

# Enhanced Dielectric Performance of a Block Copolymer-Polythiophene Nanocomposite

## **Electronic Supporting Information**

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## **1. FTIR Spectroscopy**

IR absorption spectra were recorded on a FTIR Jasco 4100 spectrophotometer. Samples were placed in an attenuated total reflection accessory (Top-plate) with a diamond crystal (Specac model MKII Golden Gate Heated Single Reflection Diamond ATR). SEBS and SEBS:P3TMA films were solvent casted from the corresponding  $\text{CHCl}_3$  solutions, while P3TMA was analyzed as powder. For each sample 32 scans were performed between 4000 and 600  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

FTIR spectra of SEBS:P3TMA films reveal absorbance peaks coming from their two individual components (Figure S2). The band associated to the C=O stretching (1731  $\text{cm}^{-1}$ ) was considered as an indicator of the presence of the conducting polymer in the insulating matrix. The intensity of this band, labelled as A in Figure S2, increases with the P3TMA concentration. In addition, the presence of P3TMA in the blend is also confirmed by the  $-\text{CH}_3$  asymmetric bending at 1431  $\text{cm}^{-1}$  (labelled as B), which is seen as a shoulder for blends with  $\leq 10$  wt. % of P3TMA, and as a well-defined peak for films with 20 wt.% of P3TMA. Bands in the range from 1000 to 1320  $\text{cm}^{-1}$  (labelled as region C) correspond to C-O-C and C=C conjugated stretching.

SEBS forms an elastomeric network in which styrene hard blocks (SB) are connected by soft ethylene butylene chains (EB).<sup>1</sup> In SEBS:P3TMA spectra, SB blocks are identified through the C=C aromatic stretching at 1453  $\text{cm}^{-1}$  (labelled as D) and the bands at 696 and 752  $\text{cm}^{-1}$  (labelled as E and E'), which are due to the ring out-of-plane deformation of the phenyl group. Besides, bands observed at 1450 and 1374  $\text{cm}^{-1}$ , which correspond to the C-H bending of  $-\text{CH}_2-$  and  $-\text{CH}_3$ , respectively, are attributed to EB blocks. Finally, the C-H rocking of  $-\text{CH}_2-$  groups is evidenced by the band at 721  $\text{cm}^{-1}$

## **2. UV-vis Spectroscopy**

UV-vis absorption spectra of SEBS:P3TMA films were obtained using a UV-vis-NIR Shimadzu 3600 spectrophotometer equipped with a tungsten halogen visible source, a deuterium arc UV source, a photomultiplier tube UV-vis detector, and a InGaAs photodiode and cooled PbS photocell NIR detectors. Spectra were recorded in the absorbance mode using the integrating sphere accessory (model ISR-3100) in the range wavelength between 300 and 850 nm. The interior of the integrating sphere was coated with highly diffuse BaO reflectance standard. Measurements, data collection and evaluation were controlled by the computer software UVProbe version 2.31. The optical  $\pi$ - $\pi^*$  lowest transition energy ( $E_g$ , eV) or band gap energy was determined considering the following expression:

$$E_g = \frac{h \cdot c}{e \cdot \lambda_{onset}} \quad (S1)$$

where  $h$  (Plank's constant) =  $6.626 \cdot 10^{-34}$  J s,  $c$  (speed of light) =  $3.0 \cdot 10^8$  m s<sup>-1</sup>,  $e$  (elementary charge) =  $1.6 \cdot 10^{-19}$  C and  $\lambda_{onset}$  is the cut off wavelength for the absorption spectra.

The doping level of the CP in SEBS:P3TMA films was assessed by UV-vis spectroscopy. Figure S3 presents the absorption spectra recorded from 300 to 850 nm for SEBS:P3TMA films with a P3TMA content of 0.5, 1, 2.5 and 5 wt. %. Unfortunately, it was not possible to obtain noise-free spectra for films with higher amount of P3TMA. All four spectra exhibit an absorbance peak that corresponds to the lowest  $\pi$ - $\pi^*$  transition of the thiophene ring of P3TMA<sup>2,3</sup> - it is not observed in the spectrum registered for individual SEBS (Figure S3). For films with 0.5 and 1 wt. % P3TMA,  $\lambda_{max}$  appears at 400 and 410 nm, respectively; while the peak becomes broader and shifts to 475 and 482 nm wavelength for films containing 2.5 and 5 wt. % P3TMA, respectively. This change indicates that the  $\pi$ - $\pi^*$  transition energy decreases since the  $\pi$ -

