

## Supporting Documents

### I. Monomer Synthesis and Characterization

*Synthesis of 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2,1-b][1,4]-oxazine]-2-amino-2-methylacrylate (SNO)*

Pd(OAc)<sub>2</sub> (0.0056 g, 0.025 mmol), NatBuO (0.0057 g, 6.0 mmol), and DABP (0.0179 g, 0.050 mmol) was purged with N<sub>2</sub> gas. Then, toluene (40 mL), SP (1.81 g, 5.0 mmol) and AEMA (0.99 g, 6.0 mmol) were added. The reaction mixture was stirred over a period of 28 h at 120°C. Upon completion, the reaction was allowed to cool at room temperature and the mixture was diluted with diethyl ether (30 mL), followed by washing it with water (20 mL). The colorless product was isolated by column chromatography using ethyl acetate/n-hexane mixture.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.25 (-CH<sub>3</sub>, H-1'), 1.48 (-C(CH<sub>3</sub>)<sub>2</sub>, H-3'), 1.65 (-CH<sub>3</sub>, H-13), 2.30 (-CH<sub>2</sub>, H-10), 2.82 (-CH<sub>2</sub>, H-11), 2.96 (-NH, H-9), 6.51 (-CH<sub>2</sub>, H-12b), 6.98 (-CH, H-5'), 7.18 (-CH, H-4'), 7.23 (-CH<sub>2</sub>, H-12a), 7.27 (-CH, H-6'), 7.42 (-CH, H-5), 7.63 (-CH, H-4), 7.70 (-CH, H-8), 7.72 (-CH, H-7), 7.75 (-CH, H-2), 7.78 (-CH, H-6), 8.53 (-CH, H-3).

Synthesis of SNO was confirmed by <sup>1</sup>H NMR spectroscopy, as illustrated in Figure S-1. The appearance of two resonances at 6.41 and 7.02 ppm due to C=C bonds and a peak at 1.48 ppm which corresponds to the methyl group of the methacryloyl moiety indicate the formation of the SP monomer. Also, aromatic protons next to the amino ethyl methacrylate group are shifted to lower fields upon elimination reactions, giving amine in position 10, thus verifying the monomer structure.

Figure S-2, A and B illustrates reversible color changes and the corresponding absorption spectra of SP monomer in CHCl<sub>3</sub> solution as a function of pH. The colorless solution of SNO (Figure S-2, A-1) turns blue immediately (Figure S-2, A-2) upon acidic conditions (pH = 1) which can be reversed under basic conditions (pH = 12, Figure S-2, A-1). The absorption

spectrum of the colorless solution exhibits characteristic bands at 314 and 348 nm, typical of a closed ring SNO form (Figure S-2, B-1). Addition of HCl converts SNO to merocyanine hydrochloride ( $\text{MCH}^+$ ) form which is confirmed by the presence of two new bands at 413 and 598 nm (Figure S-2, B-2) specifying both zwitterionic and  $\text{MCH}^+$  species. Again, reversibility is achieved by changing pH to 12, manifested by the disappearance of bands at 413 and 598 nm (Figure S-2, B-3).

## II. Polymer Synthesis and Characterization

*Synthesis of poly(methyl methacrylate/n-butylacrylate/1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2,1-b][1,4]-oxazine]-2-amino-2-methylacrylate)*

