Thermomechanical Characterization of a Tailored Series of Shape Memory Polymers

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Polymers with shape memory effect have garnered increased attention recently for use in real world applications. Compared with the shape memory alloys (SMAs), the shape memory polymers (SMPs) have the advantages that: (i) the transition temperature and the rubbery modulus can be tailored according to the application and (ii) the recoverable strain can exceed several hundred percent. One of the potential uses of these interesting materials is as a medical plastic; specifically, SMPs offer potential use as "smart" tubes and stents for both surgical implements and implantable devices. As tubes and stents, SMPs can be initially fixed in a form needed and subsequently heated for strain recovery during surgery. In our lab, we have designed and prepared a new type of shape memory polymer that features good shape recovery with tailored transition temperatures and recovery strength. We present thermomechanical characterization data for the new materials and briefly discuss their potential uses as medical plastics.

INTRODUCTION:

Shape memory materials are those materials that can be "fixed" to a temporary and dormant shape under specific conditions of temperature and stress and later, under thermal, electrical, or environmental command, the associated elastic deformation can then be almost completely relaxed to the original, stress-free, condition. The primary class of shape memory materials studied and utilized are the shape memory alloys (SMA) (1) based on nickel and titanium; i.e., nitanol. Such alloys have shape memory effects that exploit the deformation-behavior difference between a high temperature austenite phase (parent phase) and the room temperature martensite phase, a first-order phase transition separating the two phases. As the "yield stress" of martensite is extremely low, the martensitic structure is very easily deformed due to the twinning of the crystalline grains, but this yielded deformation is quite reversible. The deformed martensitic sample maintains its form until it is heated above the critical temperature associated with transformation to the austenitic phase. At that point, structural recovery occurs to achieve the original shape that existed before martensitic deformation. Such a material is now well known and used in such industries as intelligent materials and biomedical engineering. Polymers intrinsically show shape memory effects; but the mechanism of strain recovery for such materials is far different from that of the cousin shape memory alloys. Specifically, the strain recovery aspect of shape memory in polymers comes from entropy elasticity, while the strain fixing aspect comes from either vitrification (glass transition) or crystallization. Thus, mechanical work performed by an external force is converted to excess chain entropy stored in the polymer chains on cooling to a temporary shape. When the temperature is raised above the transition temperature (T_g or T_m) again, the frozen polymer chains are released and will recover to their original form as driven by the restoration of network chain conformational entropy.

Figures-of-merit for SMPs will be closely linked to the network architecture, controlling the energy storage capacity, and to the sharpness of the transition separating the rigid and rubber states, controlling the rate of recovery. Compared with SMAs, SMPs have an advantage of high strain (to several hundred percent) because of the comparatively large rubbery compliance, while the maximum strain of the SMA is less than 8%. Of additional advantage, the transition temperature can be tailored according to the application requirements, a factor that is very important in real world implementations. To the best of our knowledge, the first reported shape memory polymer is a methacrylic acid ester by the Vernon-Benshoff Co. and used as a denture material (2). Since then, numerous polymers have been found to have particularly attractive shape memory characteristics, most notably the polyurethanes, polynorbornene, styrene-butadiene copolymers, cross-linked polyethylene (3), and recently, crosslinked polycyclooctene (4). A nice review of this area of polymer science has been given by Lendlein and Kelch (5).

We have studied polynorbornene (PN) and modifications to this polymer for use as a shape memory polymer that derives from its availability in high molecular weight (over 10^6 g/mol) that leads to a large number of entanglements per chain and thus a quite long relaxation time (6). In this sense, the entanglements of long PN molecules serve as a type of physical crosslink, giving rise to the formation of three-dimensional network, so that application of stress even far above T_g leads only to elastic deformation, but not to viscous flow. Thus, when applying an external force above T_g, the shape can be deformed and the secondary shape can be fixed when cooled to glassy state due to the decrease in the mobility of PN molecules at low temperature. The work performed on the PN elastomer during deformation is stored in the glassy polymer after fixing. The advantages of PN as an SMP are two-fold: (i) it can recover almost 100% of strain due to almost pure elastic deformation, and (ii) the recovery rate is fast on heating due to the sharpness of the PN T_g. However, the use of entanglements as the sole origin of elasticity leads to significant difficult in the processing thus leading to the required use of plasticizers that ultimately hamper shape memory performance. This severe limitation has led us to the present study that looks into the use of castable, reactive formulations, in which the stress-free state is formed during the polymerization process in the form of films or coatings.