conjugation length increases. This phenomenon has been attributed to the delocalization of  $\pi$ -electrons because of the  $\pi$ - $\pi$  stacking interactions arising from the intramolecular aggregation of P3TMA polymeric chains in films with higher CP concentration. A similar red shift was observed by Manna *et al.* after reactive blending P3TMA with poly(vinylidene fluoride) under melt-cooled conditions.<sup>4</sup> The optical  $\pi$ - $\pi^*$  lowest transition energy ( $E_g$ ), which was determined considering Eq. (S1), for films containing 0.5, 1, 2.5 and 5 wt. % of P3TMA is 2.14, 2.11, 1.85 and 1.84 eV, respectively.

### **3. Figure of merit (FOM)**

Dielectric elastomer actuators (DEAs) are thin elastomeric films - bulk insulators - that when placed between two compliant electrodes under an electrical field result in a deformable capacitor: the electronic polarization of the non-conducting material accumulates charges in the electrodes that are attracted by electrostatic stress, provoking pressure on the film. Consequently, the thickness of the film decreases leading to mechanical deformation. As elastomers conserve their volume when submitted to deformation, the film is elongated in the direction perpendicular to the applied electric field until equilibrium is reached between electrostatic and elastic stress.<sup>5</sup> The electromechanical actuation strain ( $S$ ) is defined as:

$$\text{Actuation strain} = S = \frac{\epsilon_r' \epsilon_0 E_{BD}^2}{Y} \quad (\text{S2})$$

where  $E_{BD}$  is the electrical breakdown,  $\epsilon_0$  is vacuum permittivity,  $\epsilon_r'$  is the relative permittivity, and  $Y$  is the Young's modulus.

According to P. Sommer-Larsen and A. Larsen,<sup>6</sup> the actuation performance of DEA films can be evaluated through a figure of merit (FOM). This single parameter combines the material properties in a universal equation:

$$F_{OM} = \frac{3\varepsilon_r' \varepsilon_0 E_{BD}^2}{Y} \quad (S3)$$

where  $E_{BD}$  is the electrical breakdown,  $\varepsilon_0$  is vacuum permittivity,  $\varepsilon_r'$  is the relative permittivity and  $Y$  is the Young's modulus.

Therefore, as discussed by the authors,  $F_{OM}$  results in a reference value with a two-fold purpose. First, it assesses that the DEA device fulfils its function, relative to its alternatives; and secondly, it guides the optimization process of the elastomer properties.<sup>7,8</sup> As it can be seen from Eq. (S3), the actuation performance depends on both the electric and mechanical properties of the elastomer. In an effort to assess that,  $F_{OM}$  for SEBS:P3TMA films was determined relative to the  $F_{OM}$  of SEBS as:

$$\frac{F_{OM}}{F_{OM}^S} = \frac{\varepsilon_r' Y^S}{\varepsilon_r'^S Y} \left( \frac{E_{BD}}{E_{BD}^S} \right)^2 \quad (S4)$$

where the superindex <sup>S</sup> indicates that those parameters correspond to SEBS films with no P3TMA.

By a simple rearrangement of Eq. (S4), it can be determined that  $F_{OM}$  for SEBS:P3TMA films is greater than  $F_{OM}$  of SEBS only when the reduction in  $E_{BD}$  upon addition of P3TMA is not higher than a certain value (R, Table S1):

$$\log \left( \frac{F_{OM}}{F_{OM}^S} \right) = \log \left( \frac{\varepsilon_r' Y^S}{\varepsilon_r'^S Y} \right) + 2 \log \left( \frac{E_{BD}}{E_{BD}^S} \right) \quad (S5)$$

$$\text{if } F_{OM} > F_{OM}^S \rightarrow \log \left( \frac{F_{OM}}{F_{OM}^S} \right) > 0 \rightarrow \log \left( \frac{E_{BD}}{E_{BD}^S} \right) > \frac{-\log \left( \frac{\varepsilon_r' Y^S}{\varepsilon_r'^S Y} \right)}{2}$$

$$\text{Hence, only when } \frac{E_{BD}}{E_{BD}^S} > 10^{\frac{-\log \left( \frac{\varepsilon_r' Y^S}{\varepsilon_r'^S Y} \right)}{2}}, F_{OM} > F_{OM}^S.$$