p(MMA/nBA) and p(MMA/nBA/SNO) copolymers were synthesized using semi-continuous emulsion polymerization process. The reaction flask was immersed in a water bath preheated to 75 °C and purged continuously with  $\text{N}_2$  gas. The reactor was first charged with 27 mL of double de-ionized (DDI) water, and after purging with  $\text{N}_2$  for 30 min, the content was stirred at 350 rpm. At this point, pre-emulsion (DDI, 38 mL; SDOSS, 0.507 g; MMA/nBA/SNO monomers at 48.53/48.55/2.92 weight ratio, and AIBN, 0.25 g) was fed at a 0.158 mL/min rate into the vessel over a period of 3.5 h. After completion, the reaction was continued for additional 2 h. The resulting colloidal dispersion was filtered upon cooling to ambient temperature. It should be noted that polymerization reaction was conducted at 75°C which result in ring open SNO structure (red color). To obtain close ring structure emulsion was heated to 95°C (colorless) and cooled down to 25°C retaining closed ring structure (colorless). The obtained molar ratio of p[MMA/nBA/MC] copolymer was 0.07/0.05/0.0013. Due to hydrophobic nature of MC and semi-continuous emulsion polymerization conditions, 0.0013 moles of MC was copolymerized.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.75 (- $\text{CH}_3$ , H-10), 0.79 (- $\text{CH}_2$ , H-15), 0.97 (- $\text{CH}_3$ , H-11), 0.98 (- $\text{CH}_3$ , H-12), 1.28 (- $\text{CH}_3$ , H-3'), 1.47 (- $\text{CH}_2$ , H-14), 1.49 (- $\text{CH}_2$ , H-18), 1.50 (- $\text{CH}_2$ , H-15), 1.52 (- $\text{CH}_2$ , H-19), 2.15 (- $\text{CH}_3$ , H-10), 2.50 (- $\text{CH}_3$ , H-13), 2.82 (- $\text{CH}_3$ , H-1'), 2.88 (-CH, H-22), 3.50 (- $\text{CH}_2$ , H-9), 3.51 (- $\text{CH}_2$ , H-16), 3.53-4.10 (- $\text{CH}_2$ , H-17, H-18, H-20, H-21), 7.28 (-CH, H-6'), 7.40 (-CH, H-5), 7.59 (-CH, H-4), 7.66 (-CH, H-8), 7.70 (-CH, H-7), 7.74 (-CH, H-2), 7.77 (-CH, H-6), 11.80 (-CH, H-3).

The presence of resonances in  $^1\text{H}$  NMR spectra due to three repeating units and the broadening of the peaks verify the copolymer synthesis. Figure S-3 illustrate  $^1\text{H}$  NMR spectra of p(MMA/nBA/SNO) copolymer with typical resonances at 0.88 ( $-\text{CH}_3$ ) and 3.60-4.81 ppm ( $-\text{CH}_2$ ) arising from copolymerization of nBA and MMA units. Furthermore, the signals of amine proton ( $-\text{NH}$ ) of SNO shift to the lower fields (11.91 ppm) along with aromatic peaks at 8.25 ppm. Also, the absence of resonances at 6.41 and 7.02 ppm due to  $\text{C}=\text{C}$  double bonds of SP monomer, thus confirming copolymerization of the monomers. Molecular weight of the copolymer was determined by dynamic light scattering and was  $8 \times 10^6$  g/mol.

Figure S-4, A and B, illustrates reversible color changes and the corresponding absorption spectra of p(MMA/nBA/SNO) films as a function of pH. Initially, colorless p(MMA/nBA/SNO) film (Figure S-4, A-1) immediately turned dark red (Figure S-4, A-2) upon exposure to acidic vapors (pH = 1) and the reversibility is achieved by exposing it to  $\text{NH}_4\text{OH}$  vapors (pH = 12, Figure S-4, A-1). The same absorption spectrum of the colorless films with characteristic bands at 314 and 348 nm due to closed ring SNO form (Figure S-4, B-1) are observed. Exposure to acidic vapors converts SNO to  $\text{MCH}^+$  form indicated by a new band at 530 nm (Figure S-4, B-2). Again, reversibility is achieved at pH = 12 with the disappearance of the band at 530 nm (Figure S-4, B-3).

### III. Stimuli-Responsive Behavior

In an effort to establish pH responsiveness of p(MMA/nBA/SNO) colloidal particles in aqueous solutions, the particle size of p(MMA/nBA/SNO) was analyzed as a function of pH. Figure S-4, C illustrate that as pH decreases from 10 to 1, the particle size increases from 290 to 327 nm, which is attributed to the protonation and the resulting ring opening of the SNO units.

pH changes also result in reversible color changes which are illustrated in Figure S-4, A-1 and A-2. Copolymer colloidal dispersions of p(MMA/nBA/SNO) were allowed to coalesce at 25 °C to form uniform films of approximately 80 μm thickness. Each specimen was cut to 25 x 7 mm size. It should be noted that coalesced films had a pinkish color and prior to further experiments they were heated at 95°C for 5 min to become clear. Healing experiments utilizing visible light were performed using a laser pointer at 580 nm (5 mW) for one hr to avoid sample heating.

