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Mechanoresponsive PS-PnBA-PS Triblock Copolymers via Covalently Embedding Mechanophore

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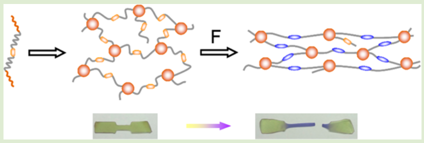
Supporting Information



ABSTRACT: A mechanically active spiropyran (SP) mechanophore is incorporated into the center of poly(*n*-butyl acrylate) (PnBA) block to construct a series of mechanoresponsive polystyrene (PS)-PnBA-SP-PnBA-PS triblock copolymers. Similar mechanical activations of SP occur in all of the copolymers in solution, whereas a unique PS fraction-dependent mechanochromism is observed in the bulk. Effective mechanical activation occurs in the copolymer with a medium PS block length, whereas a very weak color change is observed in the samples bearing low PS fractions and activation appears only in the vicinity of the fracture point in the copolymer bearing long PS blocks. The difference in chemical compositions of the triblock copolymers leads to different microphase separated structures in the bulk and consequently the unique stress−strain responses and mechanochemistry. This platform promises to open way to the design of a wide range of useful mechanoresponsive triblock copolymers having different hard/soft blocks and various types of mechanoresponsive motifs.

Over the past few decades there has been tremendous interest in responsive polymers which are capable of exhibiting property changes in response to external stimuli.[1] A great number of polymers that are thermally, electrically, chemically, optically, or otherwise responsive have been successfully developed. Mechanical properties are of paramount importance to many applications of polymers. However, in stark contrast to the naturally abundant mechanically responsive materials, artificial polymers which can respond to mechanical stimuli in a selective and useful manner have comparably been less studied.[2] The past decade has witnessed great progress in the utilization of mechanical stress for the induction of changes in chemical properties, optical properties, and other properties in polymers.[3] Rational design of functional mechanoresponsive polymeric materials has been possible. Indeed, a variety of novel functions including, but not limited to, biased and facilitated reactivity,[4] force sensing through color change,[5−10] damage healing,[11−14] catalysis,[15−18] remodeling of polymers,[19,20] as well as radical generation[21] and chemiluminescence,[22] among others,[23−28] have been created by utilizing mechanical activation of mechanophores. Studies have also indicated that the molecular weight of polymers, the position of mechanophore, and the environmental effects are critical for effective stress transfer across the mechanophore.[4−11,22−28]

Block copolymers have found numerous applications in areas ranging from self-assembly to a thermoplastic elastomer (TPE) to a compatilizer.[29] For the use as TPEs, block copolymers combine the physical properties of vulcanized rubbers with the processing and recyclable characteristics of thermoplastics.[30] It is well-established that most TPEs owe their elastomeric properties to a microphase separated structure. Rational design of the chemical structure and the architecture of the blocks in TPEs plays important roles to the microphase separation and consequently their processing and mechanical properties.

So far several mechanophores have been incorporated into elastic, ductile, or glassy polymers.[5−10,22] Of the various types of block copolymers, triblock copolymers including those based on styrenic triblock copolymers are commercially produced in the largest volume. Here we investigate the incorporation of spiropyran (SP) into the center of the soft block to construct polystyrene-*b*-poly(*n*-butylacrylate)-SP-poly(*n*-butylacrylate)-*b*-poly styrene (PS-PnBA-SP-PnBA-PS) triblock copolymers, aiming at creating mechanoresponsive TPEs of triblock copolymers and demonstrating the correlation between the activation of mechanophore and the microphase separation in triblock copolymer materials.