Figure S7 depicts the graphical representation of Eq. (S5) for each SEBS:P3TMA film composition, which results in parallel lines with slope 2 and y-intercept that depends on the experimental parameters (relative permittivity and Young's modulus). As it can be observed, SEBS:P3TMA films with a P3TMA content of 2.5 and 20 wt. % achieve positive  $\log\left(\frac{F_{OM}}{F_{OM}^S}\right)$  for lower  $\log\left(\frac{E_{BD}}{E_{BD}^S}\right)$  values.

Thus, the maximum reduction allowed in  $E_{BD}$  ( $R$ ) for which  $F_{OM}$  of SEBS:P3TMA films is greater than  $F_{OM}$  of SEBS can be defined as:

$$E_{BD} = E_{BD}^S \cdot 10^{\frac{-\log\left(\frac{\epsilon_r^I Y^S}{\epsilon_r^I S Y}\right)}{2}} \quad (S6)$$

$$|R|\% = \left| \frac{E_{BD} - E_{BD}^S}{E_{BD}^S} \right| \% = \left| 10^{\frac{-\log\left(\frac{\epsilon_r^I Y^S}{\epsilon_r^I S Y}\right)}{2}} - 1 \right| * 100\% \quad (S7)$$

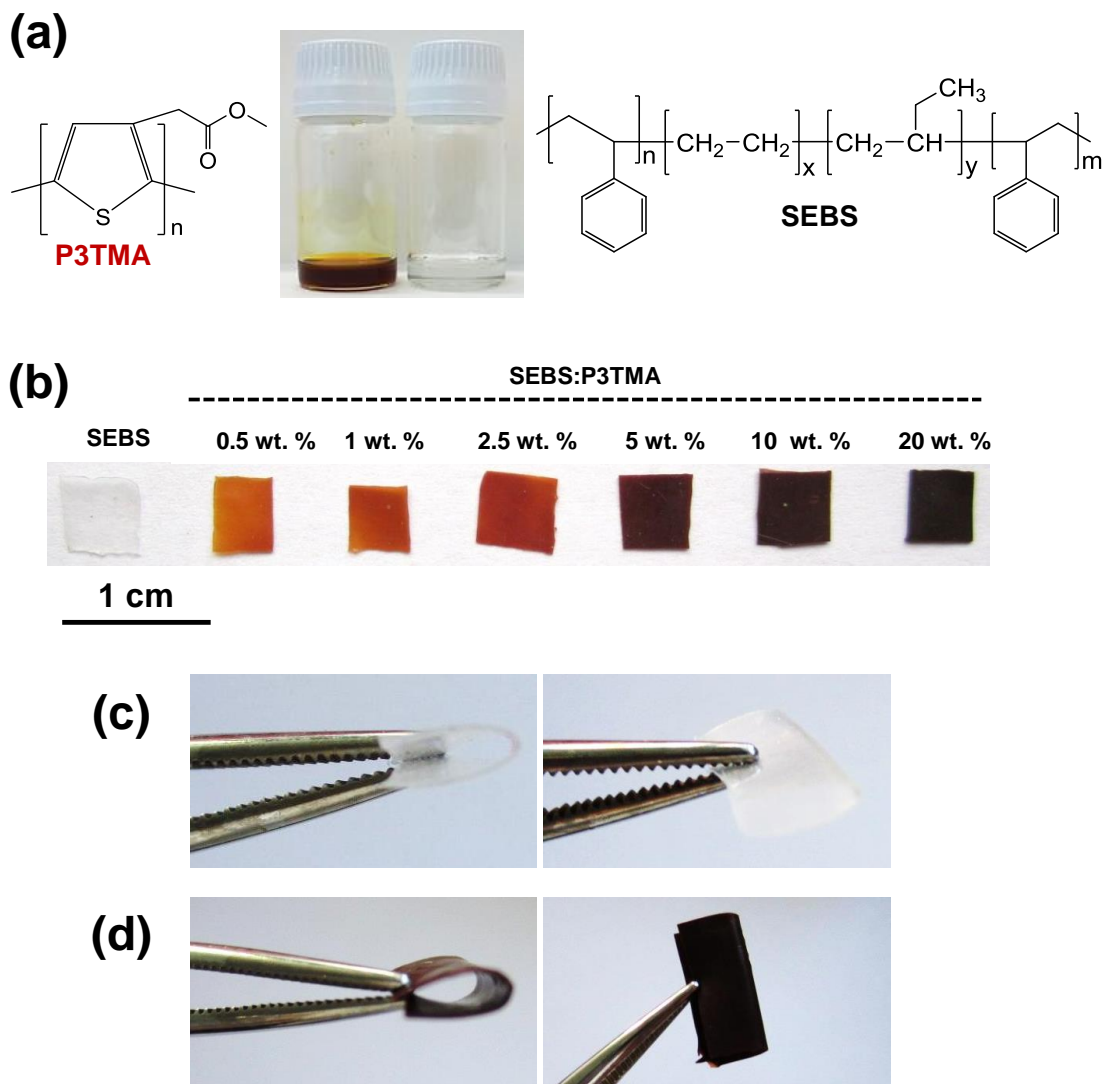
**Table S1.** Maximum reduction allowed in  $E_{BD}$  ( $R$ ) for which  $F_{OM}$  of SEBS:P3TMA films is greater than  $F_{OM}$  of SEBS;  $F_{OM}$  values according to the definition described by Kofod *et al.*<sup>9</sup>