Along these lines, it is important to note that copolymers have also been used to design shape memory polymers. The most often used idea has been to copolymerize monomers that normally lead to an amorphous polymer with a comonomer that would otherwise form a semicrystalline polymer and the melting points of the crystals are employed as the transition temperatures (6~9). When the polymers are heated up to melting point of the semicrystalline phase, the melting of the crystallites will occur to yield a rubber that is easily deformed. When the deformed rubber is cooled below the melting point, re-crystallization occurs for the fixing of the deformed state. In the case of amorphous shape memory polymers, such as might be required for optical applications or applications demanding a sharp transition, glass transition temperatures of the SMPs can be tailored by copolymerizing two kinds of monomers whose polymers have vastly different glass transition temperature (8). The given polymer will have a T_g between that of the two homopolymers. Most often, the Fox equation is used with satisfactory accuracy to predict the transition temperatures. In all cases, thermoplastic examples can be modified by common methods to create thermosetting SMPs. In these cases, the cured SMPs are fixed by the glassy transition or crystallization phenomena, while the rubbery rheological properties are determined by crosslinking rather than entanglement concentration (7, 9).

Recently, we have conceived, synthesized, and characterized a novel series of shape memory polymers that can be processed as castable formulations in the form of coatings and films. For simplicity we refer to this class of polymers as castable shape memory polymers, CSMP. Two vinylidene monomers that lead to polymers with quite different glass transition temperatures—one is 118°C and another is 22°C—were copolymerized. Furthermore, we have incorporated a difunctional monomer so that the copolymer is crosslinked during polymerization to form a thermoset network. In our system, the transition temperature (T_g) is adjusted by the ratio of the monomers, while the degree of crosslinking controls the rubbery modulus plateau. The latter, in turn, dictates the energy stored during a given deformation and thus the energy that is available to release when the polymers recover. We show, finally, that the new polymers exhibited very good shape memory effect and that the transition temperature can be adjusted as broad as from 22~118°C. The polymers have potential to be as coatings in the processing of novel medical devices.

EXPERIMENTAL

Materials and Synthesis. Alkyl-methacrylate monomers (methyl methacrylate, MMA; and butyl methacrylate, BMA) and the cross-linking agent (tetraethylene glycol dimethacrylate, TEGDMA) were purchased from Aldrich. The inhibitors were removed by passing the liquid monomers through an initiator removal column purchased from Scientific Polymer Products, Inc. AIBN, purchased from Aldrich and used as received, was used as thermal initiator. The purified monomers and the cross-linking agent were mixed in varying proportion (here referred to as %MMA) with AIBN at room temperature by stirring. The mixture was then prepolymerized in a flask using an oil bath at 65°C for 40 minutes in order to increase the viscosity to certain value amenable to casting. The viscous fluid was then filled between two casting glass plates with a designed spacer inserted for sealing and the assembly then placed into an oven and kept at 40°C for 60 h. The temperature was then raised to 80°C for 24 h and 100°C for 6 h to ensure maximal conversion. The samples were then cooled down and made ready for measurement and characterization. This prolonged curing time minimized shrinkage and led to samples free of residual stress, voids, or cracks.

Thermal Characterization. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done using Perkin-Elmer instruments (models 951 and 2910, respectively). For TGA, the samples were heated in a nitrogen atmosphere from room temperature to 600°C at a rate of 20°C/min. The onset temperature of weight loss and the percentage of weight loss were recorded. For DSC, the samples were first heated from -50°C to 150°C at a rate of 10°C/min to erase all of the prior thermal history; then the samples were quenched to -50°C at a rate of 80°C/min and the samples finally were reheated to 150°C at a rate of 10°C/min. The temperature corresponding to the midpoint in heat capacity for such second heating runs was used to determine the glass transition temperature of the polymers.

