM).

Experimental Setup. *Materials.* The initiator *tert*-butyl peroxide (TBPO, 98% from Aldrich), the switching element *tert*-butyl acrylate (tBA, 98% from Aldrich), and the cross-linker di(ethylene glycol) divinyl ether (DEGDVE, 99% from Aldrich) are used without any further purification. tBA is held in a liquid monomer jar at a constant temperature of 30 °C while DEGDVE is held in a second jar at 60 °C. The initiator TBPO is kept at room temperature. Poly(acrylic acid) (PAA, 99%, Aldrich) is used as the sacrificial layer.

iCVD System. The deposition is performed in a custom-built cylindrical chamber with a removable quartz top allowing visual inspection and real-time thickness measurements using laser interferometry. The base pressure of the system is roughly 1 mTorr, and typical pressures during the deposition are 900−1000 mTorr. Flows of the monomer species can be independently controlled with needle valves while the initiator flow is controlled with a mass flow controller (MKS Type 252).

A filament array consisting of 14 parallel nickel−chromium filaments is heated up to 275 °C using a dc power supply (Sorenson DHP series). The substrate temperature is maintained at 30 °C for all depositions using a water chiller (VWR) for backstage cooling.

Laser interferometry is done with a He−Ne laser (JDS) reflected off the sample. The thickness of the deposited film is determined from the intensity oscillations of the reflected right.

Characterization. Chemical characterization of the polymer films is performed with Fourier transform infrared (FTIR) spectroscopy using a Nexus 875 with a liquid nitrogen cooled MCT-A detector in transmission mode with a resolution of 4 cm^{-1}.

The transition temperature and mechanical properties are measured with a TA Instruments Q800 dynamic mechanical analyzer (DMA) using the oscillating force mode. This oscillating force is applied to the sample for a range of temperatures while the stress and strain of the polymer are measured. The measurement starts at a temperature of 30 °C and is increased to 90 °C with a rate of 3 °C/min to ensure uniformity of the sample temperature. The oscillation frequency is set to 1 Hz with an amplitude of 50 μm. Slack of the sample is taken up by applying a force of 0.001 N before each experiment.

A scanning electron microscope (SEM, JEOL JSM-6060) is used for real-time monitoring of the sample deformation

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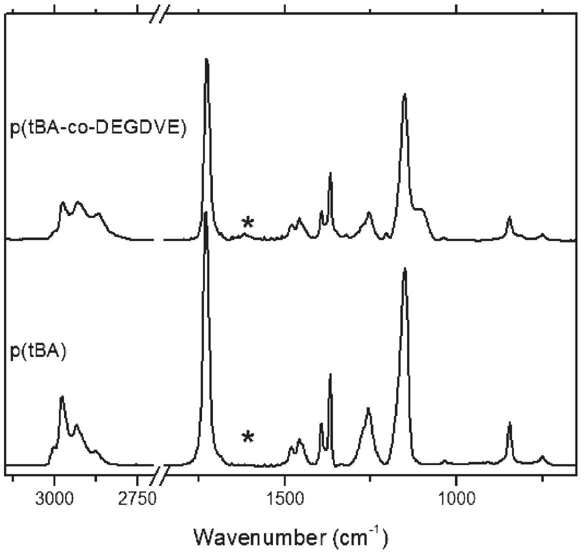

Figure 1. Infrared absorption spectra for the SMP thin film (top) and pure p(tBA). The asterisks label the vinyl bonds present in the monomer.

and recovery. A maneuverable arm with a glass tip (diameter of 1 μm) is inserted in SEM in a fixed position, while the sample stage can be freely moved. The sample is mounted on a small heating pad and connected to a power supply outside the vacuum chamber. The sample is heated to a temperature above its transition temperature, e.g., 60 °C. Subsequently, the stage is moved in order to let the tip deform the sample.

Sample Preparation. Free-standing films are fabricated by depositing the polymers on a sacrificial layer (50% PAA and 50% water) spin-coated on the silicon wafer. After the deposition, the sacrificial layer is etched by dipping the sample in water and the SMP layer is released. The deposited thickness of the iCVD polymers is 1−3 μm. The sample sizes for the DMA tests are 3 cm in length and 8 mm in width.

For all depositions, the substrate and the filament temperatures are kept at 30 and 275 °C while the reactor is maintained at 1 Torr. The flow rates of tBA, DEGDVE, and TBPO are maintained at 16, 0.5, and 2 sccm, respectively.

Results and Discussion. Fourier transform infrared spectroscopy (FTIR) is used to analyze the composition of the deposited films. Figure 1 shows the FTIR absorption spectra of the samples coated with p(tBA-*co*-DEGDVE) as well as pure p(tBA) for comparison. The peak at 1734 cm^{-1} corresponds to the carbonyl peak, and the peaks at 1390 and 1180 cm^{-1} correspond to the *tert*-butyl ester peaks. On the other hand, the peaks at 1142 and 1246 cm^{-1} originate from the C−O stretching vibrations of DEGDVE. In order for a DEGDVE unit to act as a cross-linker, both of its vinyl bonds must react. Complete reaction of the vinyl bonds, thus complete polymerization, is confirmed by the absence of the 1618 cm^{-1} C=C peak in sample S1 (Figure 1).