| P3TMA wt. % | $R(\%)$ | $F_{OM}$ |
|-------------|---------|----------|
| 1           | 7.9     | 24.1     |
| 2.5         | 14.7    | 16.6     |
| 5           | 5.2     | 6.2      |
| 10          | 8.4     | 7.6      |
| 20          | 19.1    | 5.9      |

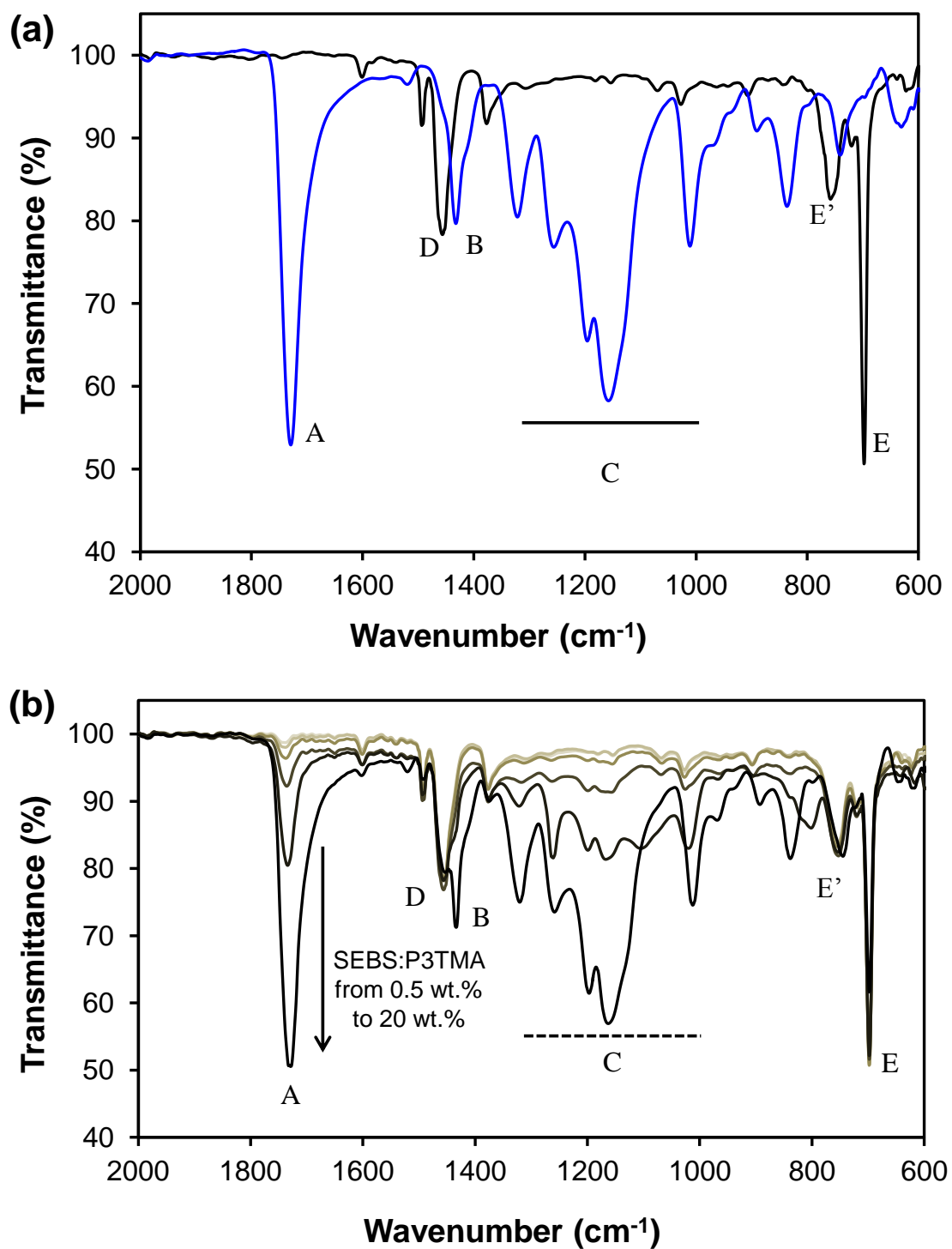
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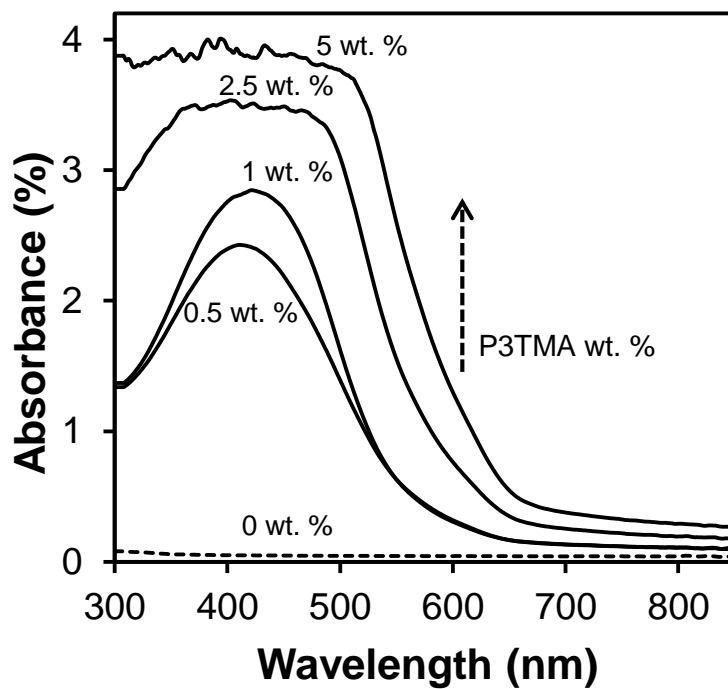