Dynamic Mechanical Analysis. The moduli of the SMPs are measured by dynamic mechanical thermal analysis (DMTA) in tensile mode using the TA Instruments DMA 2980. The method we adopted was a temperature ramp at fixed mechanical oscillation frequency of 1 Hz. The temperature was ramped from −100°C to 200°C at the heat rate of 4°C/min. A rectangular film was chosen and the geometry of the film was length × width × thickness of 15 × 2 × 1.2 mm, respectively.

Shape Memory Experiments. Stress-free shape recovery experiments were performed as we now describe in order to assess the ability of the prepared samples to recover strain induced in the rubbery state and frozen into the glassy state. Samples were first cut to a rectangular shape and stained to a red color to impart optical contrast. Samples were then bent into a circular shape about the width axis to an inner diameter of 0.737 cm while heating in a warm water bath with T = 90°C. The deformed sample was then quenched in ice water to fix the form through vitrification. This bent sample was subsequently dipped into a warm water bath at a prescribed temperature using a customized plunger and the shape recovery monitored visually with a video camera and digital framegrabber collecting images at a rate of 20 frames-per-second.

RESULTS AND DISCUSSION
TGA of the SMPs With Different Monomer Ratios

A series of shape memory polymers with different ratio of MMA to BMA (from 0% to 100%) were synthesized and the thermal stability of the polymers are measured by TGA. Results are plotted in *Fig. 1*. It can be seen that with pure polymer of BMA (0% of MMA), the film is quite stable and does not decompose below 250°C. When the MMA is incorporated in the

copolymers, the decomposition temperature of the copolymers shifts to higher temperatures. Further increasing of monomer MMA can increase the decomposition temperature further, with the homopolymer of PMMA having the highest decomposition temperature, which is about 50°C above homopolymer PBMA. This means that the monomer PMMA is more stable than monomer PBMA and that all of the polymers are stable enough for use in medical devices. All of the polymers can be totally decomposed in N_2 when further heated above 450°C; i.e. char yields are negligible.

DSC of SMP With Different Monomer Ratios

The glass transition temperatures of the SMPs with different ratio of monomer MMA from 0% to 100% were measured by DSC and the results plotted in *Fig. 2*, and summarized in *Table 1*. From *Fig. 2* we find that the copolymers form only one T_g, which suggests that the copolymers are reasonably random in the distribution of monomers along the backbone. While pure poly(butyl methacrylate) features a measured T_g of 22.2°C addition of MMA leads to a systematic transition in the glass transition temperature to higher temperatures. Ultimately, pure PMMA prepared in this way features a T_g of 117.7°C. Thus the transition temperature for shape memory behavior can be easily tailored through composition variation of the two monomers. The T_g's of the polymers are listed in *Table 1* and were fit well by the Fox equation, as shown in *Fig. 3*.

DMTA Comparison of CSMPs With and Without Crosslinking

The storage modulus of the polymers with and without crosslinking were compared at fixed monomer ratio using DMTA, the results being shown in *Fig. 4*. The
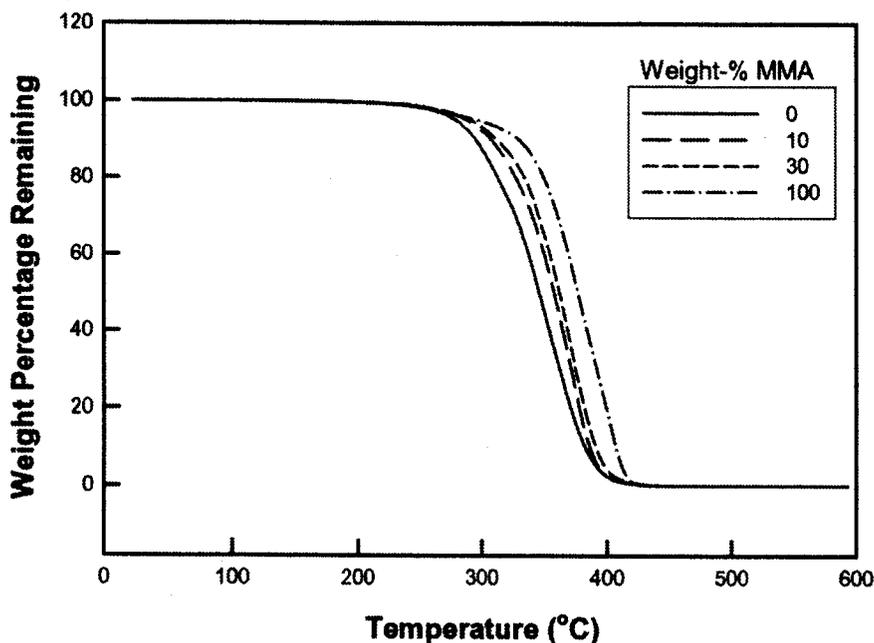

