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PAPER

Environmental effects on mechanochemical activation of spiropyran in linear PMMA†

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Mechanophore-linked linear poly(methyl methacrylate) (PMMA) was synthesized using bisfunctionalized spiropyran (SP) as an atom transfer radical polymerization initiator. The resulting polymer had a T_g of 127 °C and molecular weight greater than 250 kDa. SP-cleavage experiments confirmed the incorporation of SP molecules approximately into the center of the polymer chain. Force-induced reaction of the SP species into a colored, fluorescent merocyanine (MC) form was investigated over a range of environmental conditions by monitoring color change or full field fluorescence during tensile loading. Activation of this glassy polymer was observed in a temperature range of 90–105 °C. At higher temperatures, approaching T_g , deformation was dominated by viscous flow at very low applied stress with no activation. At lower temperatures, brittle failure preceded activation unless the polymer was plasticized by exposure to methanol. Mechanically induced activation of SP in plasticized PMMA at room temperature (22 °C) was achieved at a critical strain (ca. 10%) substantially below that required in previous systems.

Introduction

Chemical reactions are traditionally driven by heat, light, catalysis, or electric potential. However, mechanical force can also alter the pathway for chemical reactions. Mechanochemical processes are abundant in nature, both in chemically induced force (e.g. ATP to force in kinesin motors),¹ or force affecting biochemistry (cell growth, wound healing, and regeneration).² Synthetic mechanochemistry is also well established in the polymer literature. Many processes are known to cause cleavage of covalent bonds in polymer chains, ranging from cold-working rubber³ to polymer scission by sonication in solution.^{4,5}

Recent work in polymer mechanochemistry has focused on development of molecular species, referred to as mechanophores, which undergo force-induced reactions at specific bonds.^{6–15} Hickenboth *et al.* demonstrated ring opening of benzocyclobutene linked into poly(ethylene glycol) chains in solution, driven by the acoustic force generated by sonication.⁶ The directional nature of mechanical force drives the reaction pathway to only

one of the isomeric products.¹⁶ Potisek *et al.* achieved ring opening of polymer-linked spiropyran (SP) in solution, marked by a change in color and fluorescence signal.⁷ More recently, sonication has been used to demonstrate mechanophores with potential for radical formation⁸ and catalysis.^{9–11}

In the solid state, mechanochemical reactivity of SP has been shown in a number of polymers.^{17,18} SP is a well characterized molecule which undergoes a reversible 6- π electrocyclic ring opening reaction to a merocyanine (MC) form. This molecule is thermochromic and photochromic. Irradiation with light in the visible range drives equilibrium to the SP form, while UV light promotes the MC form.¹⁹ The MC species is of interest because it is vibrantly colored and fluorescent. When incorporated into a bulk polymer, force can be transmitted across the spiro bond of the SP molecule, reducing the barrier for electrocyclic ring-opening.¹⁶ Conversion to the MC form occurs when the strain on the weak C–O spiro bond reaches a critical level.¹⁷

So far SP has been incorporated into elastomeric or ductile polymers such as linear poly(methyl acrylate) (PMA) or polyurethane (PU). SP activation in these polymers occurs at relatively large deformations, on the order of hundreds of percent strain.^{17,18} Here we investigate the incorporation of SP into a linear engineering polymer, poly(methyl methacrylate) (PMMA), with the goal of imparting higher force to the mechanophore at lower strains, and achieving low-strain activation of SP. The linear PMMA has a relatively high glass transition temperature and exhibits brittle fracture at room temperature. At higher temperatures, approaching T_g , the yield stress decreases and PMMA exhibits the ability to be drawn.^{20,21}

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The glass transition temperature of PMMA can also be reduced by plasticizing with a dilute concentration of solvent, allowing yielding at lower temperatures.^{22–24} In this work, we exploit the ductile response at high temperature or after plasticizing to achieve activation in SP-linked PMMA.