SP was selected due to its well-defined mechanochromic properties.[5−10] The ring-closed SP form is colorless or yellow, while proper mechanical activation leads to its ring-opened merocyanine (MC) form, which is red or purple blue, through rupture of the weak spiro carbon−oxygen bond. In this study, SP-linked triblock copolymers were synthesized through ATRP by using SP as a bifunctional initiator. Experimentally, SP-linked PnBA ($PnBA_N$-SP-$PnBA_N$) was first synthesized, followed by copolymerization of PS blocks (Scheme 1). The subscripts N and M in $PnBA_N$ and PS_M correspond to the polymer's approximate M_n in kDa. In a first set of experiments, by varying the ratio of PS and PnBA block lengths while keeping the PnBA block length constant, three triblock copolymers with high (PS_9-$PnBA_{15}$-SP-$PnBA_{15}$-PS_9), medium

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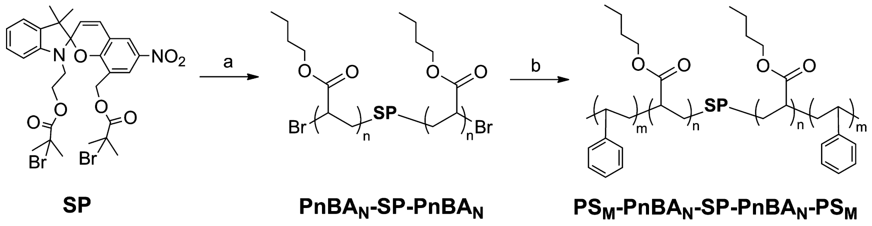
Scheme 1. Synthetic Route of SP Mechanophore Linked PnBA Polymers and PS-PnBA-PS Triblock Copolymers via ATRP by Using SP as a Difunctional Initiator[a]



[a](a) *n*-Butyl acrylate, CuBr, PMDETA, 70 °C, N_2; (b) styrene, CuBr, PMDETA, 75 °C, N_2.

(PS_5-$PnBA_{15}$-SP-$PnBA_{15}$-PS_5), and low (PS_3-$PnBA_{15}$-SP-$PnBA_{15}$-PS_3) PS fractions were synthesized. A control triblock copolymer (PS_4-$PnBA_{19}$-SP-$PnBA_{19}$-PS_4) with similar ratios of PS length to PnBA length to that of PS_3-$PnBA_{15}$-SP-$PnBA_{15}$-PS_3 but having a molecular weight in between those of PS_9-$PnBA_{15}$-SP-$PnBA_{15}$-PS_9 and PS_5-$PnBA_{15}$-SP-$PnBA_{15}$-PS_5 was also synthesized to study the effect of the molecular weight of the copolymer. In terms of polydispersity (Tables S1 and S2), the polymerization achieved here was as good as or slightly better than those used in the preparation of other mechanophore linked polymers.[5,23,24]

Previous work has demonstrated that there are molecular weight thresholds for the mechanical activation of mechanophores.[4,23−25,27] This molecular weight dependent mechanical activation has been studied for benzocyclobutene,[4] Diels−Alder based cyclooctyl,[23] clicked triazolyl,[24] bicyclo[3.2.0]heptane,[25] and cyclobutane[27] mechanophores, but not for SP of any form. Before studying the mechanochromic properties of the SP-linked triblock copolymers, the mechanical activation of SP in SP-linked PnBA was first studied by using sonication in solution. A series of SP-linked PnBA chains of various molecular weights ($PnBA_N$-SP-$PnBA_N$, see Supporting Information) were synthesized by ATRP from SP initiator and were individually subjected to sonication in CH_3CN for 10 min in an ice bath. The results were summarized in Table S1 and Figure S8 (see Supporting Information). Similar to the results reported by Moore,[4,27] Bielawski,[23,24] and Craig[25] groups, there is a molecular weight dependent mechanical activation of SP in SP-linked PnBA polymers. The sonication of PnBA polymers with $M_n > 14$ kD resulted in mechanochromism, whereas polymers with M_n lower than 14 kD showed no color change. Collectively, these results suggested to us that ultrasound induced mechanical activation could be readily achieved when SP was embedded in the center of the polymer chain and the attached polymer chain was sufficiently long, for instance, higher than 14 kD. As the M_n of the SP-linked PnBA macroinitiators used for syntheses of triblock copolymers were 30 and 38 kD, all of the resulting SP-linked block copolymers are thus believed to be capable of exhibiting ultrasound induced mechanochromic properties. Indeed, when subjected to sonication, similar mechanical activations were observed for all of the four triblock copolymers in solution (Figure S9).