To determine conformational changes in p(MMA/nBA/SNO) coalesced films upon exposure to VIS radiation (580 nm), acidic vapors, and temperature, Raman spectra were collected as a function of exposure time. Analysis of the Raman data discussed below provides detailed information about conformational and structural features responsible for color change and self-repair.

Figure S-5, A, Traces a, b, and c illustrate Raman spectra of p(MMA/nBA/SNO) recorded as a function of the 580 nm exposure time (0, 30, 60 min). As seen, after 60 min exposure, the intensity of the band at 1648 cm<sup>-1</sup> decreases which is responsible for conversion of MC to SNO form. At the same time, reappearance of the band at 3027 cm<sup>-1</sup> due to the C-O-C ring closure (Trace c) is observed. Also, the intensity of the bands at 2773 and 1407 cm<sup>-1</sup> associated with the symmetric C-H stretching (N-CH<sub>3</sub>) and the aromatic C=C-H ring stretching vibrations of MC decrease, manifesting reversibility of the ring opening-closure resulting to MC to SNO conversion. The mechanism of ring opening-closure process upon exposure to UV/VIS radiation is shown in Figure S-5, B.

Figure S-6, A, Traces a, and b illustrate Raman spectra of p(MMA/nBA/SNO) recorded as a function of time at 10 min intervals (0, 20 min) at pH =1 and Trace c illustrates the reversibility upon exposure to 580 nm radiation for 10 min. As seen, after 20 min exposure,

Trace b exhibits bands at 1569 and 1648  $\text{cm}^{-1}$  due to C=C and C=N stretching vibration indicating the presence of MC-HCl. The decrease of the 2773 (N-CH<sub>3</sub>), 1407 (ar. C=C-H) and 843 (CCN) bands accompanied by reappearance of the band at 3027  $\text{cm}^{-1}$  is also associated with C-O-C ring closure, thus indicating MC-HCl to SNO conversion upon exposure to VIS radiation. The forward reactions shown in Figure S-6, B illustrate protonation process of the SNO component (Step I), where H<sup>+</sup> reacts with the C-O functionality. Reversible reactions upon exposure to VIS radiation or temperature result in MCH<sup>+</sup> form to go back to the SNO form.

Figure S-7, A Traces a, b, and c illustrates Raman spectra of p(MMA/nBA/SNO) copolymer recorded as a function of time (0, 10, 30 min) in the 25 to 95 °C temperature range. After 30 min exposure (Trace c), the band at 1648  $\text{cm}^{-1}$  disappears, again signifying conversion of MC to SNO form. Furthermore, reappearance of the band at 3027  $\text{cm}^{-1}$  due to the C-O-C ring closure (Trace c) is detected which is accompanied by the decrease of the 2773 and 1407  $\text{cm}^{-1}$  bands due to symmetric C-H stretching (N-CH<sub>3</sub>) and aromatic C=C-H ring stretching vibrations of MC, manifesting the reversibility of the ring opening and closure. Figure S-7, B illustrates the mechanism of ring opening-closure process upon exposure 25 and 95 °C temperature range. It should be also noted that when spironaphthoxazine (SNO) monomer is dissolved in ethyl acetate it will turn blue after exposure to 365 nm UV light, but will return to colorless solution immediately after UV source removal. However, only slight color changes are observed when SNO is copolymerized and forms a film. This is likely attributed to the polymer matrix surroundings which, due to steric hindrance, restricts the ring-opening reactions as well as the polarity of the surroundings matrix, favoring ring-closed state.

To elucidate a stimuli-responsive behavior of the p(MMA/nBA/SNO) copolymer (Figure 2-II, Main Doc.), several controlled experiments were performed. Figure S-8, A illustrates an

optical image of p(MMA/nBA/SNO) films before mechanical damage. The Raman images of the 1648 and 1732  $\text{cm}^{-1}$  bands are shown in Figure S-8, B. As seen, distribution of both species responsible for these vibrations is uniform and being due to MC form, also supports earlier conclusions obtained from Raman measurements obtained from area **a** in Figure S-8, A.

