

Supporting Information

Enabling Room-Temperature Mechanochromic Activation in a Glassy Polymer: Synthesis and Characterization of Spiropyran Polycarbonate

Yuval Vidavsky,^{†,||} Steven J. Yang,^{†,||} Brooks A. Abel,[‡] Iris Agami,[§] Charles E. Diesendruck,[§] Geoffrey W. Coates,[‡] and Meredith N. Silberstein^{*,†}

^{||}Both authors contributed equally to this manuscript

[†]Sibley School of Mechanical and Aerospace Engineering, and [§]Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301, United States

[‡]Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 3200003, Israel

Table of Contents

General	2
Simultaneous Tensile Test and Fluorescence Measurement.....	3
Simultaneous Tensile Test and Fluorescence Analysis Methods.....	3
Dihydroxyspiropyran Synthesis	5
¹ H and ¹³ C NMR Spectra of Dihydroxyspiropyran.....	5
Triphosgene Reaction Mechanism	6
SP-BPA-PC Synthesis.....	7
Material Processing	8
Effect of Reaction Conditions on iMC formation During SP-BPA Copolymerization	9
Calculated pK _a Values for the Conjugate Phenols	10
¹ H and ¹³ C NMR Spectra of SP-BPA-PC	10
Thermal Properties: SP-BPA-PC vs. Commercial PC	11
Mechanical Properties: SP-BPA-PC vs. Commercial PC	12
SP-MC Isomerization in Solid State: SP-BPA-PC vs. Unattached SP	12
Polymer Chain Relaxation Timescale	14
Film Lamination and Beam Bending	15
Digital Image Correlation (DIC) for Beam Bending	17
Crosshead Strain vs. Digital Image Correlation (DIC) for Tensile Test.....	18
Film Preparation Setup.....	18
References	19

General

All reactions performed using triphosgene were conducted in a fume hood since triphosgene decomposes to phosgene on heating and upon reaction with moisture.

Unless otherwise noted, solvents and reagents were purchased and used without further purification. Dihydroxyspiropyran synthesis and polycarbonate polymerizations were carried out under inert atmosphere. The SP-BPA-PC ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 500 MHz instrument at room temperature using CDCl_3 as the solvent. Gel permeation chromatography (GPC) analyses were carried out using an Agilent 1260 Infinity GPC System equipped with an Agilent 1260 Infinity autosampler and a refractive index detector. The Agilent GPC system was equipped with two Agilent PolyPore columns (5 micron, 4.6 mm ID) which were eluted with THF at 30 °C at 0.3 mL/min and calibrated using monodisperse polystyrene standards. Fluorescence spectra were obtained using an Edinburgh FLS1000 spectrometer with monochromic 532 nm excitation light. CH_2Cl_2 used for polymerizations was sparged vigorously with nitrogen for 40 minutes before passing through two packed columns of neutral alumina under nitrogen pressure. Bisphenol A (Alfa Aesar) was initially recrystallized from a mixture of water/acetic acid followed by a second recrystallization from toluene. The recrystallized BPA was dried under vacuum at 50 °C before use. Triphosgene was purchased from Oakwood Chemical. Triethylamine was purchased from Millipore-Sigma. 5-hydroxy-1,2,3,3-tetramethyl-3*H*-indolium iodide (**1**) and 2,3-dihydroxy-5-nitro-benzaldehyde (**2**) were synthesized according to literature procedures.^{1,2} Differential scanning calorimetry (DSC) measurements of polymer samples were performed on a Mettler-Toledo Polymer DSC instrument equipped with a chiller and an autosampler. Samples were prepared in aluminum pans. All polycarbonates were analyzed using the following heating program: -70 °C to 200 °C at 25 °C/min, 200 °C to -70 °C

at 10 °C/min, and –70 °C to 200 °C at 25 °C/min. Data were processed using StarE software. All reported glass transition temperatures were observed on the second heating cycle.

Simultaneous Tensile Test and Fluorescence Measurement

Tensile tests were performed on a Zwick-Roell Z010 system with a 500 N capacity load cell (X-Force HP, Zwick-Roell). Constant strain rate, cyclic, and stress relaxation tests, were performed with displacement control using engineering strain rates and assuming an effective gage length of 19.54 mm. Both the cyclic and stress relaxation tests were conducted at an engineering strain rate of 0.001 s⁻¹. For the cyclic test, change in crosshead direction is specified by displacement when loaded and by force (0.1 N) when unloaded. The test measuring the persistence of SP activation begins with displacement control at a strain rate of 0.001 s⁻¹ during loading and unloading followed by force control at 0.02 N for 2 h.

During tensile tests, SP to MC conversion was measured by MC fluorescence intensity. Fluorescence was excited by a 4.5 mW 532 nm green laser (CPS532, Thorlabs). The laser was diffused using a tophat engineered diffuser (ED1-S20-MD, Thorlabs) projecting a ~110 x 110 mm uniform intensity light pattern resulting in irradiance of ~3.7 W/m² on the specimen. Images of the resulting fluorescence were photographed using a monochrome CCD camera (Exi-Blue, Q-Imaging) and a 75 mm lens at an aperture of f/2.8 (M7528-MP, Computar) with 1 s exposures. A 575 nm longpass filter (84-751, Edmund Optics) was placed in front of the camera lens to capture the MC fluorescence peak while blocking the excitation light. To minimize photobleaching, a servomotor shutter blocks the laser source between images.

Simultaneous Tensile Test and Fluorescence Analysis Methods

Stress and strain were calculated from force and crosshead displacement recorded during tensile tests. True strain is given by $\epsilon_{true} = \ln(L/L_0)$ where L_0 is the initial length with a value of 19.54

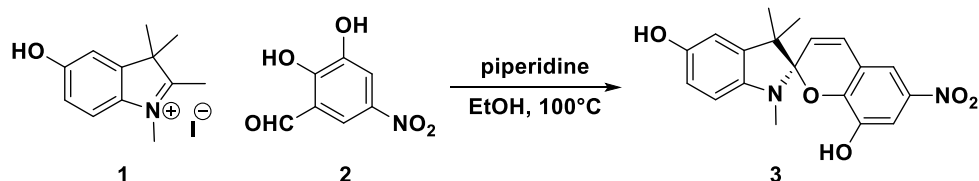
mm obtained by linear finite element simulation of the tensile specimen geometry. The crosshead-based strain measurement was verified against digital image correlation strain measurement (Figure S15). True stress is given by $\sigma_{true} = F/A$ where F is the recorded force and A is the deformed specimen cross-sectional area. The cross-sectional area is determined by approximating the material as incompressible (a typical assumption for plastic deformation) and is given by $A = A_0(L_0/L)$ where A_0 is the initial specimen cross-sectional area. Elastic moduli were determined by linear fit of the stress-strain curve between the 0 and 0.02 strain. Yield strengths were determined by the 0.5% offset method.