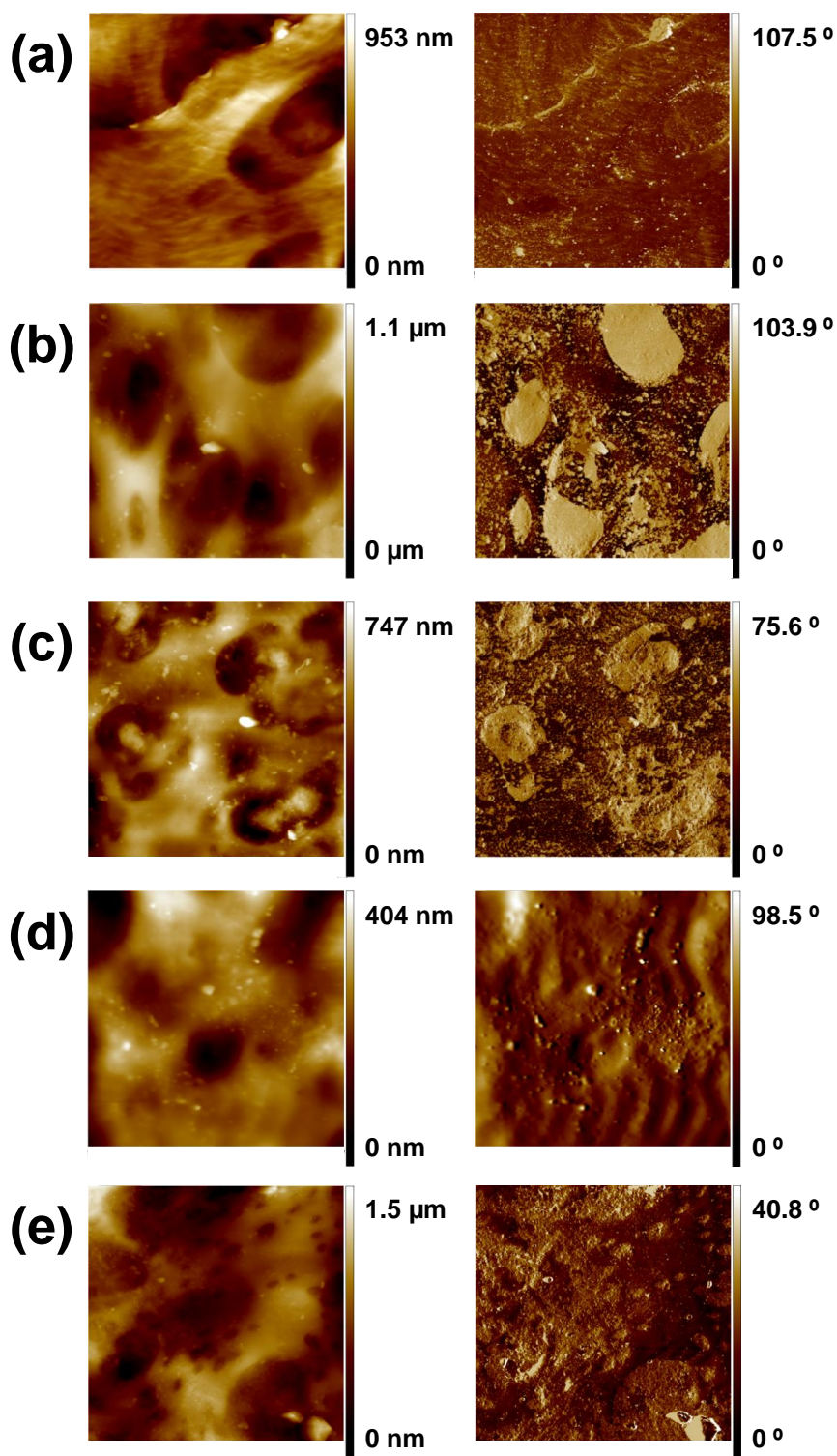
**Figure S1.** Optical images of (a) stock solutions of P3TMA (left) and SEBS (right); (b) SEBS and SEBS:P3TMA films with increasing wt. % P3TMA; flexible response of (c) SEBS and (d) 20 wt. % SEBS:P3TMA films.