Next, we set out to investigate the mechanoresponsive properties of the SP-linked block copolymers in the solid state. Nonstandard dogbone shaped specimens[6,7] of the four triblock copolymers were subjected to monotonic tensile loading to failure at a controlled strain rate of 0.05 s^{-1} at room temperature. At the same time, the mechanically induced color changing behaviors were monitored by a camera. Interestingly, the first three specimens exhibited different tensile (Figure 1) and mechanical activation behaviors (Figure 2); that is, stress−strain responses and mechanical activation in the bulk were dependent on the composition of the triblock copolymers. The specimen with a high PS hard-phase fraction (PS_9-$PnBA_{15}$-SP-$PnBA_{15}$-PS_9) behaved more like a glassy polymer, as shown by the low yield strain (ca. 8%), low elongation at break (lower than 40%), and highest Young's modulus (ca. 240 MPa). A mechanically induced color change (blue) was only observed in the vicinity of the fracture points in the PS_9-$PnBA_{15}$-SP-$PnBA_{15}$-PS_9 specimen. Notably, characteristic tensile behaviors of triblock TPEs[29] and intense color change were observed throughout the gauge section in the PS_5-$PnBA_{15}$-SP-$PnBA_{15}$-PS_5. On the contrary, the specimen of PS_3-$PnBA_{15}$-SP-$PnBA_{15}$-PS_3 exhibited a stress−strain response typical of soft plastics. Despite that this specimen with low PS fraction could be elongated to very high strain without breaking, a very weak mechanical activation of the SP was observed. Very light purple blue emerged only at high strains (greater than 600%) and changed little with further deformation. The control sample showed similar tensile and mechanochromic behaviors to those of the PS_3-$PnBA_{15}$-SP-$PnBA_{15}$-PS_3, except that a relatively higher tensile strength was found, due to its higher molecular weight.

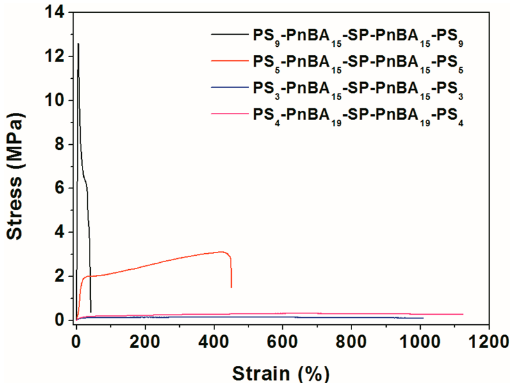


Figure 1. Stress−strain curves of SP-linked PS-PnBA-SP-PnBA-PS triblock copolymers under tensile loading.

To gain insights into the remarkable mechanical activation behaviors in the block copolymers, efforts were directed toward investigating the structure and morphology of the bulk specimens of the triblock copolymers. The microphase morphology was first investigated by TEM on drop casted thin films (Figure 3).[30,31] Relatively clear microphase separated morphology was only observed in the TEM image of PS_5-$PnBA_{15}$-SP-$PnBA_{15}$-PS_5 (Figure 3b). The microphase separation was further studied by SAXS. As can be seen from the