For each fluorescence image, a single intensity value was obtained by averaging the intensity values over a 1.5 x 2.5 mm region located at the centroid of the specimen using the software Fiji.¹ Throughout this paper, a normalized and thickness corrected fluorescence measure at each point in time referred to as Fluorescence Change is defined as:

$$\text{Fluorescence Change}(t) = \frac{I(t) - I(t = 0)}{I(t = 0) \times \left(\frac{L}{L_0}\right)^{-0.5}}$$

Where $I(t)$ is the average intensity value in the centroid region at a given strain, $I(t = 0)$ is the average intensity value at zero strain, and $(L/L_0)^{-0.5}$ is the change in specimen thickness.

Dihydroxyspiropyran Synthesis



Dihydroxyspiropyran **3** was synthesized according to a literature procedure³

1 (400 mg, 1.26 mmol, 1 equiv), **2** (231 mg, 1.26 mmol, 1 equiv), and piperidine (0.25 mL, 2.5 mmol, 2.1 equiv) were dissolved in EtOH (12.4 mL) and heated to reflux. After 3 h, the reaction mixture was cooled to room temperature and the resulting solids isolated by vacuum filtration,, washed with EtOH, and dried under high vacuum to yield **3** (410 mg, 0.760 mmol, 91.8%) as a dark green powder. ¹H NMR (400 MHz, DMSO-d₆, DCl): δ 8.66 (s, 1H), 8.28 (d, *J* = 16.5 Hz, 1H), 7.78 (dd, *J* = 24.8, 10.4 Hz, 3H), 7.24 (s, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 4.10 (s, 3H), 1.69 (s, 6H). ¹³C NMR (100 MHz, DMSO-d₆, DCl): δ 178.56, 160.03, 153.41, 148.30, 146.18, 143.18, 140.23, 134.07, 121.11, 117.63, 116.98, 116.04, 115.40, 110.02, 108.94, 57.07, 52.06, 35.03, 25.95.