Figure S-9, A-1, A-2 and A-3 shows optical images, whereas B-1, B-2 and B-3 are Raman images of p(MMA/nBA/SNO) scratched films after 30 ( $t$ ) and 60 ( $t_1$ ) minutes without any external stimulus. As shown, no spectroscopic changes are observed without stimulus (C-1, C-2 and C-3). To further realize molecular changes resulting from this process and its influence on the dynamics of the copolymer backbone, computer simulations were conducted. The polymer backbone shows a random coil-like conformation (D) due to the presence of MC form upon mechanical damage. The damaged area does not show any repair after 60 min, indicating the presence of open-ring MC form. Furthermore, the polymer backbone shows the same random coil-like conformation (D').

Figure 10-I, A-1, A-2 and A-3, illustrate optical images of mechanically damaged and repaired p(MMA/nBA/SNO) films, and **a**, **a'** and **a''** represent the areas subjected to nanoindentation after 30 and 60 min. Figure 10-II show the results of nanoindentation measurements, where each cycle **a**, **a'**, and **a''** illustrates the force ( $\mu\text{N}$ ) plotted as a function of displacement (nm) of undamaged (A-1), mechanically damaged (A-2) and repaired (A-3) film surfaces without any external stimuli. Compared to the initial values of 28.7 (A), 28.9 (B) and 28.6 (C) MPa for undamaged area (**a**), the loss moduli in the damaged area (**a'**) diminishes to 18.6 (A), 18.9 (B), and 18.5 (C) MPa. After 60 min, no change was observed for the loss moduli

values [18.8 (A), 19.0 (B) and 18.6 (C) MPa ( $\mathbf{a''}$ )] indicating no self-repair. The same trend is observed for nano-hardness measurements which initially were at 5.1, 5.2 and 5.1 MPa, to be diminished to 2.4, 2.35, 2.38 MPa upon damage, and no change was detected after 60 min (2.48, 2.39 and 2.41 MPa).

Figure S-11, A-1 shows optical image of mechanically damaged p(MMA/nBA) control sample and A-2, A-3 after 30 and 60 min without external stimulus. Figure S-11, B-1, C-1 and D-1 shows optical images of damaged p(MMA/nBA) control samples whereas B-2, C-2, D-2 and B-3, C-3, D-3 upon exposure to VIS radiation, pH and temperature as a function of time. The control samples does not show any change in the damaged area upon exposure to external stimuli indicating that SNO and MC units as pending groups is required for the self-repair process. Figure S-11, E and E' illustrates computer modeling experiments performed on p(MMA/nBA) control sample as a function of temperature. The polymer backbone shows an extended conformation. No conformation changes of the copolymer backbone were observed after exposure to elevated temperature, indicating that SNO and MC forms are responsible for changing the conformation of the polymer backbone from extended to collapsed state.

#### IV. Materials and Characterization Methods

Methyl methacrylate (MMA, 99.9 %), n-butyl acrylate (nBA, 99.9 %), di(1-adamantyl)-n-butyl phosphine (DABP, 98 %), 5-Chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-(3H)naphth[2,1-b](1,4) oxazine] (SP, 99.0 %), sodium tertiary butoxide (NatBuO, 98.2 %), palladium (II) acetate (Pd(OAc)<sub>2</sub>, 99.5%), 2-amino ethyl methacrylate (AEMA, 99.0 %), dioctyl sulfosuccinate sodium salt (SDOSS, 98%), 2, 2'-azobisisobutyronitile (AIBN, 98.2 %), anhydrous toluene (99.9 %), ammonium hydroxide (NH<sub>4</sub>OH, 28 %), sodium hydroxide (NaOH, 0.1 N) and hydrochloride acid (HCl, 36.7 % , 0.1 N) were purchased from Aldrich Chemical Co.