Fig. 1. Dependence of thermal stability in nitrogen on MMA content in the copolymers.

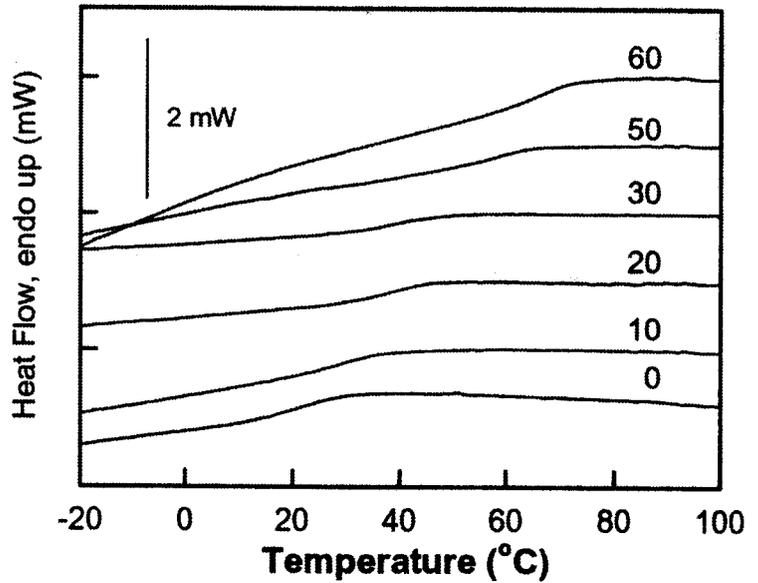*Fig. 2. DSC traces for copolymers with MMA weight percentage indicated.*

Table 1. Glass Transition Temperatures of the Copolymers With Different Monomer Ratios.

Monomer ratio (MMA/MMA+MBA)	0	0.1	0.2	0.3
Tg (°C)	22.2	27.2	38.3	44.2
Monomer ratio (MMA/MMA+MBA)	0.4	0.5	0.6	1.0
Tg (°C)	50.7	59.0	65.6	117.7

particular samples compared in this figure have MMA/BMA/TEGDMA weight percentages of 30/70/0 and 28.5/66.5/5 for the uncrosslinked and crosslinked samples, respectively. Both polymers show glassy mechanical response with a tensile modulus ~3 × 10⁹

Pa for temperatures below 70°C. Then, when the temperature reaches 70°C, the modulus begins to drop dramatically and reaches its rubbery state at 100°C. For this system, it is interesting to point out that for low TEGDMA concentrations (this case, 5 wt%) the glass transition temperature is unaffected, thus allowing independent control over T_g and rubber modulus. Without crosslinking, the rubbery modulus of the polymer falls rapidly with increasing temperature until viscous flow occurs; no rubber plateau is sustained. With crosslinking, the sample shows a flat modulus plateau and does not flow until thermal degradation. This tunability of thermomechanical properties with MMA and TEGDMA content yields a powerful material system that can be adjusted for given applications that define the critical temperature and rubber modulus (mechanical work) requirements.