¹H and ¹³C NMR Spectra of Dihydroxyspiropyran

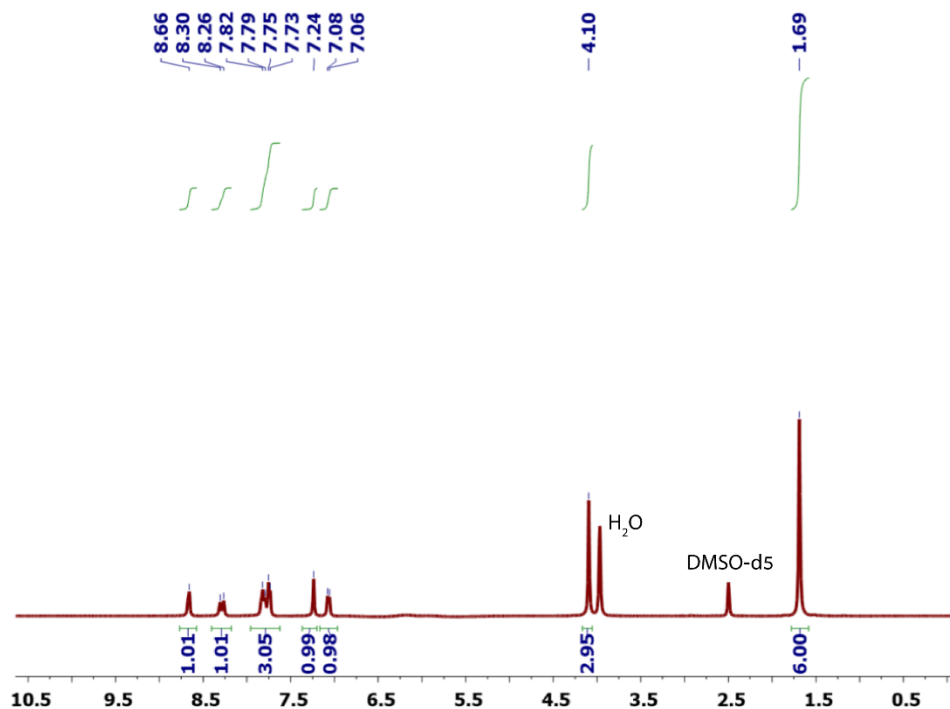


Figure S1. ¹H NMR spectrum of Dihydroxyspiropyran

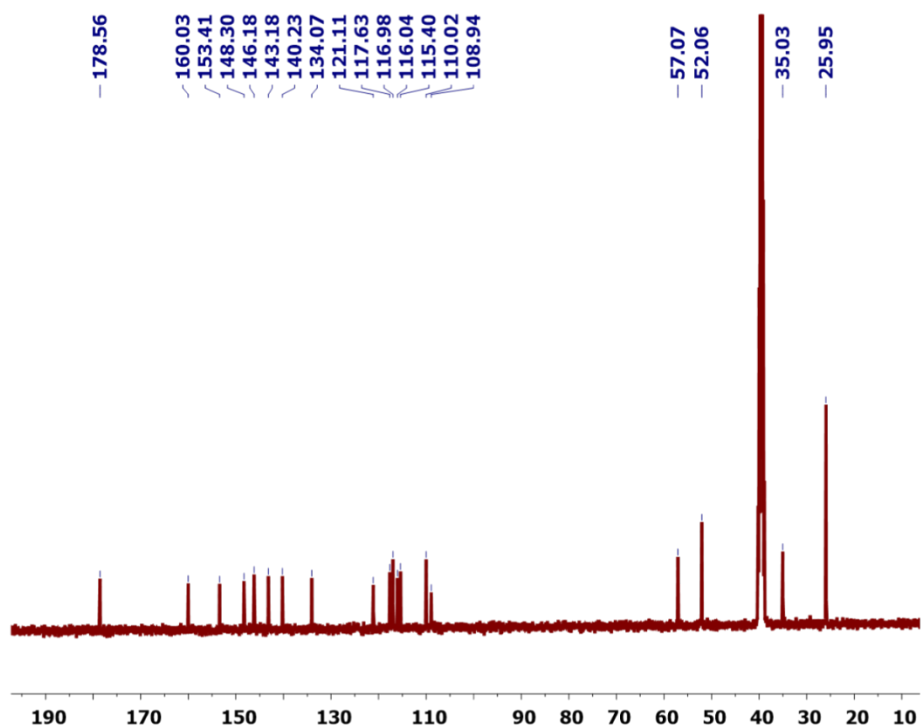


Figure S2. ^{13}C NMR spectrum of Dihydroxyspiropyran

Triphosgene Reaction Mechanism⁴

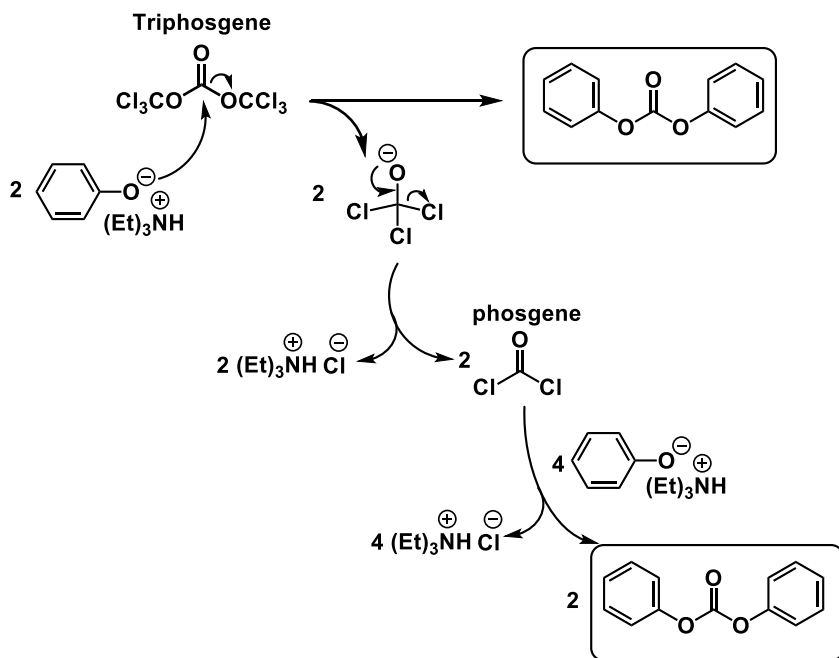


Figure S3. Mechanism for the reaction of triphosgene with phenoxides. Triphosgene reacts with two phenoxides to produce diphenyl carbonate while generating two trichloro-methoxides. Each trichloro-methoxide turns to phosgene while releasing chloride anions. Each phosgene then reacts with two additional phenoxides to produce a total of three diphenyl-carbonates.

SP-BPA-PC Synthesis

All the work with triphosgene was performed in a fume hood, since triphosgene decomposes to phosgene on heating and upon reaction with moisture.

Phosgene-Starved Conditions

Recrystallized Bisphenol A (39.3 g, 172 mmol), triethylamine (59.0 ml, 420 mmol), and dihydroxyspiropyran (73 mg, 0.20 mmol) were combined in dry CH₂Cl₂ (500 ml) in round bottom flask containing a magnetic stir bar. The mixture was cooled in an ice bath and a solution of triphosgene (17.0 g, 57.0 mmol) in dry CH₂Cl₂ (100 ml) was added dropwise (over approximately 4 h to ensure phenol excess) while irradiating the reaction with white light (Bescor LED-500K). After the addition of triphosgene was completed, the reaction mixture was stirred for an additional 2 h at 0 °C. Reaction progress via change in molecular weight was monitored by GPC analysis of aliquots taken during the reaction. Prior to GPC analysis, the polymer samples were precipitated from a 1:1 (v:v) water/acetone mixture (5mL), the solids isolated by vacuum filtration, washed with acetone, and dried in vacuo before redissolving in THF at a concentration of 1 mg/mL. Additional quantities of triphosgene ($[\text{phosgene}] = \frac{1}{2}[\text{phenol}]_t$) were added according to the concentration of remaining phenol end-groups $[\text{phenol}]_t$ calculated from the number average molecular weight determined by GPC. After each addition of triphosgene, an aliquot was taken, and the molecular weight was evaluated by GPC analysis. This process was repeated until the number average molecular weight of the synthesized SP-BPA-PC was above 40 kDa. On reaching the desired molecular weight, SP-BPA-PC was purified by precipitation from a 1:1 (v:v) acetone/water mixture (1 L), filtered on Buchner funnel, washed three times with acetone (300 ml), and dried under vacuum for 24 h to obtain 40.3 g (92% yield) of an off-white powder. ¹H NMR (500 MHz, CDCl₃): δ 7.27-7.28 (4H), 7.18-7.20 (4H), 1.70 (6H). ¹³C NMR (125 MHz, CD₃Cl): δ 152.16, 148.96, 148.26, 127.94, 120.34, 42.58, 30.95. $M_n = 49.0 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.34. $T_g = 156.3 \text{ }^\circ\text{C}$. The

resulting coarse powder was dissolved in CH₂Cl₂ (300 mL) and the solution was filtered through sintered glass to remove any macroscopic impurities. The solvent was removed under a stream of nitrogen before being processed (see below).

Excess Phosgene Conditions

Recrystallized Bisphenol A (1.42 g, 6.22 mmol), triethylamine (2.09 ml, 15.0 mmol), and dihydroxyspiropyran (1 mg, 0.003 mmol) were combined in CH₂Cl₂ (20 ml) in a round bottom flask containing a magnetic stir bar. A solution of triphosgene (0.68 g, 2.3 mmol, 1.1 equiv. phosgene) in dry CH₂Cl₂ (4 ml) was added via a syringe. The reaction mixture was stirred for 4 hours at room temperature. Reaction progress via change in molecular weight was monitored by GPC analysis of aliquots taken during the reaction. Prior to GPC analysis, the polymer samples were precipitated from a 1:1 (v:v) water/acetone mixture (5mL), the solids isolated by vacuum filtration, washed with acetone, and dried in vacuo before redissolving in THF at a concentration of 1 mg/mL. SP-BPA-PC was purified by precipitation from a 1:1 (v:v) acetone/water mixture (100 ml), filtered using a Buchner funnel, washed three times with acetone (30 ml), and dried under vacuum for 24 h to obtain 1.32 g (84% yield) of a light pink-orange powder. $M_n = 37.1 \text{ kg} \cdot \text{mol}^{-1}$, $\bar{D} = 1.85$. A solution of the resulting polymer did not exhibit the typical reversible SP-MC photochromic behavior.

Material Processing

SP-BPA-PC films with a thickness of 110 μm ($\pm 6 \mu\text{m}$ SD) were made by dissolving SP-BPA-PC (1.1 g) in CH₂Cl₂ (12 mL) and casting in a flat bottom 95 mm Petri dish. The CH₂Cl₂ was allowed to evaporate at room temperature producing the film. Film uniformity was improved through controlling solvent evaporation by covering the Petri dish with a stainless-steel mesh (80x80 mesh size 0.007" opening, McMaster-Carr) and leveling the dish on a clear leveling table (TrippNT). A

white LED panel was placed under the leveling table to shift the solution equilibrium to SP (Figure S16). Tensile specimens were cut from the film to the ASTM D638 Type V geometry using a die cutter and a hydraulic press (Carver Press). The excess film was dissolved, filtered, and recast.