Experimental

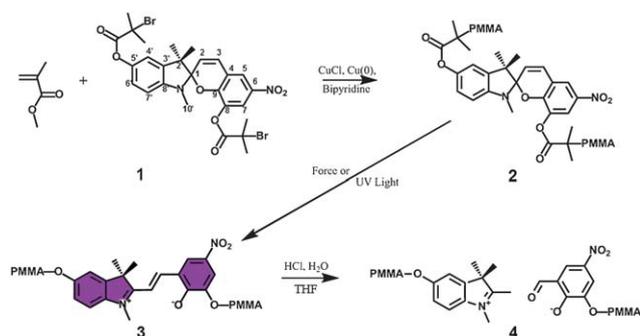
Polymer synthesis

An atom transfer radical polymerization (ATRP) reaction was used to synthesize PMMA based on the methods described by Matyjaszewski²⁵ and further studied by Wang *et al.*²⁶ Copper powder (99%), CuCl ($\geq 99\%$), and 2,2'-bipyridine (BPY) ($\geq 99\%$) were purchased from Sigma-Aldrich and used as received. Plain PMMA was synthesized using methyl-2-bromopropionate as an initiator. Mechanochemically active polymer was initiated by bisfunctional α -bromo ester spiroopyran, which was synthesized *via* the methods outlined by Potisek *et al.*^{7,17} Scheme 1 depicts the method for polymerization of methyl methacrylate (MMA) with an SP initiator (**1**). Positions 5' and 8 were chosen as the attachment points on the SP mechanophore since this configuration is known to transmit force across the SP C–O spiro bond.^{7,17,18} A difunctional SP control was also prepared as reported previously.¹⁷ ATRP was then used to link polymer chains to only one side of the spiro junction, at the 5' and 10' positions. This placement allowed the transfer of force to the SP, but not across the relevant C–O bond in the spiro junction.

Solid reactants were weighed to molar proportions of 1 : 1 : 2 : 2 in terms of SP : CuCl : Cu(0) : BPY. All reactants and a stir bar were added to a dried flask under N₂ atmosphere. MMA was added in a proportion calculated based on the desired molecular weight. A 1 : 1 proportion, with respect to MMA, of acetonitrile was introduced as a solvent. The reaction vessel was then subjected to three freeze–pump–thaw cycles in order to remove water vapor and oxygen and introduce a N₂ atmosphere. The vessel was held in an oil bath at 70 °C for 24 hours while stirring. The resulting polymer was dissolved in tetrahydrofuran, followed by filtering through silica and basic alumina powders. The polymer was precipitated in methanol and dried under vacuum for 24 hours.

Characterization

Gel permeation chromatography (GPC) was used to characterize the molecular weight of the polymers. Measurements were



Scheme 1 Synthesis, ring-opening and hydrolytic cleavage of mechanochemically active SP-linked PMMA.

performed in THF at 30 °C with a Waters 515 HPLC pump and Viscotek TDA 3000 detector. Chemical cleavage of SP subspecies was performed *via* the method introduced by Stafforst²⁷ and outlined in Scheme 1. A 100 mg polymer sample was dissolved in 2 mL THF, and 0.5 mL 1 M HCl was added, and the solution was irradiated with UV light to keep the active species in the open MC form **3**, which was hydrolyzed to species **4**. The solution was then refiltered by the method described above and GPC was run on the resulting polymer to measure molecular weights after cleavage.

The glass transition temperature was determined by both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Mettler-Toledo model DSC821 and TA Instruments RSA3 were used, respectively with a temperature ramp of 3 °C min⁻¹.

Sample molding

Polymer powder was molded into tensile dog-bone samples *via* compression molding in a closed mold at approximately 75% relative humidity (RH). A pressure of 200 psi was applied to the mold at a temperature of 160 °C, for 10 minutes. The mold was then quenched in water. Samples were polished before testing. Sample dimensions are shown in the ESI†. Thermal energy from molding at high temperature (160 °C) led to some ring opening. Molded samples exhibited a red or orange appearance, indicating a combination of the clear/yellow SP form and the purple MC form. Although visible spectrum light is known to drive the MC isomer to the SP form,¹⁹ illuminating with 530 nm light at room temperature (~22 °C) did not effectively revert all species to the SP form. Irradiation at higher temperature (100 °C) did allow reversion of MC to SP. SP-linked polymer, held at 100 °C, was irradiated with a 530 nm diode lamp for 24 hours to drive the active species to the closed SP form **2**.

Mechanical testing

Dog-bone specimens were tested in tension over a range of temperatures, using the DMA environmental chamber to control the temperature. Prior to testing, samples were equilibrated for 5 minutes at the desired test temperature under a small tensile preload (0.1 N). The samples were then loaded in displacement control at a rate of 5 μm s⁻¹. Initial gauge lengths varied between 5 and 7 mm.