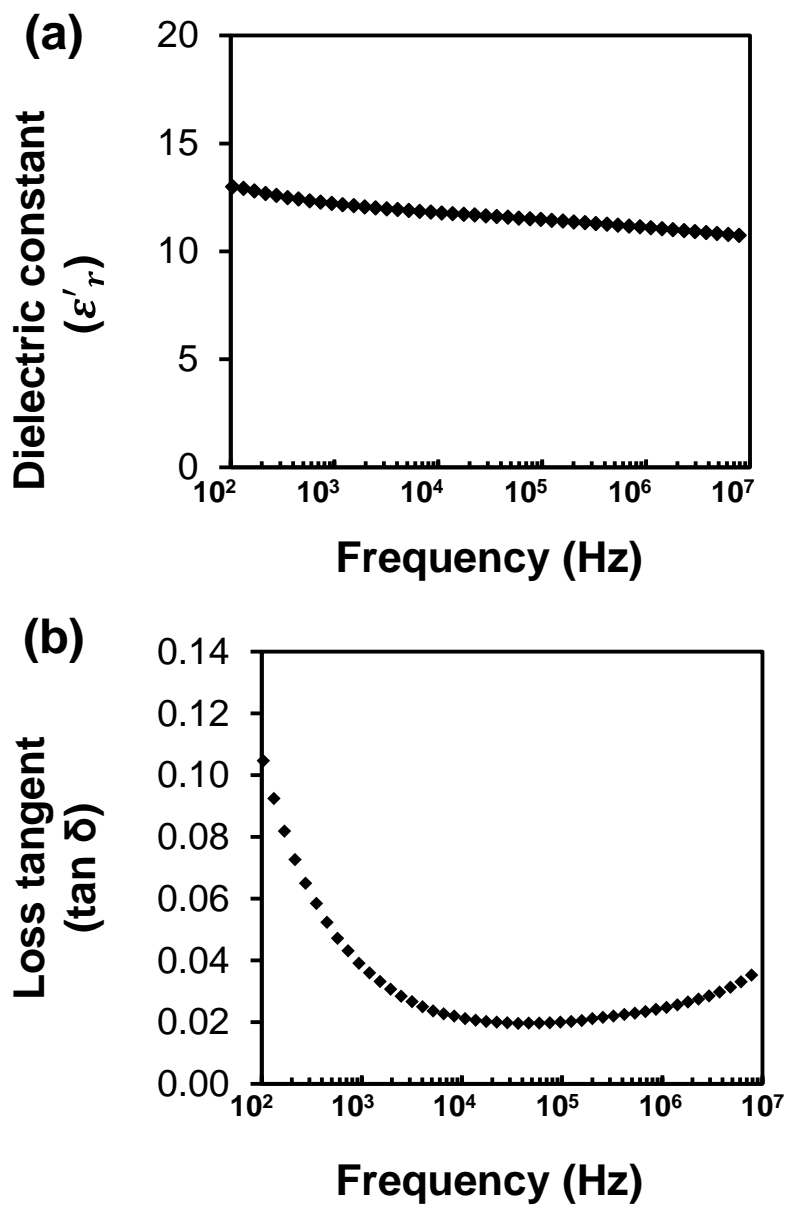
**Figure S2.** FTIR spectra for (a) P3TMA powder (blue line) and SEBS (black line); (b) SEBS:P3TMA films.