Effect of Reaction Conditions on iMC formation During SP-BPA Copolymerization

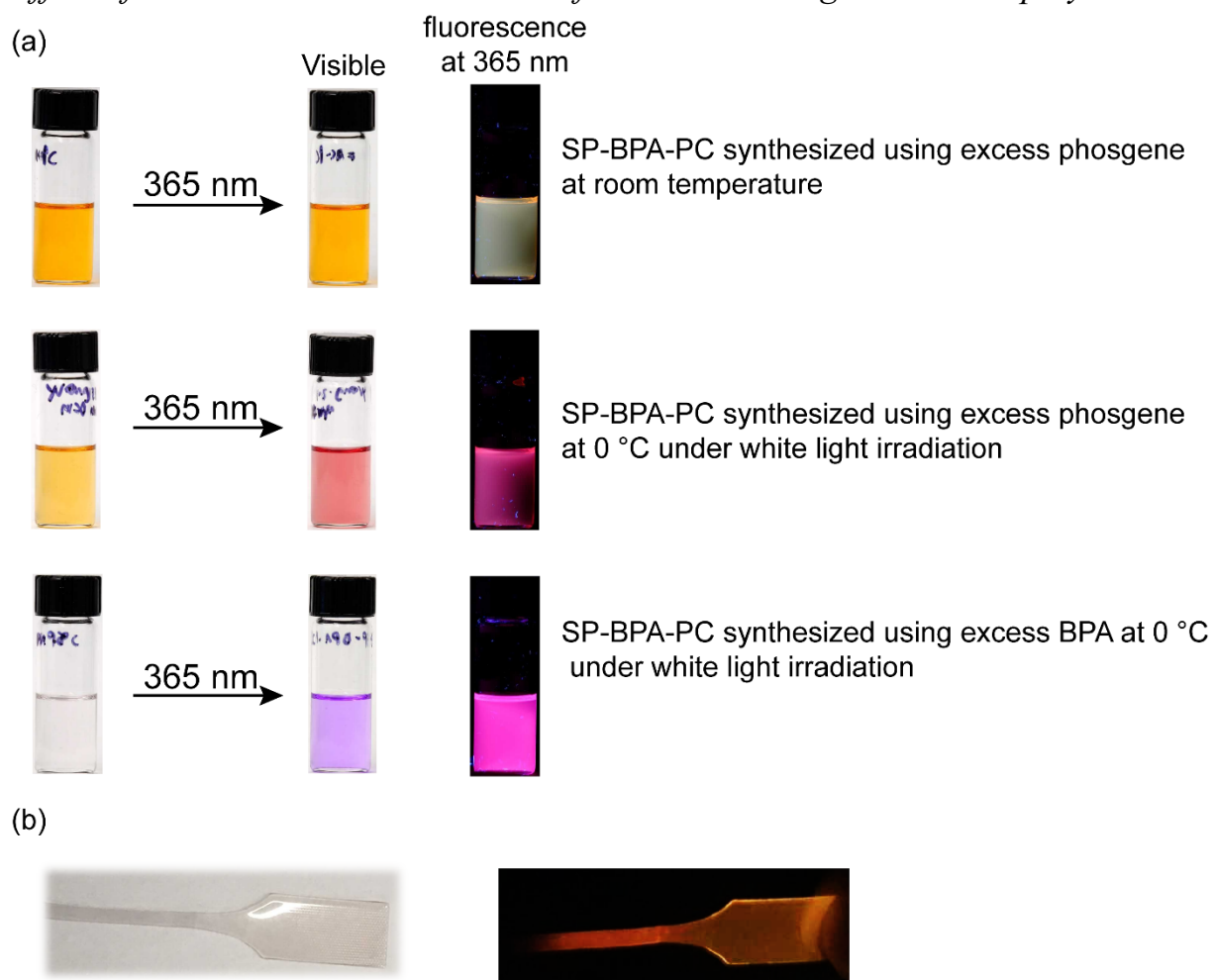


Figure S4. (a) Influence of white light irradiation, temperature, and [phenol]:[triphosgene] stoichiometry on iMC formation. (b) A stretched sample of SP-BPA-PC synthesized using excess phosgene and white light irradiation at 0 °C visualized using visible light (left) and UV fluorescence through a longpass filter (right).

Calculated pK_a Values for the Conjugate Phenols⁵

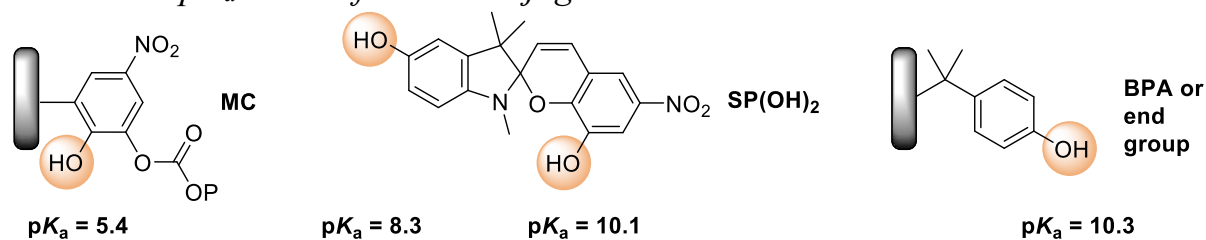


Figure S5. Calculated (ACD/Labs Software) pK_a values for the conjugate phenols of the different phenoxides present in the polycondensation reaction. The MC conjugate phenol exhibits a relatively low pK_a value hence, lower reactivity.

1H and ^{13}C NMR Spectra of SP-BPA-PC

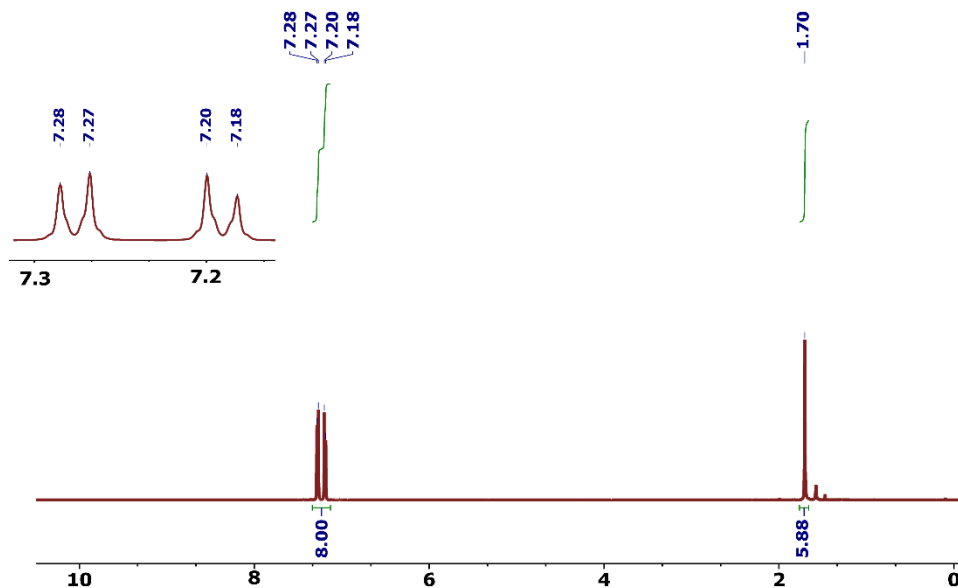


Figure S6. 1H NMR spectrum of high molecular weight SP-BPA-PC.