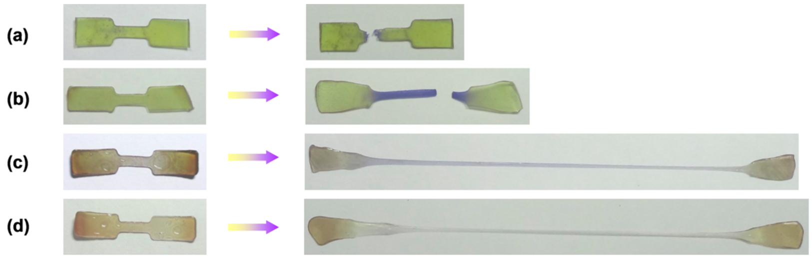


Figure 2. Mechanochromic response of SP-linked PS-PnBA-SP-PnBA-PS triblock copolymers under tensile loading. (a and b) Optical images of PS$_9$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_9$ and PS$_5$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_5$, respectively, after failure; (c and d) optical images of PS$_3$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_3$ and the control PS$_4$-PnBA$_{19}$-SP-PnBA$_{19}$-PS$_4$, respectively, after being strained to 1000%.

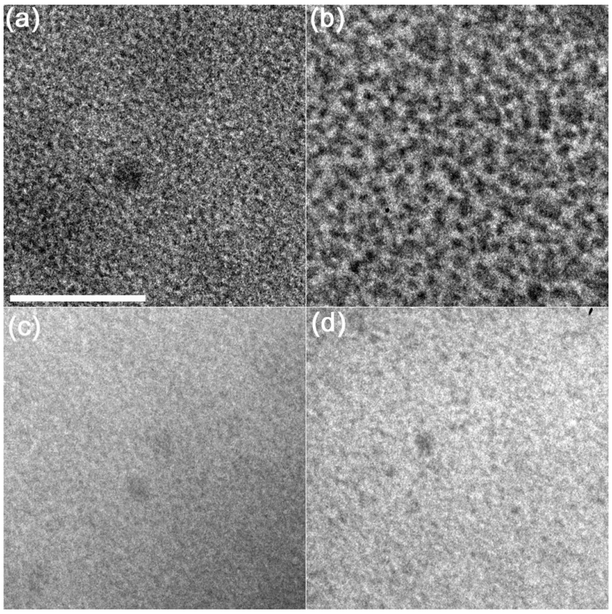


Figure 3. TEM images of the four triblock copolymers (a) PS$_9$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_9$, (b) PS$_5$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_5$, (c) PS$_3$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_3$, and (d) PS$_4$-PnBA$_{19}$-SP-PnBA$_{19}$-PS$_4$. The scale bar is 200 nm.

scattering profiles (Figure S19), the PS$_5$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_5$ clearly exhibits a broad smeared primary Bragg diffraction peak, while none of the other triblock copolymers show distinct scattering patterns. Since the electronic contrast between the PS and PnBA blocks is low (Supporting Information), the observation of the microphase separated morphology by TEM and SAXS can be difficult.[32] Therefore, indirect techniques, that is, modulated differential scanning calorimetry (MDSC) and dynamic mechanical analysis (DMA) measurements, were performed. As shown by MDSC (Figure S20), the T_g values of the PnBA blocks and PS blocks are around −40 and 80 °C, respectively. The T_g values of the PnBA and PS blocks in PS$_9$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_9$ and PS$_5$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_5$ were also determined by DMA measurements (Figures S21 and S22). However, no DMA measurements were performed for PS$_3$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_3$ and PS$_4$-PnBA$_{19}$-SP-PnBA$_{19}$-PS$_4$, because these two samples are too soft to be tested. The measured T_g values are consistent with those reported for PS-*b*-PnBA-*b*-PS triblock copolymers.[33−35] These results suggest that microphase separation is present at least in the PS$_9$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_9$ and PS$_5$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_5$ triblock copolymers.[33−35]

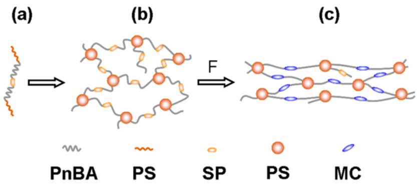


Figure 4. Schematic illustration of the simplified structure and the proposed mechanism of mechanical activation of the SP-linked triblock copolymers in solid state.