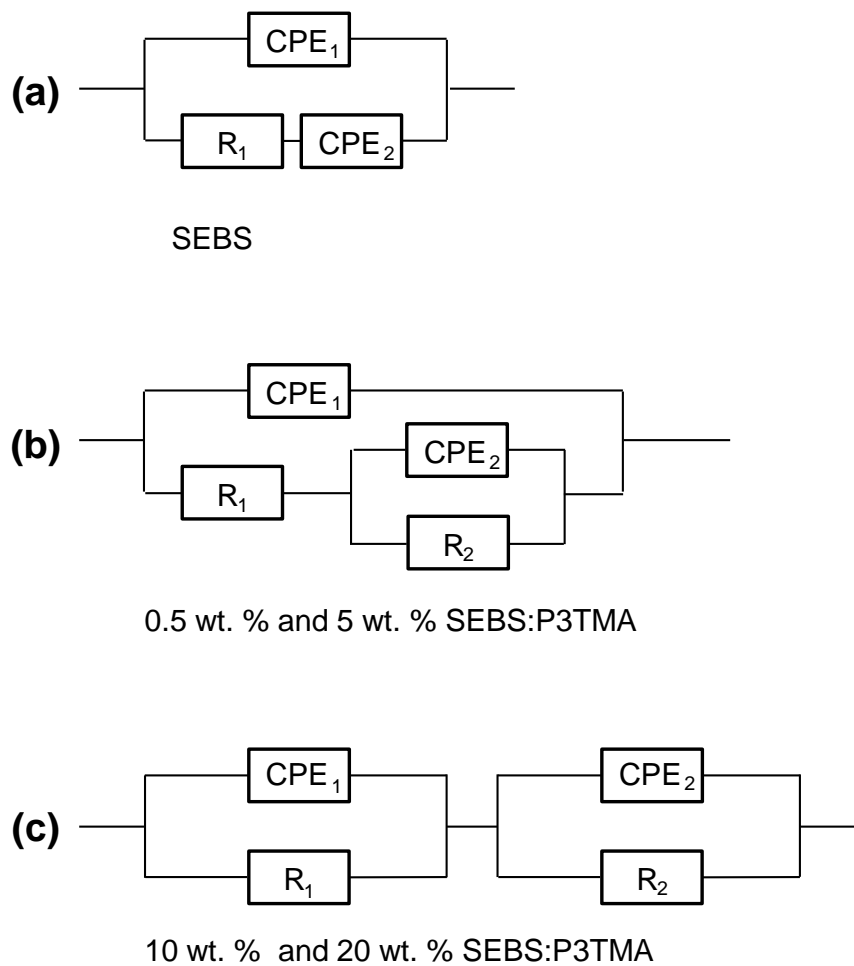
**Figure S3.** UV-vis spectra for SEBS (dashed line) and SEBS:P3TMA films with increasing P3TMA wt. % content (solid lines).