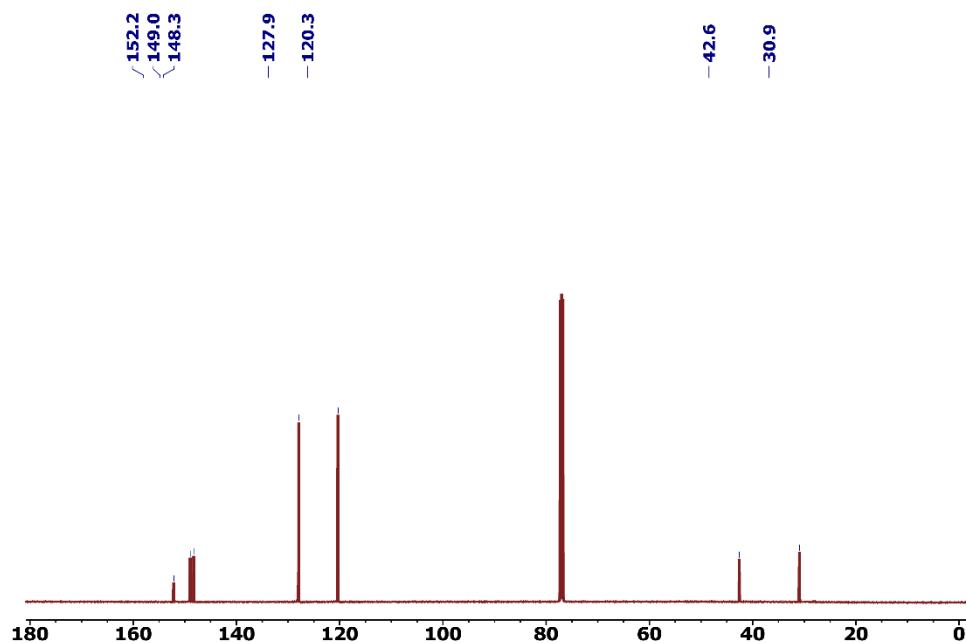


Figure S7. ^{13}C NMR spectrum of high molecular weight SP-BPA-PC.

Thermal Properties: SP-BPA-PC vs. Commercial PC

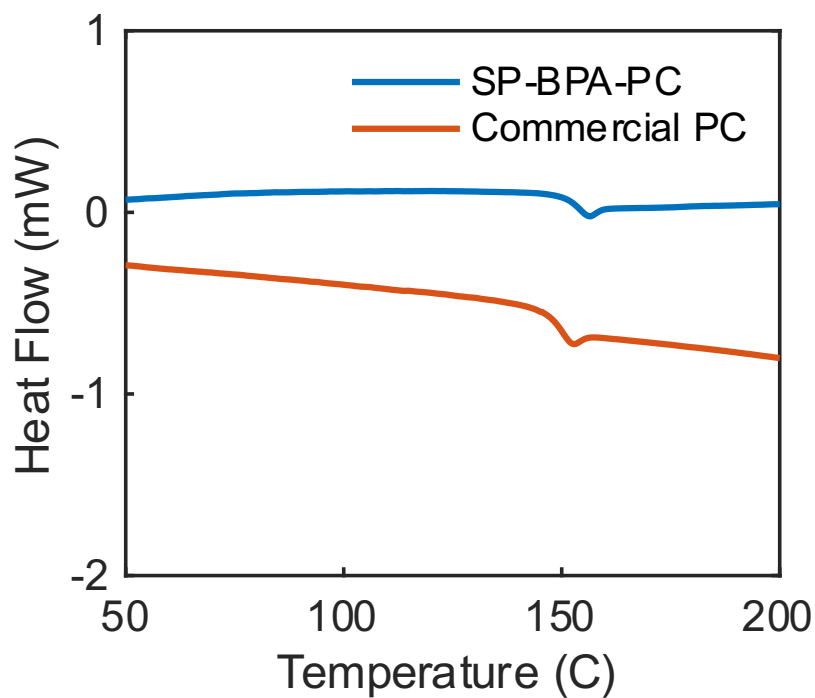


Figure S8. DSC analysis of commercial polycarbonate $T_g = 152.5\text{ }^{\circ}\text{C}$ (red) and SP-BPA-PC $T_g = 156.3\text{ }^{\circ}\text{C}$ (blue).

Mechanical Properties: SP-BPA-PC vs. Commercial PC

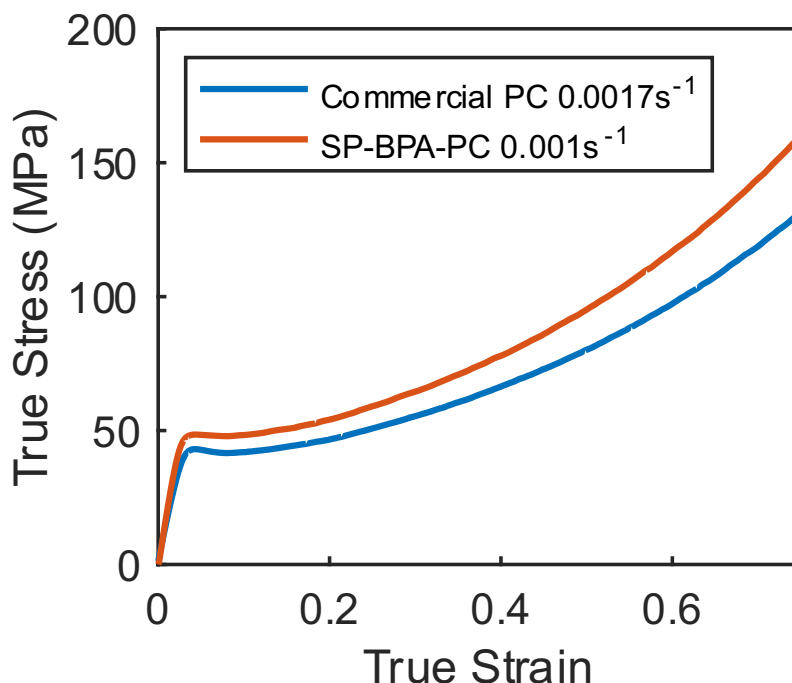


Figure S9. Mechanical properties of SP-BPA-PC (red) vs. commercial BPA-PC (blue)

SP-MC Isomerization in Solid State: SP-BPA-PC vs. Unattached SP

The sample for the unattached SP was prepared by dissolving 1.5 mg (4 mmol) of 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrrolospiran with 1.1 g of commercial BPA-PC in CH_2Cl_2 and processed using the same method described for SP-BPA-PC (see Material Processing).