In contrast to the similar mechanically induced ring-opening of SP of the four triblock copolymers in solutions by ultrasound, which is solely dependent on the overall molecular weights of the copolymers, the unique mechanoresponsive properties in the bulk should be ascribed to their different solid state structures and dynamics. We present in Figure 4 a schematic illustration of the simplified structure and the proposed mechanism of mechanical activation of the SP-linked triblock copolymers in solid state. Based on the results described above, it is clear that self-assembly of PS blocks led to the disordered microphase separated structure and the PS spheres behaved as the physical cross-linkings in the matrix to give mechanical properties. The chemical composition dependent mechanically induced color change in bulk films is thus believed to be a consequence of the differences in the morphological structures and relaxation times (polymer mobility/chain dynamics) in the solid state. In PS$_3$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_3$ with the lowest PS fraction, the PS phase was sparsely present, and there was little physical cross-linking. Consequently, disentanglement by chain reptation prevailed and effectively reduced stress transfer across the SP mechanophore when the specimen was stretched, leading to very weak mechanochromism. In the cases of PS$_5$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_5$, there were longer PS blocks and therefore a denser and larger PS phase, leading to better physical cross-linking and more effective transfer of force across SP. However, when the lengths of the PS blocks were further increased in PS$_9$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_9$, the fraction of the hard PS phase was too high to afford large plastic flow of the soft PnBA phase and the copolymer. Therefore, the orientation of the chains along the tensile direction at larger scale was greatly hindered; effective distribution of the strain along the polymer chains was suppressed, and only a small fraction of localized activation was expected in the vicinity of fracture. Although the molecular weight of the control was increased to as high as in between those of PS$_5$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_5$ and PS$_9$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_9$, it had similar ratios of PS to PnBA and ineffective physical cross-linking to those of PS$_3$-PnBA$_{15}$-SP-PnBA$_{15}$-PS$_3$.

Similar tensile and mechanical activation behaviors were thus found for the control sample and PS_3-$PnBA_{15}$-SP-$PnBA_{15}$-PS_3. Collectively, it is the combination of the morphological effects (microphase separated structure) and relaxation times, which are dependent on the ratio of PS and PnBA block sizes, but not the overall molecular weight of the triblock copolymer or the global strain that resulted in the composition-dependent mechanical activation behaviors in the triblock copolymers studied in this work. The morphological effects on the mechanical activation of SP found here can also be supported by the recent findings on environmental effects on activation of mechanophores by Moore[7] and Sijbesma et al.[17] groups.

In conclusion, we have successfully incorporated a mechanically active SP mechanophore into the centers of linear PnBA homopolymers and PS-PnBA-PS triblock copolymers to prepare various mechanoresponsive PnBA-SP-PnBA homopolymers and PS-PnBA-SP-PnBA-PS triblock copolymers. Unique mechanically induced activation was observed in bulk films of the triblock copolymers, by varying the molecular weights of the PS blocks while keeping the length of PnBA block constant. This unique chemical composition, that is, the ratio of PS to PnBA block length, dependent mechanical activation in the bulk was demonstrated to be coincident with the stress−strain behaviors and the microphase separated structures of the bulk triblock copolymers. Collectively, within the molecular weight range of the triblock copolymers studied here, a proper microphase separated structure (moderate size and volume fraction of the hard PS phase) is critical to specific mechanical properties and effective mechanical activation of covalently embedded mechanophore. Therefore, incorporation of mechanophore into the triblock copolymer and subsequent investigation on the mechanically induced chromic change behaviors enabled the sensing and mapping of stress, deformation, and to some extent, the structure, for example, microphase separation, in the copolymers. This platform promises to open way to the deeper understanding and design of a wide range of useful mechanoresponsive triblock copolymers having different hard/soft blocks and various types of mechanoresponsive motifs. We also envision the use of mechanophore as an effective probe for sensing and mapping structure, deformations, stresses, and damage in supramolecular polymers carrying supramolecular moieties at the ends as well as in the backbone and in the side chain.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, NMR, GPC, DSC, DMA, SAXS, sonication results, and additional information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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