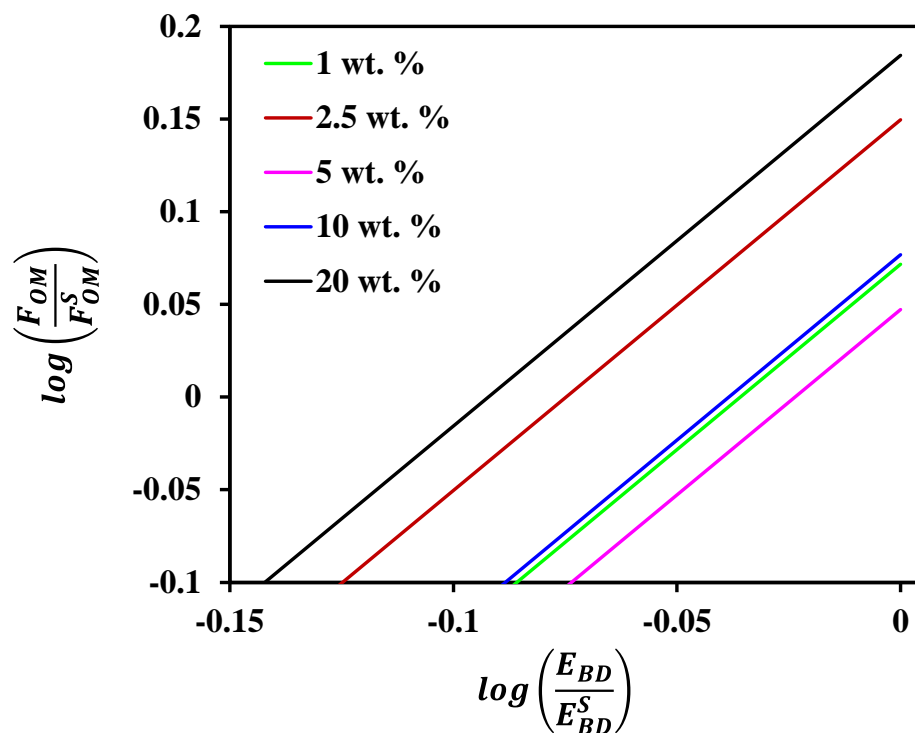
**Figure S4.** AFM height (left column) and phase (right column) images for (a) SEBS (25 × 25 μm<sup>2</sup>) and (b-e) SEBS:P3TMA films surface with increasing P3TMA content: (b) 2.5 wt. % (15 × 15 μm<sup>2</sup>); (c) 5 wt. % (15 × 15 μm<sup>2</sup>); (d) 10 wt. % (15 × 15 μm<sup>2</sup>); and (e) 20 wt. % (25 × 25 μm<sup>2</sup>).



**Figure S5.** (a) Dielectric constant and (b) dielectric loss tangent as a function of frequency at room temperature (23 °C) for pressed P3TMA powder.



**Figure S6.** Equivalent electric circuits (EECs) for SEBS and SEBS:P3TMA films containing 0.5, 5, 10 and 20 wt. % P3TMA.



**Figure S7.** Graphical representation of Eq. (S5) for each SEBS:P3TMA film composition, which results in parallel lines with slope 2 and y-intercept that depends on the experimental parameters (relative permittivity and Young's modulus).