### **<sup>1</sup>H NMR Spectroscopy**

<sup>1</sup>H NMR spectra were acquired using the Varian Mercury 300 MHz NMR spectrometer. Typical measurement conditions involved 45° pulse, relaxation delay 1 s, acquisition time of 1.998 s and each spectrum represents a co-addition of 256 scans. For <sup>1</sup>H NMR measurements, 5.0 % w/v of p(MMA/nBA/SP) and p(MMA/nBA) copolymers were dissolved in dimethyl sulfoxide (DMSO), respectively, and 5.0 % w/v of SP was dissolved in chloroform (CDCl<sub>3</sub>).

### **FT-IR Spectroscopy**

Microscopic attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra were collected on a Bio-Rad FTS-6000 FT-IR single-beam spectrometer set at 4 cm<sup>-1</sup> resolution equipped with a deuterated triglycine sulfate (DTGS) detector. A 2 mm Ge crystal with a 45° face angle maintaining constant contact pressure between the crystal and the specimens was used.

### **Particle Size Analysis and Molecular Weight Determination**

Particle size analysis was performed using a Microtrac Nanotrac particle size analyzer (model NPA 250) with an accuracy of ±10 nm. Potentiometric titrations were performed at 22 °C using Orion pH meter Model 350 with a glass combination electrode (Orion 9202 BN). Auto calibration against standard buffer solutions was completed before the titration. Standard hydrochloric acid and sodium hydroxide were utilized to adjust pH values of aqueous dispersions.

Molecular weight was determined using gel permeation chromatography (Waters, Inc.) equipped with a 515 HPLC pump and a 2414 model refractive index detector. Each sample was precipitated in tetrahydrofuran/triethylamine (THF/TEA= 9:1) and eluted through a 5 μm



MIXED-C column. Elution times were referenced against polystyrene standards, and molecular weights ( $M_w$ ) of p(MMA/nBA), and p(MMA/nBA/SNO) were  $\sim 7.8\text{-}8 \times 10^6$  g/mol, respectively.

### **Film Formation**

Polymeric films were prepared by casting colloidal dispersions onto poly(tetrafluoroethylene) (PTFE) substrate and allowed to coalesce in an environmental chamber at 42 % relative humidity (RH) for 78 h at 25 °C. In a typical experiment, approximately 80  $\mu\text{m}$  thick and 10 $\times$ 3 mm size films were utilized controlled humidity, temperature, vapor exposure, or UV exposure conditions.

### **Raman Spectroscopy**

Raman spectra were obtained using a Renishaw Raman microscope equipped with a computer controlled three-axis encoded (X, Y, Z) motorized stage, a RenCam CCD detector, and a Leica microscope (DMLM series). The 785 nm diode laser provided an excitation source with a maximum power output of 300 mW. The films were placed on the gold surface and each Raman spectrum was collected at a 100 mW laser power and an acquisition time of 10 sec.

### **UV-Vis Spectroscopy**

UV-Vis absorption spectra were measured using a Varian Cary 500 scan UV-Vis-NIR spectrophotometer. SNO monomer was diluted with  $4 \times 10^{-5}$  mol/L of  $\text{CHCl}_3$  and p(MMA/nBA/SNO) colloidal dispersions with DDI water ( $6 \times 10^{-5}$  mol/L) and placed in a quartz cell with a 10 mm path length. The same dispersions were coalesced to form solid films which were attached on a quartz substrate with 0.5 mm path length. In a typical experiment,  $3.5 \times 10^{-4}$  mol/L solution was placed in a capped quartz cell with a 10 mm path length.

### **Computer Modeling**

Quantum mechanical semi-empirical calculations were conducted using Material Studio software (Accelrys Inc., Version 4.1) and computer modeling simulations were performed using the PCFF force field conditions. In the first step, we created infinite copolymer long chains containing MMA, nBA, and SNO monomer units. In an effort to determine thermodynamic responses of molecular segments a  $25 \times 25 \times 25 \text{ \AA}^3$  periodic unit cell containing 972 atoms (972 asymmetric units) was constructed, and temperature as well as protonated state MC of the photochromic SNO component were the control parameters to calculate conformational changes and energy differences resulting from temperature and protonation conditions.