Additionally, samples were plasticized by soaking in solvent in order to reduce *T_g*. Dibutyl phthalate, methanol and ethanol are documented plasticizers for PMMA.^{22–24} Of these three solvents, methanol diffused most effectively into compression molded PMMA. Samples were soaked in methanol (MeOH) for approximately 48 hours. Samples mass was measured prior to soaking in MeOH, and again before testing. Solvent uptake of 15–20 wt% was observed. At this MeOH content, mechanical behavior was similar to unplasticized PMMA at 90 °C. Plasticized tensile specimens were tested at room temperature (RT) with a custom-built load frame at a displacement rate of 5 μm s⁻¹.

A bi-directional screw-driven rail table allowed tensile testing of samples with both grips translating simultaneously and in opposite directions, keeping the center of mass of the sample stationary. The load was measured *via* a 220 N capacity

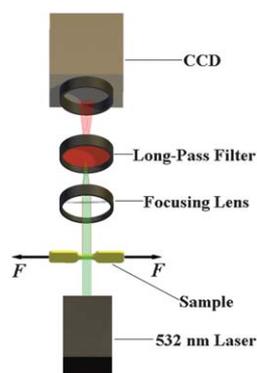


Fig. 1 Experimental apparatus for *in situ* fluorescence imaging of plasticized tensile specimens.

Honeywell Sensotech load cell. Fluorescence imaging was accomplished with a 532 nm diode laser (CrystaLaser) to excite the sample, focusing lenses, and a long pass filter (>575 nm) to transmit only fluorescence, followed by an AVT Stingray model F-125C CCD detector (Fig. 1). The fluorescence intensity was defined as the red channel intensity of the CCD averaged over the entire sample. Laser power and CCD exposure settings were kept constant between all tests.

Results and discussion

Physical properties

PMMA was synthesized using SP as an ATRP initiator. As summarized in Table 1, the resulting molecular weights were as high as 260 kDa (polystyrene standardized). Polydispersity indices (PDIs) varied from 1.4–2.1. Chemical cleavage²⁷ of SP reduced the molecular weight of active material roughly in half, while the PDI was not substantially increased, implying that SP was centrally located in the PMMA chains (Scheme 1). Plain PMMA and difunctional SP-linked control PMMA showed negligible change in molecular weight under SP cleavage conditions, thus the polymer itself was unaffected by SP cleavage conditions.

The glass transition temperatures of the three types of polymer were determined by DSC and DMA testing, and results are listed in Table 1. DSC and DMA traces are included in the ESI†. T_g values calculated by the two methods agreed closely. The glass transition occurred within a narrow range (~ 3 °C) for plain, active and difunctional SP-linked control PMMA, indicating that the presence of the mechanophore had a negligible effect on the thermal transition of the polymer.

Effect of temperature on mechanical activation

The stress–strain response of the active PMMA is shown in Fig. 2a over a range of temperatures from 22 °C to 120 °C. Specimens tested in tension at 22 °C and 80 °C failed in a brittle manner ($\epsilon_{ult} < 10\%$). No color change was detected in these specimens prior to failure, and fluorescence imaging indicated no measurable activation at the fracture surface. At higher temperatures, 90 °C and 105 °C, the yield stress dropped

Table 1 Physical properties of as-synthesized and SP-cleaved PMMA

PMMA type	Plain	Active	Difunctional SP-linked control
$T_g/^\circ\text{C}$	126	127	129
Synthesized M_N/kDa	78	260	185
SP cleaved M_N/kDa	82	123	181
Synthesized PDI	1.5	2.0	2.1
SP cleaved PDI	1.5	2.0	2.0

significantly and substantial plastic flow was observed. Visible evidence (purple color) of the mechanochemical reaction was detected at *ca.* 10% applied strain in samples tested at 90 °C, appearing shortly after yielding of the polymer. Color change was localized and coincided with drawing regions of the gauge section. As strain increased, the color became more vibrant in the drawn section of specimens tested at 90 °C and 105 °C. Qualitatively, samples tested at 90 °C exhibited more intense color change than at 105 °C, presumably due to higher stress in the sample during drawing. At temperature of 120 °C, just below the glass transition, deformation was dominated by viscous flow. Samples deformed over 100% strain at low stress and no color change was observed. Representative images of samples tested at various temperatures are included in Fig. 2b.