Fig. 3. Dependence of T_g on copolymer composition expressed as T_g^{-1} vs. MMA weight fraction. Straight line is the Fox equation prediction.
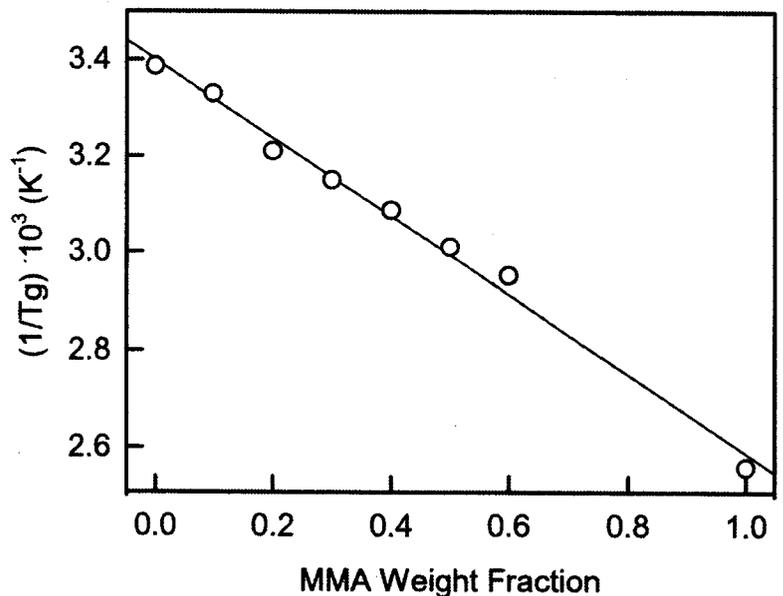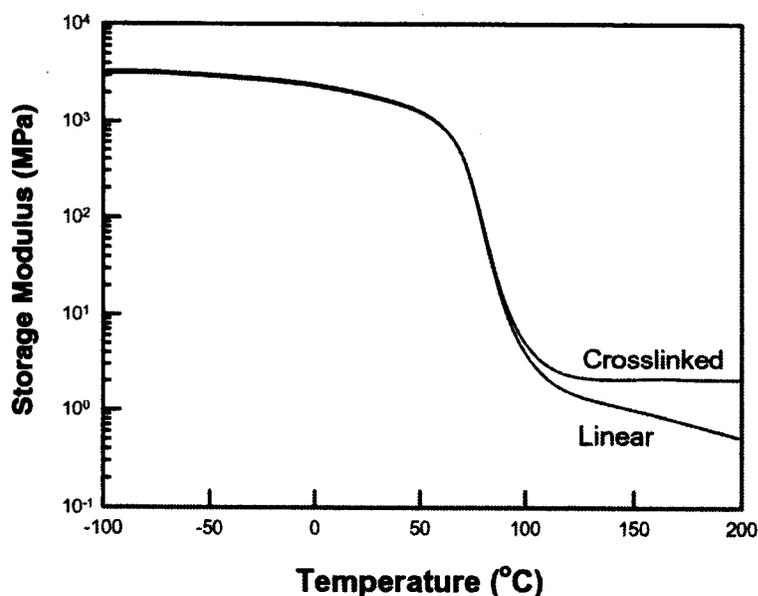
Fig. 4. Temperature dependence of tensile storage modulus with and without crosslinking for an MMA and TEGDMA weight fractions of 28.5 and 5, respectively.