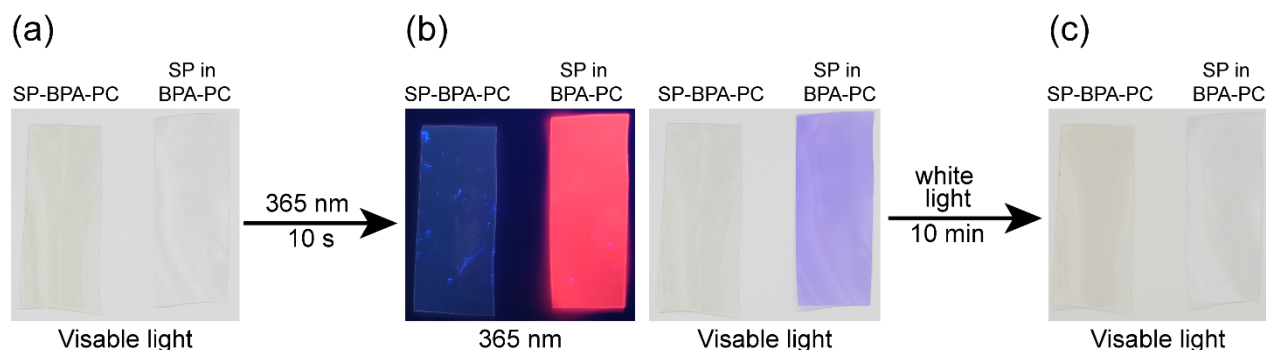


Figure S10. SP-BPA-PC and SP dispersed in commercial BPA-PC before irradiation with UV light (a), after irradiation with UV light for 10 seconds (b), and after irradiation with white light for 10 minutes (c). The non-bonded SP shows the reversible SP-MC isomerization while the bonded SP is unchanged.

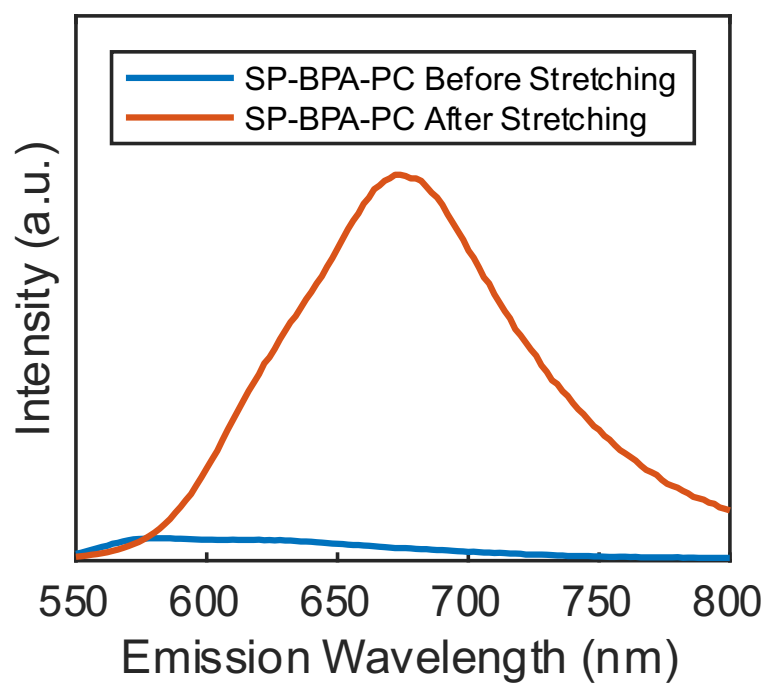


Figure S11. Fluorescence spectra with 532 nm excitation light of SP-BPA-PC before (blue) and after stretching (red).

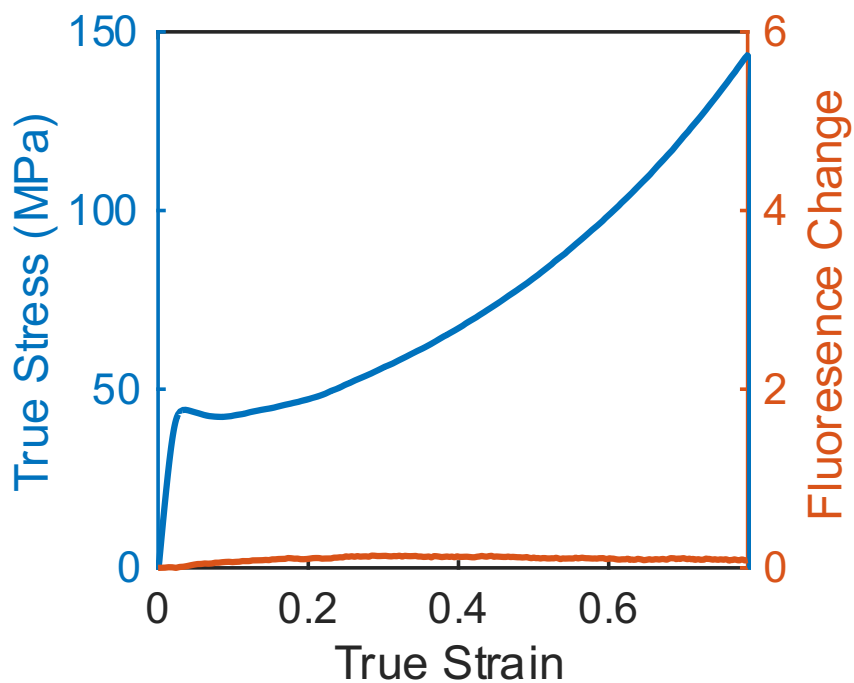


Figure S12. True stress vs strain vs fluorescence change for the dispersed SP in commercial BPA-PC measured at a strain rate of 0.001 s^{-1} .

Polymer Chain Relaxation Timescale

It has been proposed that the reorientation timescale of polymer chains can be measured from the initial rate of stress relaxation after the polymer was deformed and held at a constant strain.^{7,8} Figure S13a shows an experiment where SP-BPA-PC is deformed at a constant strain rate of 0.01 s⁻¹ and then held at constant strain at increments of 0.1 engineering strain. Stress (σ) reduces over time when the material is held at constant strain. Figure S13b is a comparison of the relaxation curves where stress is normalized by the initial stress (σ_0) and time is shifted to the start of the stress relaxation period (t_0). We followed the procedure from Lee *et. al.*⁹ where the relaxation timescale (τ) is given by the inverse of the initial rates shown in Figure S13b. As a function of stress, τ is given by the following equation.

$$\frac{1}{\tau} = -\frac{1}{\sigma} \frac{d\sigma}{dt} \Big|_{t=t_0}$$

The changes of the relaxation timescale (τ) at various strain values (ϵ) is shown in Figure S13c. The relaxation time is found to span from 30 to 70 s.