Control samples were mechanically tested at 90 °C. Both plain PMMA (without SP incorporated) and difunctional SP-linked control PMMA behaved mechanically similar to active polymer, with no significant variation in yield stress, yield strain, or strain at failure. Difunctional SP-linked control samples tested at 90 °C did not exhibit a color change, indicating that the color change in active samples was due to mechanically induced opening of SP, and not thermal activation. Mechanical properties and optical images of controls are included in the ESI†.

Effect of plasticizer on mechanical activation

As molded PMMA specimens were exposed to methanol to increase the polymer mobility at room temperature. Samples with 15–20% MeOH uptake by mass exhibited similar mechanical behavior at RT compared to unplasticized samples at 90 °C. Samples with <15 wt% MeOH uptake exhibited brittle failure and no activation at RT. Samples with >20 wt% MeOH uptake showed significant nonuniformity and inconsistent mechanical behavior. RT testing of plasticized PMMA allowed for *in situ* fluorescence imaging; a feature which was prevented by the thermal control chamber used for high temperature testing of unplasticized polymer.

Fluorometry in the visible spectrum (see ESI† for spectra) showed little fluorescence signal for untested active samples, indicating that the mechanophore is predominantly in the SP form. However, mechanically activated samples exhibit strong fluorescence, with broad excitation and emission bands peaking at 560 nm and 620 nm, respectively. These peaks correspond to the MC form of the mechanophore.

Representative stress–strain and fluorescence intensity data are plotted in Fig. 3 for methanol soaked (~ 15 wt% uptake) samples of plain PMMA, active PMMA, and difunctional SP-linked control PMMA. All three polymers had similar stress–

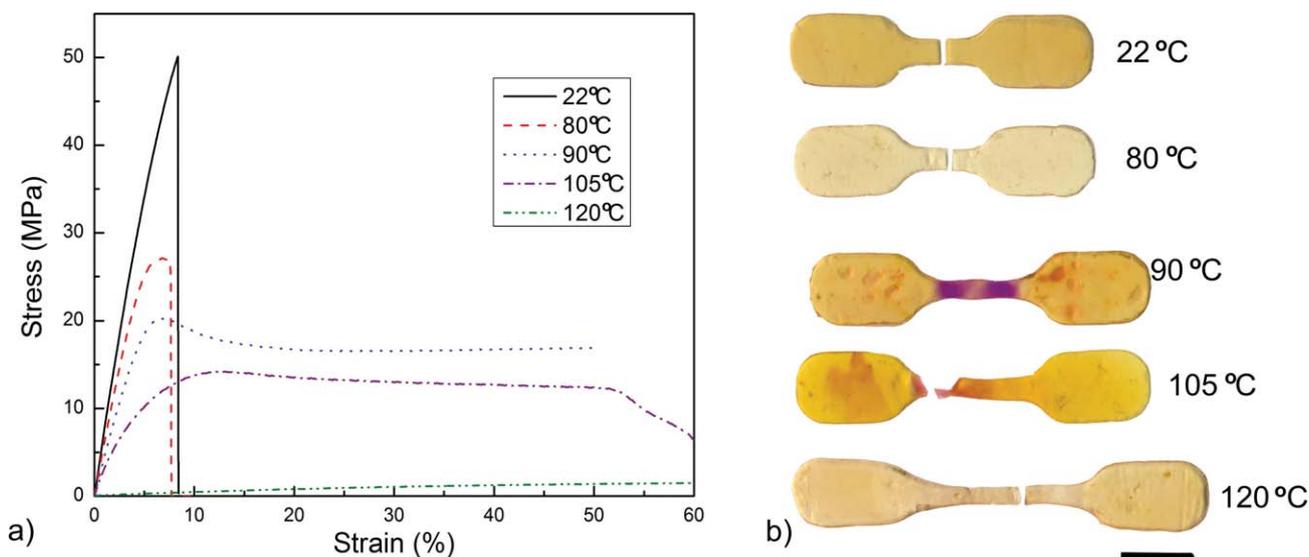


Fig. 2 Effect of temperature on mechanochemical behavior of active PMMA. (a) Mechanical response at various testing temperatures. (b) Optical images of samples after testing. Scale bar = 6 mm.