Shape Memory Behavior of the CSMPs

The stress-free strain recovery of a castable shape memory polymer strip was performed and the results are shown in *Fig. 5*. Here, the composition chosen was MMA/BMA/TEGDMA (28.5/66.5/5) in weight percentage. The original form of the polymer (permanent form) is a strictly flat rectangular strip, but the strip was first deformed to a circle (secondary form) and fixed as described in the experimental section above. Heating above the critical temperature triggered the shape memory of the deformed strip by being immersed into a warm water bath at 90°C quickly. As can be
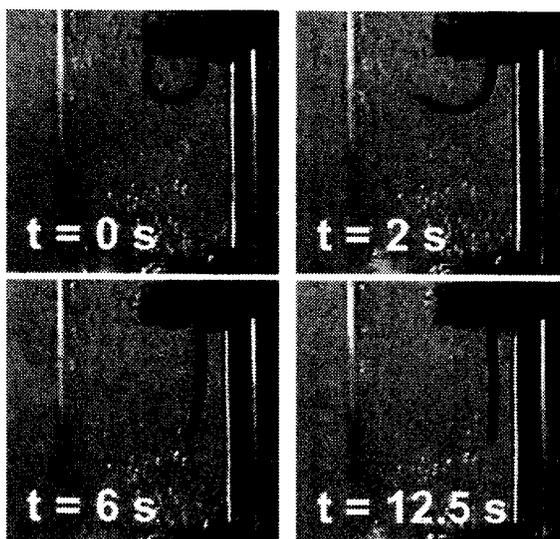

Fig. 5. Strain recovery of crosslinked MMA/BMA/TEGDMA (28.5/66.5/5 wt%) upon rapid exposure to a water bath at T = 80°C.

seen in *Fig. 5*, the speed and the extent of recovery of the strip, recorded digitally, show that the strip has a good shape memory effect and can recover to its original shape totally in 10 sec. Most of the strain is recovered within the first five seconds, however.

Potential Uses of CSMPs in Medical Devices

Because of their unique "memorizing" properties, shape memory materials are being considered increasingly in the medical device industry for self-triggering stents, catheters and auxiliary devices (11, 12). The devices can be thermomechanically "trained" and surgically manipulated with the body, then treated with heat or other ways during the operations to trigger the transitions for the device to perform certain mechanical actuation in the body. Our materials have a great potential for modifying existing medical devices because we can design both the transition temperatures (T_g) and the recovery force (rubber modulus) according to the surgical requirements. Moreover, the extent of deformation can be as large as 200%, while the SMA devices can only deform to as much as 8% and the critical temperatures are hard to adjust.

CONCLUSIONS

We have designed and prepared a new type of shape memory polymer that features good shape recovery with tailored transition temperatures and recovery strength. Thermo-mechanical characterization data for the new materials has quantified this versatility and revealed independent synthetic control over the critical temperature and rubber modulus. Our present research is focusing on novel schemes to trigger the actuation process that will be amenable to surgical procedures.

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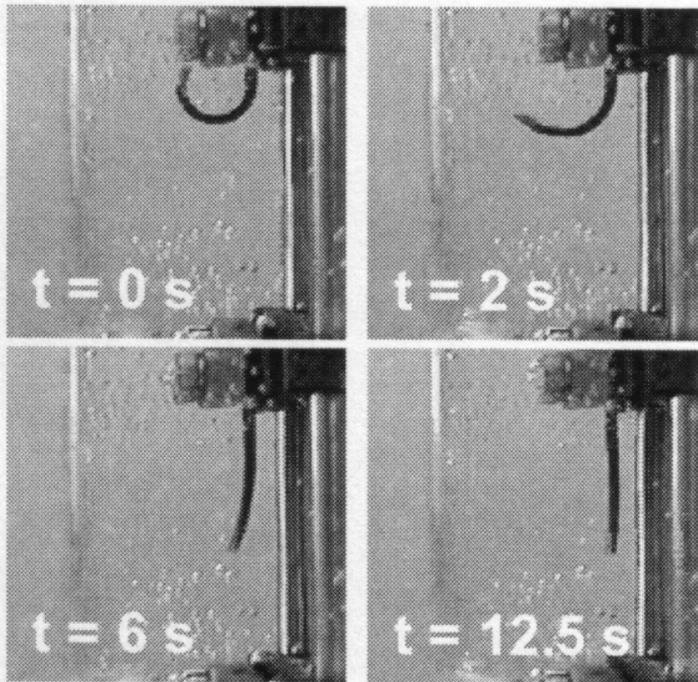12. T. Duerig, A. Pelton, and D. Stockel, *Materials Science and Engineering*, **A273–275**, 149–160 (1999).

Fig. 5. Strain recovery of crosslinked MMA/BMA/TEGDMA
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