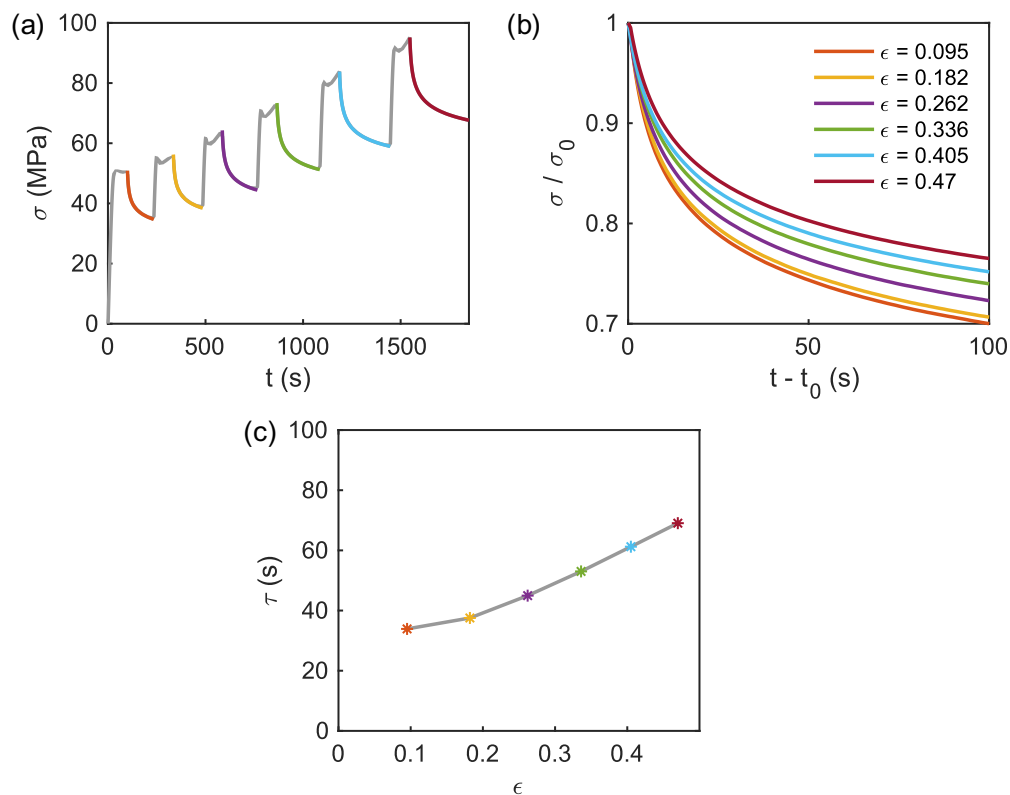


Figure S13. (a) True stress (σ) vs. time (t) for an experiment where SP-BPA-PC is deformed at a rate of 0.01 s^{-1} and then held constant in increments. (b) Stress relaxation response from the data in Figure S13a where stress is normalized by the initial relaxation stress (σ_0) and time is shifted to the start of the relaxation period (t_0). (c) The relaxation timescale (τ) at each strain (ϵ).

Film Lamination and Beam Bending

The SP-BPA-PC film was laminated onto a commercial polycarbonate beam (McMaster-Carr) with a light-cure adhesive (Loctite AA 3103, Henkel). The adhesive was cured for 90 s using a 6 W 365 nm hand lamp (VWR) followed by white LED lamp (Bescor) for 20 min. The beam was bent via four-point bending with a support span of 70 mm and a loading span of 20 mm. The height and width of the beam are 12.7 mm and 25.4 mm respectively. The beam was loaded at 5 mm/min in increments of 2 mm up to 12 mm. At each displacement increment, the test was paused for 60 s to photograph the fluorescence field. Fluorescence was excited by a 6 W 365 nm lamp and captured with a color CMOS camera (XE-2s, Fujifilm) and a tele-macro lens (180 mm f/3.5, Tamron).

Images were taken with 1 s exposures at 3200 ISO, f/3.5 aperture, Fuji Velvia color setting, and 6434 K white balance.⁶ The excitation light was blocked between images. For the resulting images shown in Figure 7b, brightness and contrast adjustments were applied equally to all color channels with a minimum of 120 and a maximum of 215. DIC tests were performed on an identical beam under the same loading. A spray paint speckle pattern was applied to the side of the beam and the beam was photographed at each 2 mm displacement increment. Images of the beam being deformed were processed with DIC software (VIC2D 2009, Correlated Solutions), to obtain full-field strain measurements.

Digital Image Correlation (DIC) for Beam Bending

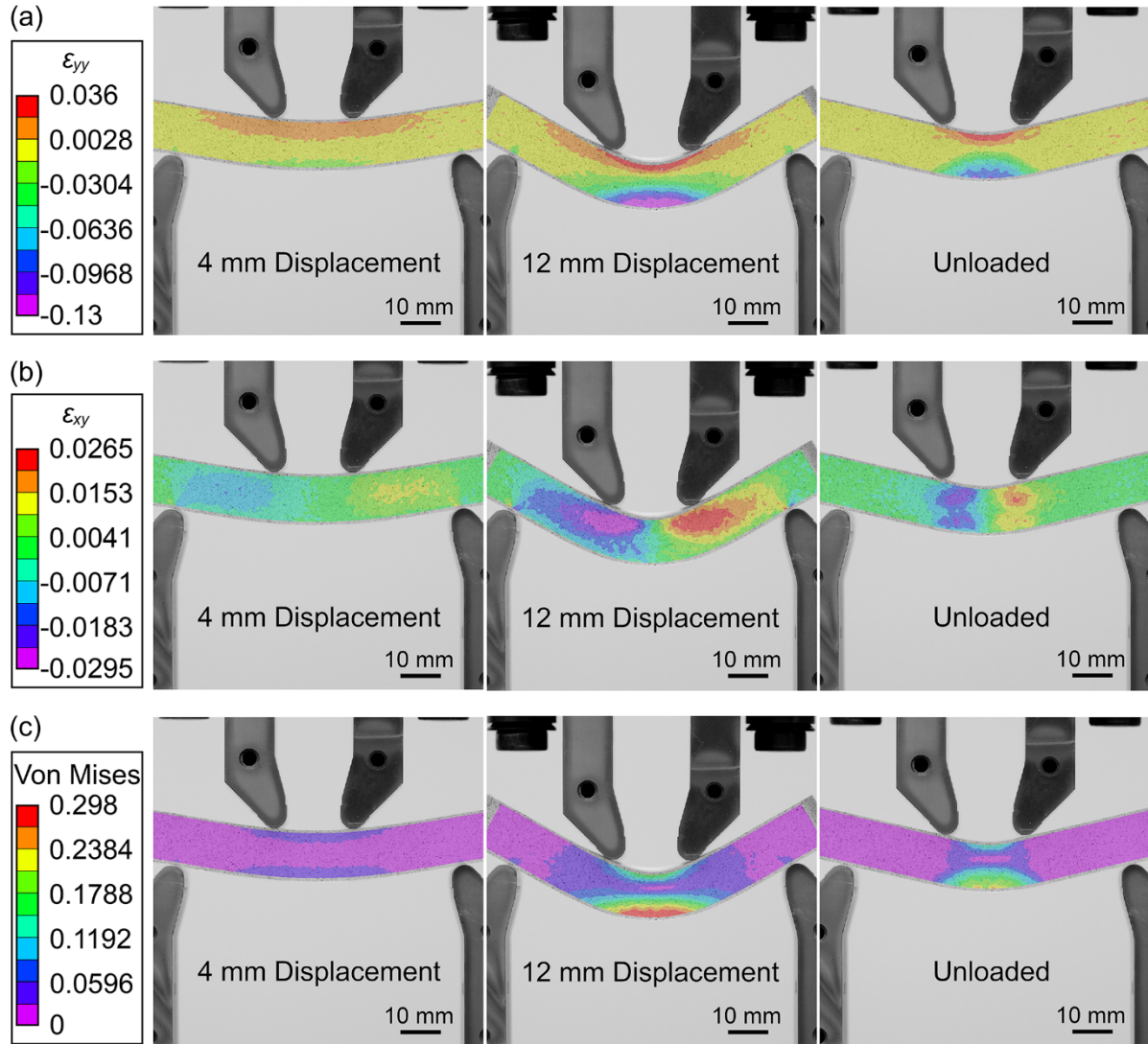


Figure S14. Digital image correlation strain fields during beam bending. (a) Transverse strain ϵ_{yy} (b) shear strain ϵ_{xy} and (c) equivalent Von Mises strain for 4 mm displacement, 12 mm displacement, and after unloading to zero force.