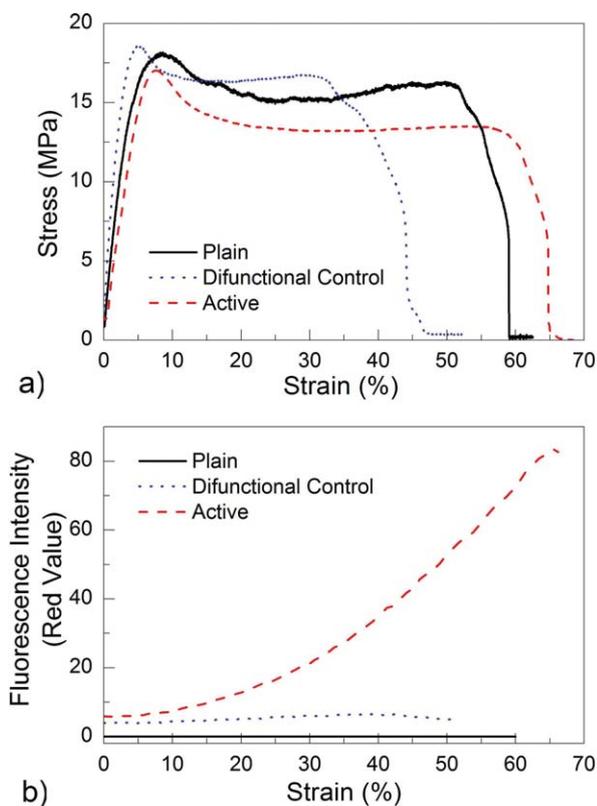


Fig. 3 Mechanical and fluorescent response of MeOH plasticized (~15 wt%) PMMA. (a) Mechanical response at room temperature. (b) Corresponding fluorescence intensity from full field fluorescence imaging during mechanical testing.

strain responses, with a significant region of drawing prior to failure. However, only the active PMMA exhibited a substantial increase in fluorescence with mechanical loading. Onset of activation at room temperature was observed below 10% strain in all

plasticized active PMMA samples, just after polymer yield. The fluorescence intensity continued to increase during drawing until failure. Plain PMMA showed no measurable fluorescence intensity before or after loading, confirming that any fluorescence is due to the incorporation of SP. A small amount of fluorescence was present in the active and difunctional SP-linked control PMMA prior to testing due to a small inherent fluorescence for the closed SP form, or trace remaining amounts of MC. Only a slight change in the difunctional SP-linked control fluorescence intensity was observed during loading, most likely due to increased scattering as the specimen deforms.

Discussion

SP-linked PMMA undergoes a force-driven reaction of SP to the MC form. Activation of the SP was achieved under conditions where PMMA has sufficient mobility to yield and draw at moderate stress levels, prior to failure. We hypothesize that the mobility afforded at elevated temperatures allows for rearrangement (in this case planarization) of the SP molecule and alignment of the polymer backbone and SP in the direction of the applied force, enhancing the transfer of force across the mechanophore. No activation occurred if the polymer was too viscous and failed in a brittle manner without significant polymer flow. At temperatures near and above T_g , the force across the mechanophore is insufficient to initiate activation. A similar range of temperatures at which activation can occur may translate to other mechanophore-linked polymers in the bulk.

Mechanochemical activation of SP-linked PMMA was demonstrated at far lower strains (below 10%) than in previous reported systems. For example, lightly cross-linked PMMA in which SP acts as a cross-linker has been shown to require a minimum of 20% strain for activation.¹⁷ The onset of activation for the linear PMMA reported here occurred at strain levels (*ca.* 10%) over an order of magnitude lower in comparison with other linear, moldable polymers.^{17,18}

Conclusions

A color changing SP mechanophore was successfully incorporated into linear PMMA with a T_g of 127 °C. This system demonstrates mechanically induced chemical activation, which is strongly dependent on polymer mobility, controlled either thermally or using a plasticizing solvent. A temperature window (90–105 °C) was observed at which activation occurred—a characteristic which other mechanochemical systems may share. Activation in PMMA occurred post-yield and was localized coincident with drawing regions. Plasticizing with 15–20 wt% MeOH allows drawing and activation at room temperature. The onset of activation was observed at *ca.* 10% strain in linear SP-linked PMMA.

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