Figure 2 shows the result of DMA testing on free-standing SMP films. The storage modulus, loss modulus, and the ratio, tan delta, are displayed as functions of temperature. The tan delta peak corresponds to the transition to rubbery state, which occurs at 71 °C. The glass transition temperature, T_g, is taken as the temperature at which the slope of the decrease in storage modulus is the steepest. In the case of a relatively long cross-linker, e.g. DEGDVE, the distance between the chains increases with the cross-linking ratio. Consequently, less energy is needed for the transition to the rubbery state, thus lowering the transition temperature.[16] For the iCVD SMP the glass transition is observed at ~60 °C.

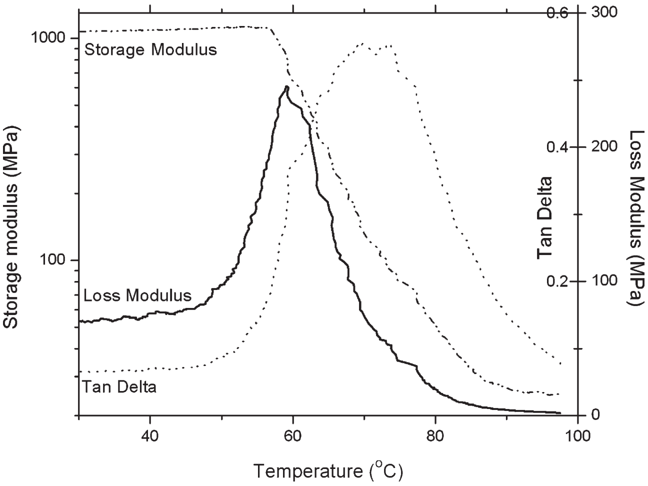

Figure 2. DMA results for the SMP thin film. The glass transition occurs at ~60 °C. The glass transition temperature is defined as the point where the storage modulus has the steepest slope.

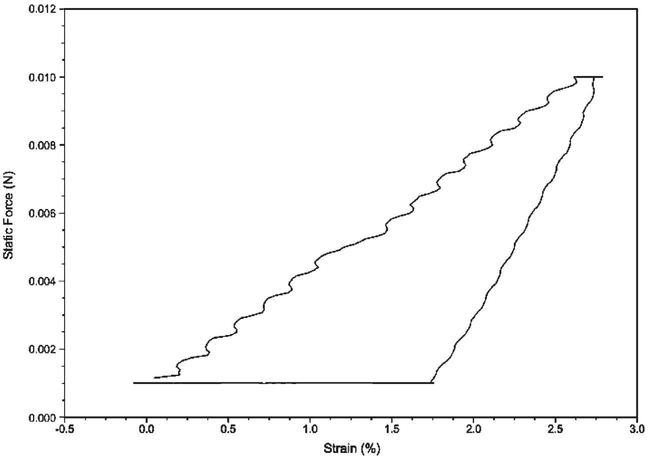

Figure 3. DMA results of a cyclic deformation test. At 0.0% strain, the sample is already heated to 75 °C. At this point a linear increasing force is applied, until a static force of 0.010 N is reached. The force is kept constant while cooling down below the transition temperature. At room temperature the force is released, while the sample retains a deformed shape. Heating to 75 °C again makes the sample return to its original shape, before manipulation.

Below T_g the polymer is in a glassy state. When heated, a phase change to a more rubbery state occurs. The polymer, then, can be easily deformed without breaking the vital cross-linked bonds needed for shape recovery. For a more effective shape-memory polymer, the range in which the glass transition takes place should be as narrow as possible.[9] Indeed, iCVD SMP has a steep and sudden drop in the storage modulus from 1100 to 50 MPa (Figure 2) over ~15 °C. Figure 2 also shows two plateaus for the glassy and rubbery states which correspond to two stable regions.

By using a dynamic mechanical analyzer (DMA), the shape memory effect is confirmed for free-standing films of 1 μm thickness. Figure 3 shows the stress−strain curve obtained from a cyclic DMA test. The first step is to heat the sample to 75 °C. The clamps of the DMA device apply a constant force during this step, but due to increasing temperature, the sample is stretched already, giving it a strain up to 10%. By taking this as an offset, we start at zero strain in Figure 3. Now, at 75 °C, we start to apply an increasing force with a ramp of 0.001 N min^{-1}, starting at 0.001 N as the minimal applicable force of the DMA device. When 0.01 N is