Crosshead Strain vs. Digital Image Correlation (DIC) for Tensile Test

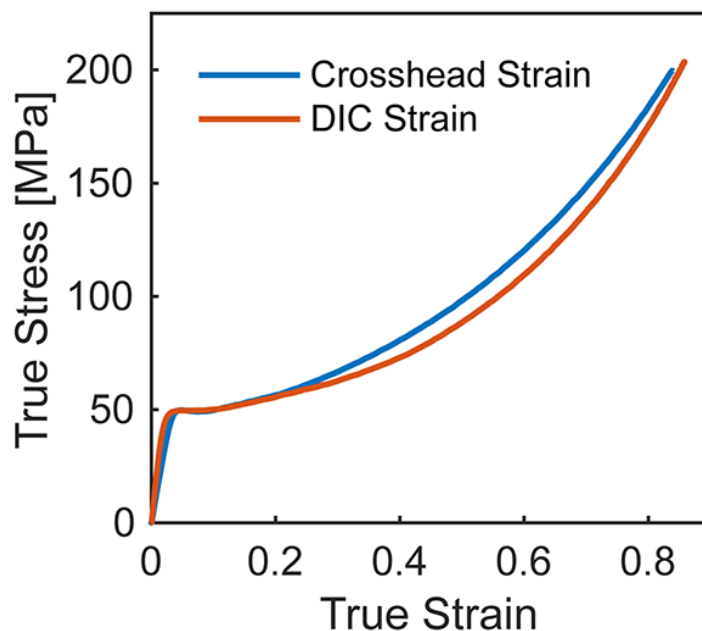


Figure S15. Comparison of monotonic tensile stress-strain response calculated from crosshead displacement (19.54 mm effective gauge length) and DIC strain measurement for the same SP-BPA-PC specimen at a rate of 0.001 s^{-1}

Film Preparation Setup

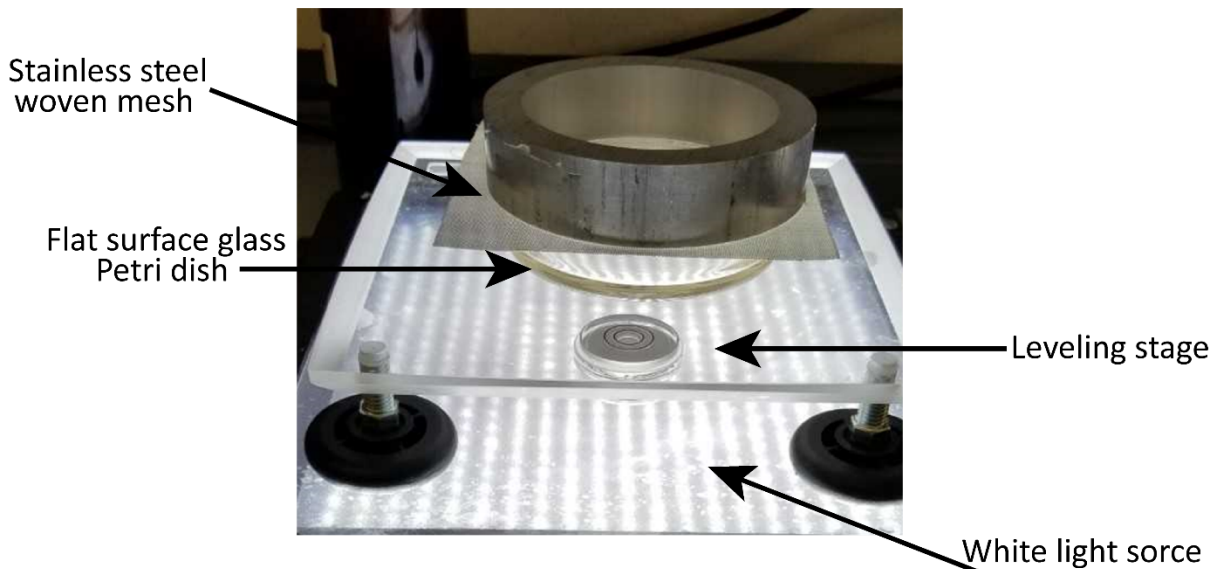


Figure S16. Film preparation setup: Stainless steel mesh for controlled evaporation of the dichloromethane. Flat bottomed Petri dish on a leveling stage to produce film with uniform thickness. White light source in order to drive the SP-MC equilibrium towards the SP species.

References

- (1) Potisek, S. L.; Davis, D. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanophore-Linked Addition Polymers. *J. Am. Chem. Soc.* **2007**, *129*, 13808–13809.
- (2) Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymeric Materials. *Nature* **2009**, *459*, 68–72.
- (3) Lee, C. K.; Davis, D. A.; White, S. R.; Moore, J. S.; Sottos, N. R.; Braun, P. V. Force-Induced Redistribution of a Chemical Equilibrium. *J. Am. Chem. Soc.* **2010**, *132*, 16107–16111.
- (4) Eckert, H.; Forster, B. Triphosgene, a Crystalline Phosgene Substitute. *Angew. Chem. Int. Ed. Eng.* **1987**, *26*, 894–895.
- (5) *Calculated Using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2019 ACD/Labs).*
- (6) Schindelin, J.; Arganda-Carreras, I.; Frise, E.; Kaynig, V.; Longair, M.; Pietzsch, T.; Preibisch, S.; Rueden, C.; Saalfeld, S.; Schmid, B.; Tinevez, J. Y.; White, D. J.; Hartenstein, V.; Eliceiri, K.; Tomancak, P.; Cardona, A. Fiji: An Open-Source Platform for Biological-Image Analysis. *Nat. Methods* **2012**, *9*, 676.
- (7) Bending, B.; Ediger, M. D. Comparison of Mechanical and Molecular Measures of Mobility during Constant Strain Rate Deformation of a PMMA Glass. *J. Polym. Sci. Part B Polym. Phys.* **2016**, *54*, 1957–1967.
- (8) Kim, J. W.; Medvedev, G. A.; Caruthers, J. M. Nonlinear Stress Relaxation in an Epoxy Glass and Its Relationship to Deformation Induced Mobility. *Polymer* **2013**, *54*, 3949–3960.

- (9) Lee, E.-W.; Medvedev, G. A.; Caruthers, J. M. Deformation Induced Evolution of Mobility in PMMA. *J. Polym. Sci. Part B Polym. Phys.* **2010**, *48*, 2399–2401.