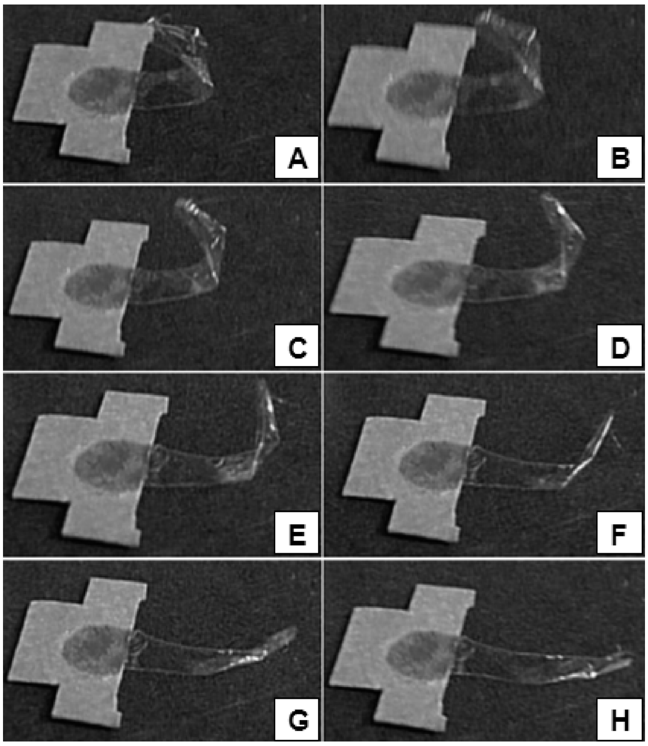

Figure 4. Shape recovery of the free-standing SMP film while begin exposed to a temperature of 75 °C: (A) temporary shape fixation; (B−G) shape recovery during exposure to heat; (H) full recovery to initial shape.

reached, the force is kept constant again while temperature is lowered to 30 °C. After this, the force was gradually removed with a rate of 0.001 N min^{-1}. The last step is to heat the sample to above its transition temperature to let it recover to its original shape, before deformation. As seen in the figure, the path of deformation and removal of the applied force follow different paths, typical for a shape-memory polymer, whereas for a normal polymer these lines would overlap. The high-frequency oscillations observed in the figure is a result of operating at too low values of applied force due to film thicknesses of micrometer scale. It should be noted that the device is optimized for films with a thickness of 1 mm.

The shape fixity ratio of this sample, which describes how well the sample holds its new temporary shape, can be calculated by comparing the final strain with the strain after cooling the sample down. The shape fixity ratio is found to be 63.6%. Bulk shape memory polymers have typical values of 90%.[6] Defects play a much bigger role in the thin films which may lead to lower fixity ratios. Also, the cooling rate might influence this number. However, Figure 3 shows that the sample fully returns to its original shape.

Figure 4 shows the behavior of the free-standing SMP film when heated in an oven above its transition temperature after a new temporary shape has been manually given to the sample. The first image shows the polymer in its temporary deformed state. It recovers to its original flat shape at a temperature of 75 °C in roughly 5 s.

In Figure 5A the SEM image of a free-standing film can be seen. At 75 °C the tip is used to deform the structure (Figure 5B). While cooling to room temperature, the tip is held in this position to keep the applied force constant. Figure 5C,D shows the recovery process after the tip has been lifted from the sample.

The films deformed in the oven and under the microscope show a clear restoration to their original shape, showing that at these scales the films behave as shape memory polymers.

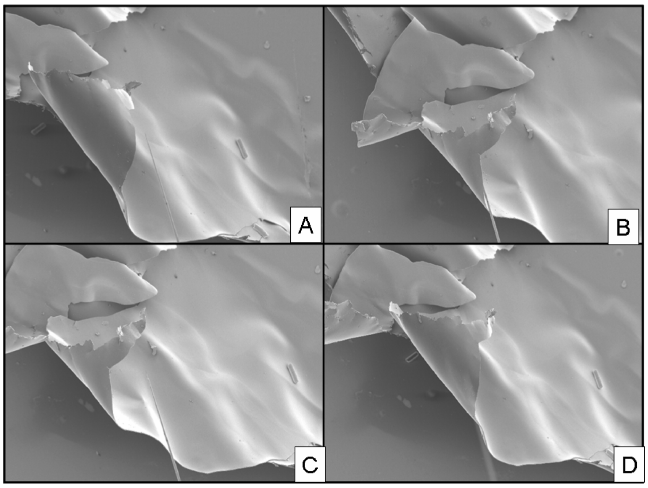

Figure 5. SEM images of (A) the free-standing thin film at room temperature, (B) shape changes using the tip at 75 °C, (C) shape fixation at room temperature, and (D) shape recovery at 75 °C.

Conclusion. Thin films of shape memory polymers of poly(*tert*-butyl acrylate-*co*-di(ethylene glycol) divinyl ether) have been synthesized for the first time in vapor phase using initiated chemical vapor deposition. The shape memory characteristics of the free-standing iCVD thin films are studied using DMA, and a glass transition temperature of 60 °C and a fixation ratio of 63.6% are measured. Shape recovery rates of the iCVD films are observed to be similar to that of the bulk SMPs, indicating that the SMP thin films can successfully be deposited using the gas phase iCVD technique.

For the future studies, the conformal nature of the iCVD technique will enable fabrication of high aspect ratio structures of shape memory polymers with potential applications in biotechnology. Furthermore, by varying the cross-linking ratio, the thermomechanical properties of the SMP structures will be tuned.

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